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Fundamentals of transport, geochemistry and sampling

Ondra Sracek

Principal transport processes

(1) Difussion

(2) Advection

(3) Dispersion

(4) Adsorption and retardation

(5) Decay

Conservative contaminant/tracer: is not adsorbed,
does not decay nor precipitate

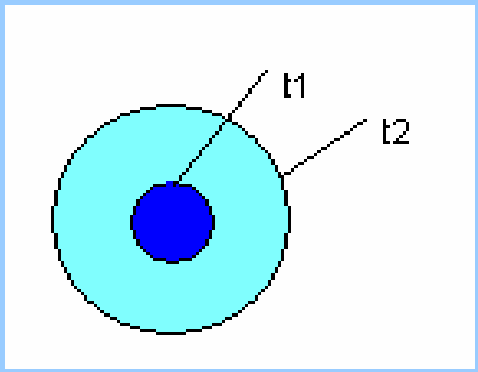
Ad (1) Difussion

- transport caused by concentration gradient, occurs also in stagnant water,

1. Fick Law:

$$J_D = -D_{ef} \cdot \frac{\partial C}{\partial x}$$

where J_D is diffusive flux, D_{ef} is effective diffusion coefficient for porous media, C and x is distance,



Ad (2) Advection

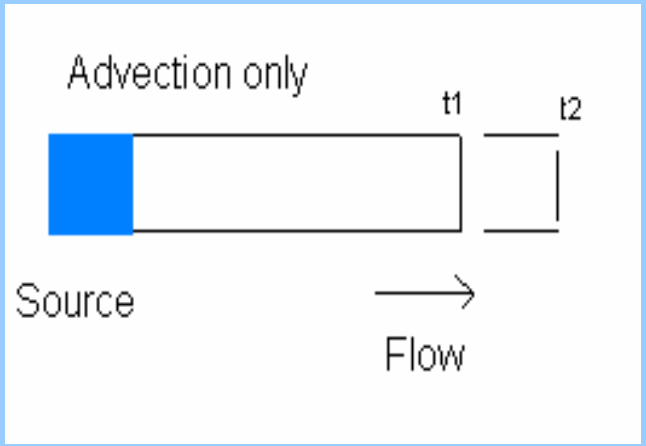
- transport caused by hydraulic gradient,

- advective flux is $J_A = q.C = v.n.C$

where v is average linear velocity calculated from Darcy Law,

$$v = \frac{k\,.I}{n_e}$$

where k is hydraulic conductivity, I is hydraulic gradient and n_e is effective porosity



Ad (3) Dispersion

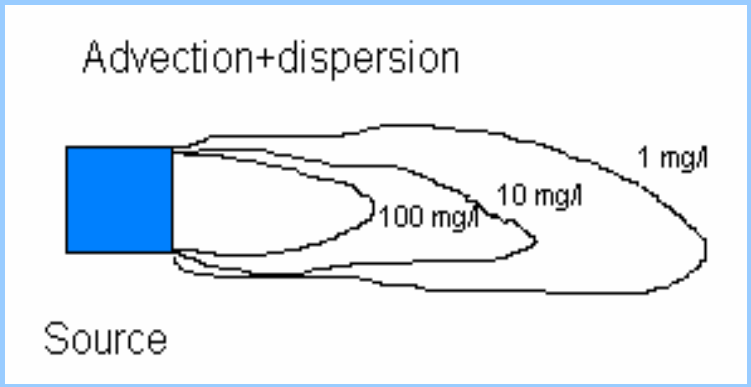
- spreading caused by differences in permeability/velocity of advection

- this parameter is described by 3 dispersivity terms (depending on direction): longitudinal α_L, transversal α_H and vertical α_v,

- diffusion and dispersion are combined in parameter called hydrodynamic dispersion D, for example, for direction of flow it is

$D_L = \alpha_L . v_x + D_{ef}$

- when dispersivity values increase, also increases the width of transition zone between contaminant plume and clean water;

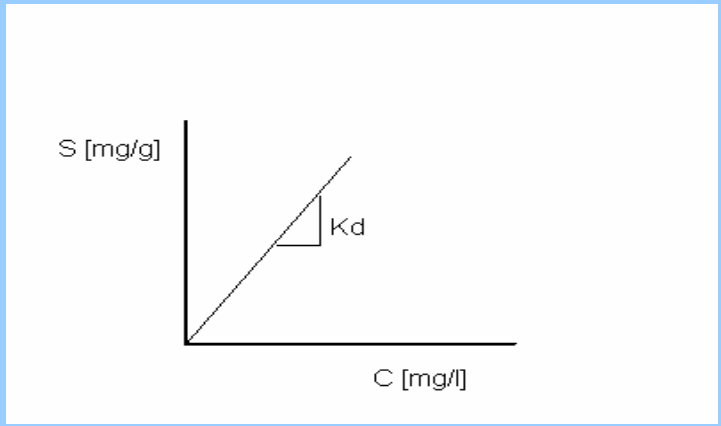


Ad (4) Adsorption and retardation

- contaminant is attached to the surface of solid phase, adsorption is frequently described by empirical isotherms such as K_d:

$K_d = dS/dC$

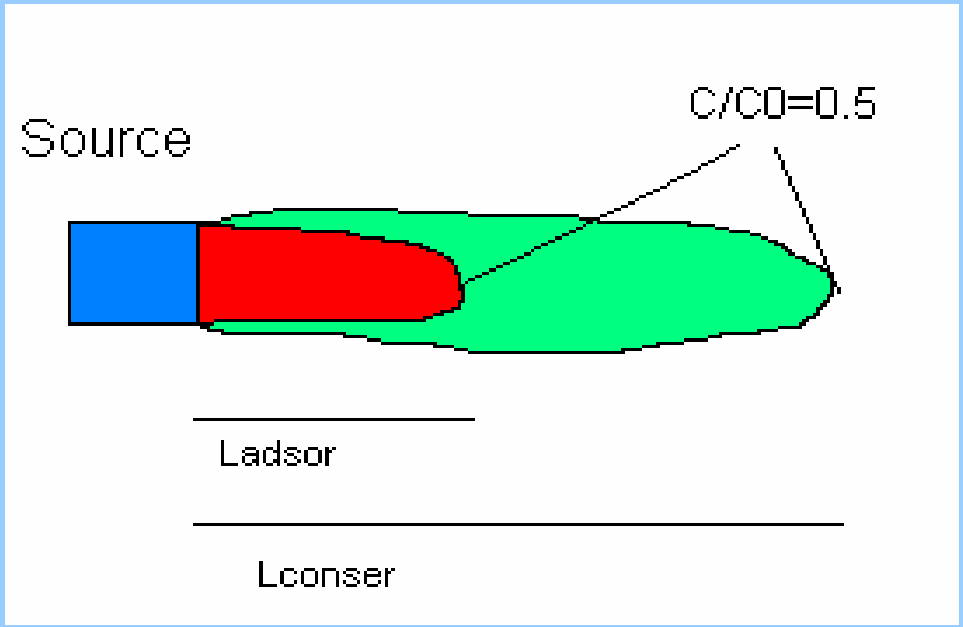
S – adsorbed concentrations, C – dissolved concentration,



- relation between retardation coefficient R and K_d is

$R = 1 + (\rho_b/n).K_d$; ρ_b is bulk density of solid phase, n is porosity

Retardation coefficient defined by lenght of plumes:



where L_{adsor} is a length of adsorbed contaminant plume and L_{conser} is a length of conservative contaminant plume;

In this case $R = L_{conser}/L_{adsor} = v_{conser}/v_{adsor} = 1 + (\rho_b/n).K_d$

When R = 1.0, there is no retardation;

Ad (5) Decay

- decomposition of a contaminant and its transformation into daughter products

- decay is frequently described by 1st order kinetics:

$C_t = C_0 .e^{-kt}$

C – concentration, k – decay constant (t^{-1}),

t – time

- decay constant is related to half-life $t_{1/2}$ (t):

$k = 0.693/t_{1/2}$

- attenuation: high value of k = fast decay, high value of $t_{1/2}$ = slow decay!

Transport equations in 1-D

- Advection-dispersion equation (ADE):

$$Dx \frac{\partial^2 C}{\partial x^2} - v_x \frac{\partial C}{\partial x} = \frac{\partial C}{\partial t}$$

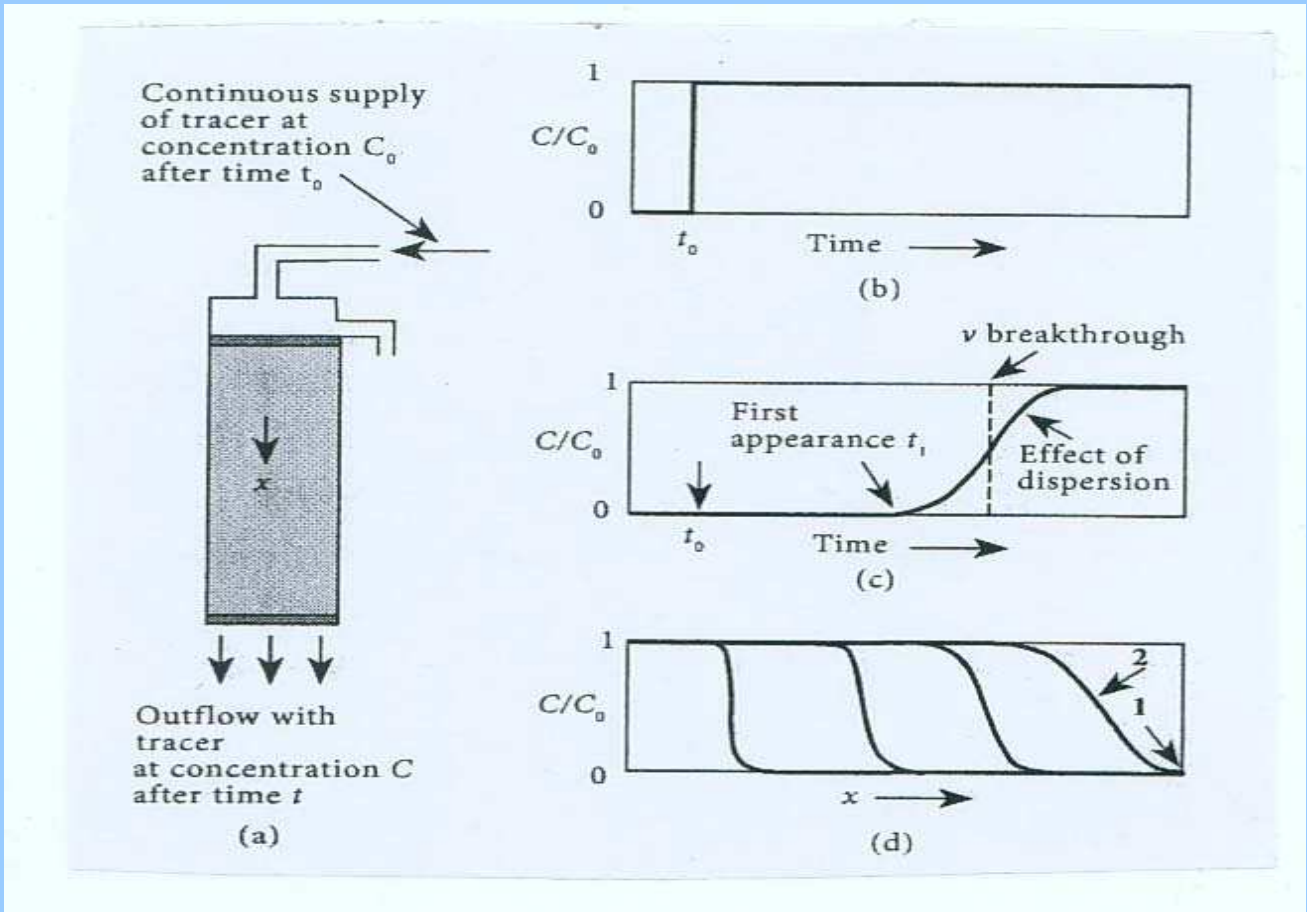
- ADE with retardation:

$$\frac{D_x}{R} \frac{\partial^2 C}{\partial x^2} - \frac{v_x}{R} \frac{\partial C}{\partial x} = \frac{\partial C}{\partial t}$$

- ADE with retardation and decay:

$$\frac{D_x}{R} \frac{\partial^2 C}{\partial x^2} - \frac{v_x}{R} \frac{\partial C}{\partial x} - kC = \frac{\partial C}{\partial t}$$

Breakthrough curve (BTC):



Freeze, Cherry, 1979

Geochemical processes

(1) Complexation / ionic strength effect

(2) Precipitation / dissolution

(3) Redox processes

(4) Adsorption

(5) Colloidal transport

Ad (1) Complexation / ionic strength impact

Total concentration of, for example, Cd is

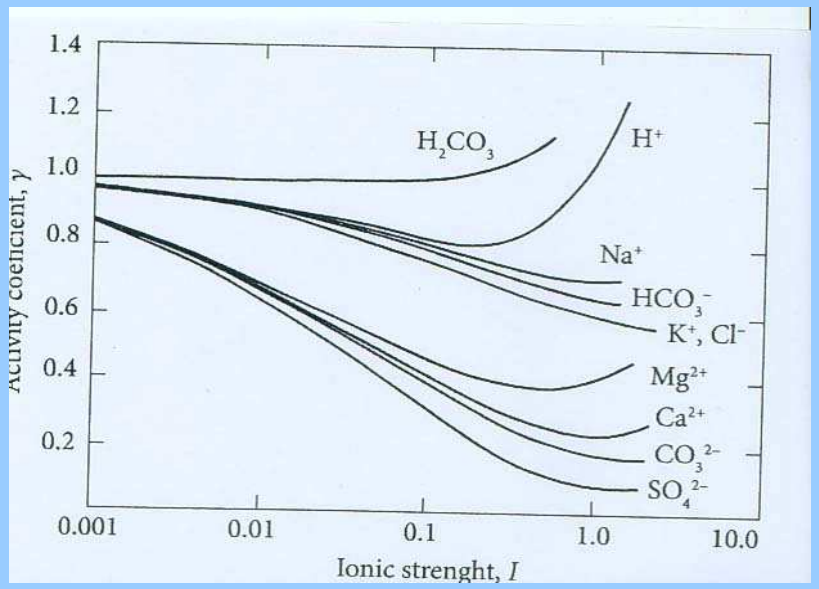
$Cd_{total} = Cd^{2+} + CdCl^{-} + CdOH^{+} + ..etc.$

Each complex is described by its association (dissociation) equation:

$Cd^{2+} + Cl^{-} = CdCl^{-}$ $K_{assoc} = 10^{-1,98}$, complexation increases solubility;

Activity a_i = thermodynamic concentration

$a_i = \gamma_i .m_i$ where γ_i is activity coefficient and m_i is concentration, γ_i depends on ionic strength I, $\gamma_i = f(I)$:



Kehew, 2001

Ad(2) Precipitation / dissolution

There is dissolution of anglesite, $PbSO_4$:

$PbSO_4(s) = Pb^{2+} + SO_4^{2-}$ then

$[Pb^{2+}].[SO_4^{2-}] = K_{sp} = 10^{-7,79}$

where K_{sp} is solubility product from literature and [ ] are activities;

when ionic strength increases, values of γ for Pb^{2+} e SO_4^{2-} decrease and solubility of anglesite increases;

In general form, $[Pb^{2+}].[SO_4^{2-}]$ is called ion activity product and saturation index SI is defined as

$SI = \log(IAP/K_{sp})$

When SI>0, water is supersaturated with respect to a mineral, which may precipitate,

When SI=0, water is at equilibrium with a mineral,

When SI<0, water is undersaturated with respect to a mineral and this mineral can dissolve;

Ad (3) Redox reactions

Oxidation = loss of electrons, reduction = gain of electrons

There is no oxidation without reduction and vice versa, example:

$Fe^0(s) = Fe^{2+} + 2e^-$.....oxidation of Fe^0

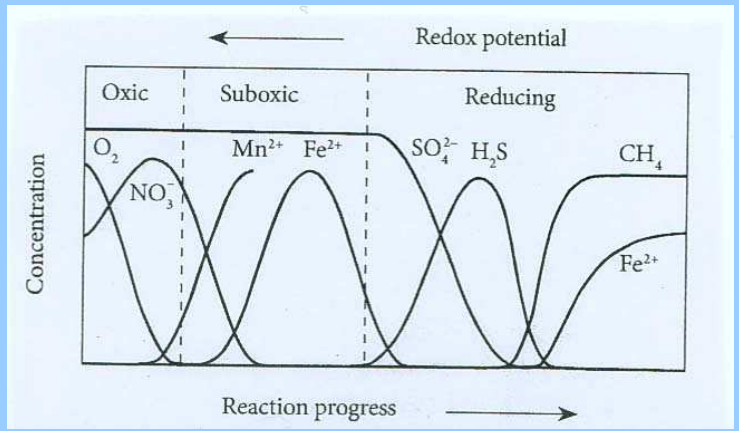
$\underline{0.5O_2{}^0(g) + 2H^+ + 2e^- = H_2O}$.....reduction of O_2

$Fe^0(s) + 0.5O_2{}^0(g) + 2H^+ = Fe^{2+} + H_2O$..complete reaction

2 types of redox notation:

Eh and pe, a conversion is Eh [V] = 0.059.pe for 25 °C

Redox sequence (*redox ladder*): $O_2 \rightarrow NO_3 \rightarrow Mn(IV) \rightarrow Fe(III) \rightarrow SO_4 \rightarrow CH_4$:

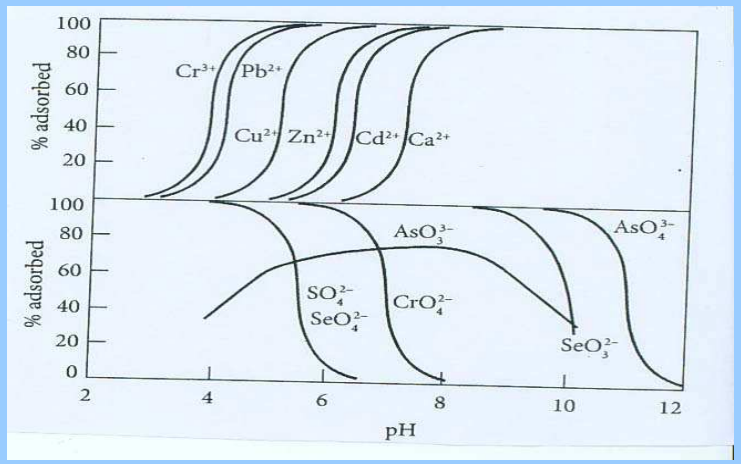


Appelo, Postma, 1996

Ad (4) Adsorption

- adsorption isotherrms like K_d are for constant pH, chemistry and temperature of water, when these parameters change, surface complexation approach is applied, principle adsorbents are hydroxides like $Fe(OH)_3$, which have pH-dependent surface charge,

- when pH is low, there is formation of $\equiv FeOH_2^+$, when pH is high, $\equiv Fe(OH)^-$ predominates, value of pH when $\equiv FeOH_2^+ = \equiv Fe(OH)^-$ is called pH_{ZPC} (zero point of charge), in this case surface charge is neutral, for $Fe(OH)_3$ value of pH_{ZPC} is 8.3, for clays it is between 2.0 – 4.0; consequencies: when pH increases, adsorption of cations like Pb^{2+} and Cd^{2+} also increases, the opposite (desorption) ocurrs for anions like $HCrO_4^-$ and $HAsO_4^{2-}$ (adsorption edge):

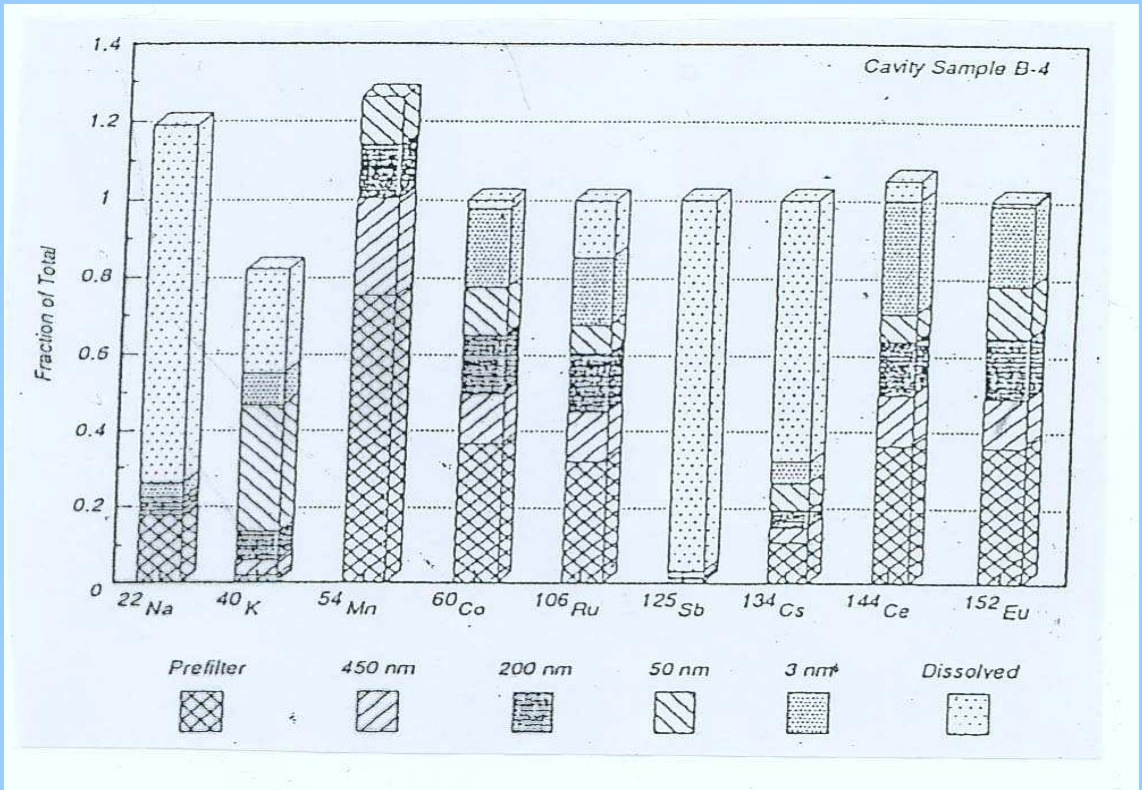


Drever, 1997

Ad (5) Colloidal transport

Formation of colloids results in a second mobile phase;

it is possible to use several sizes of filters or to take 2 samples: one filtered and one unfiltered, both samples are acidified, if there are colloids, the concentration in unflitered sample is higher;



Buddemeier, Hunt, 1988

Processes during sampling:

There are 2 reactions caused by contact with the air:

$Ca^{2+} + 2HCO_3^- = CaCO_3 + CO_2 + H_2O$

This reaction increases pH and reduces concentration of Ca and alkalinity:

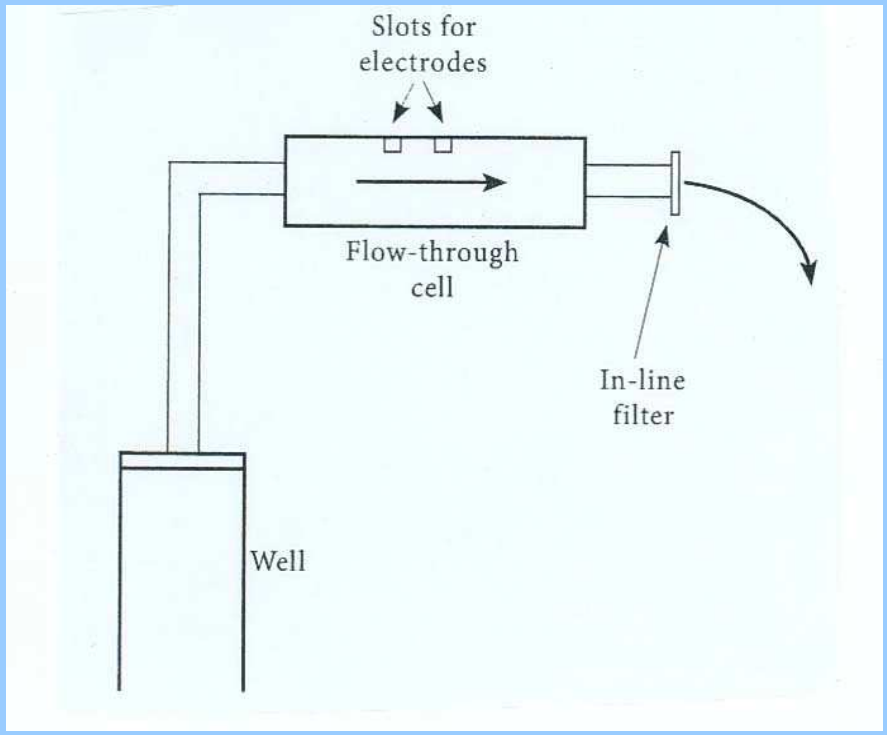
$Fe^{2+} + 0.25O_2 + 2.5H_2O = Fe(OH)_3 + 2H^+$

This reaction decreases pH and concentration of iron and other metals (by adsorption);

Field parameters:

Temperature T, pH, redox potential Eh, dissolved oxygen DO, eletrical conductivity EC

flow-through cell:



Sracek, Zeman, 2004

Preservation of samples:

- samples for cation and metal analyses: filtering in the field with 0.45 μm filter and acidification with HCl to pH less than 2.0 ;

- samples for anion analyses: no acidification, but filtration is recommended;

- alkalinity: determination in the field is recommended, if this is impossible, take a sample dedicated to alcalininity determination;

- sampling for volatile organics : sub-atmospheric pressure should be avoided;

CONCLUSIONS

- Principal transport processes are difussion, advection, dispersion, adsorption/retardation and decay, advection is the most important process,

- transport processes are included in advection/dispersion equation, which can be solved by analytical or nunerical methods,

- principal geochemical processes are complexation/ionic strenghth impact, precipitation/dissolution, redox reactions, adsorption/desorption and formation of colloids:

CONCLUSIONS (continuation)

- several parameters have to be measured in the field: T, pH, Eh, DO, and alkalinity,

- it is necessary to avoid contact with the air using flow-through cell,

- samples for cation and metal analyses have to be filtered and acidified; filtered and unfiltered samples, both acidified are taken to confirm presence of colloids;

RISK ASSESSMENT HANDBOOK FOR SHUT DOWN AND ABANDONED MINE SITES IN NAMIBIA

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B1: Guides to Estimate the Probability Index for each Contamination Hazard Scenario
B2: Supporting Material for the Simplified Contamination Risk Area

ANNEX C: **COMPLEMENTARY INFORMATION FOR THE DETAILED RISK ASSESSMENT FOR CONTAMINATION**
C1: Guideline Concentrations for Assessment of Chemicals of Potential Concern in Environmental Media
C2: Basic Considerations for Reviewing Studies in the Detailed Risk Assessment for Contamination

ANNEX D: **COMPLEMENTARY INFORMATION FOR THE DETAILED RISK ASSESSMENT FOR SAFETY**
D1: Basic Considerations for Reviewing Studies in a Detailed Risk Assessment for Safety

ANNEX E: **RISK ASSESSMENT RECORD FORMS**

ANNEX F: **FIELD GUIDE**

ANNEX G: **SHUT DOWN AND ABANDONED MINE SITE INVENTORY DATA SHEET**

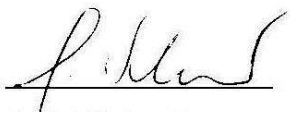
FOREWORD

Namibia has 157 registered and probably in excess of 250 abandoned mine sites in total. These mines may pose a serious threat in terms of groundwater and soil contamination, dust pollution, the impending physical impact of hazardous structures, and negative visual impact. There is a variety of types of abandoned mines, both, in terms of size, and in terms of the commodity that was mined. Some are underground mines, while others are open pits and quarries. Associated structures are overburden dumps, tailings facilities, and beneficiation plants in various stages of deterioration and decay.

The Ministry of Mines and Energy has recognized the hazardous potential and the negative environmental impact of these abandoned mines. However, due to the wide variety of types, there is no standard solution for dealing with them, and remediation measures need to be tailor-made for individual cases.

Faced with the same problem in Chile, the Federal Institute for Geosciences and Natural Resources (BGR) of Germany developed a manual to assist with prioritizing old mines sites in terms of the risks that they pose to the health and safety of people and the biophysical environment. This manual was edited, adapted and customized to the Namibian situation with the help of highly recognized specialists in this field in the southern African region, such as Bryony Walmsley of SAIEA, Peter Terbrugge of SRK and Willie van Niekerk of Infotox.

This resulting Namibian manual will assist greatly in the difficult task of dealing with the inherited problem of abandoned mine sites and allocating funding to rehabilitate those mines which pose the greatest risk. As it has been designed to suit the Namibian circumstances, it also forms the basis for dealing with orphan mine sites in the entire southern African region.





Dr Gabi Schneider
Director Geological Survey of Namibia
(GSN)

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Head of Technical Cooperation
BGR-GSN Project

INTRODUCTION TO ACID MINE DRAINAGE

Ondra Sracek

Acid Mine Drainage (AMD): types of mining wastes

There are 2 basic types of mining wastes: mine tailings and waste rock;

- mine tailings: fine grain particles, highly saturated by water, oxygen transport by difussion, they are in topographic depressions and thickness of unsaturated zone is low (generally 1 - 5 m),

- waste rock piles: highly variable size of particles, oxygen transport by both diffusion and convection, fast oxidation of pyrite results in high temperatures, they form topographic elevations and thickness of unsaturated zone is frequently high (> 30 m, sometimes 100 m);

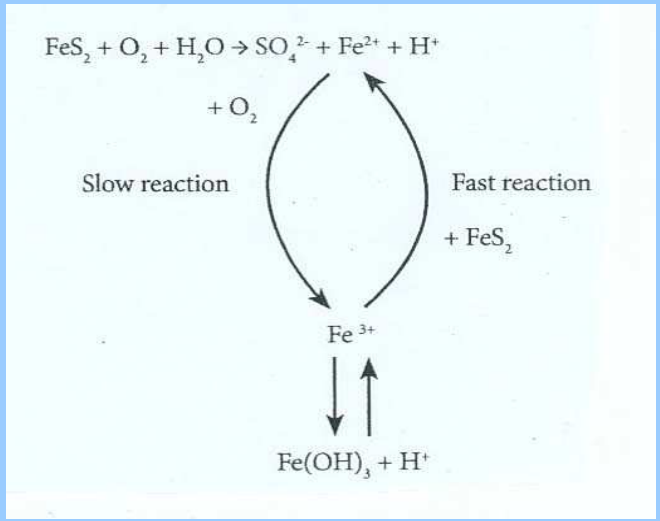
Mine tailings, Mindolo, Copperbelt, Namibia



Waste rock pile, Mine Doyon, Québec, Canada



Principal process responsible for formation of acid mine drainage is the oxidation of sulphides such as pyrite:



Stumm, Morgan, 1981

Balanced equations are:

(1) $FeS_2(s) + 3{,}5O_2(g) + H2O = Fe^{2+} + 2SO_4^{2-} + 2H^+$

(2) $Fe^{2+} + 0{,}25O_2 + H^+ = Fe^{3+} + 0{,}5H_2O$

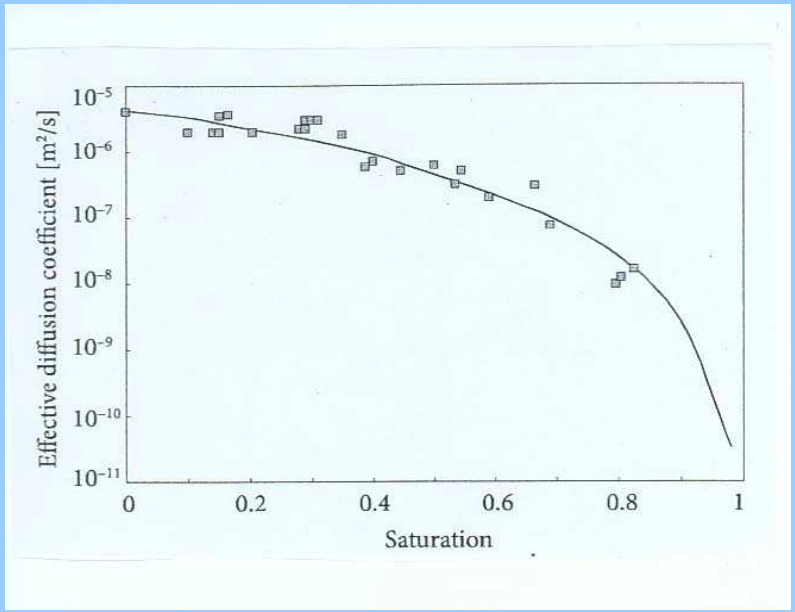
(3) $Fe^{3+} + 3H_2O = Fe(OH)_3(s) + 3H^+$

(4) $FeS_2(s) + 14Fe^{3+} + 8H_2O = 15Fe^{2+} + 2SO_4^{2-} + 16H^+$

Oxygen transport in mine tailings is by diffusion, described by 1. Fick`s Law:

$$J_{O_2} = -D_{O_2} \cdot \frac{\partial C_{O_2}}{\partial x}$$

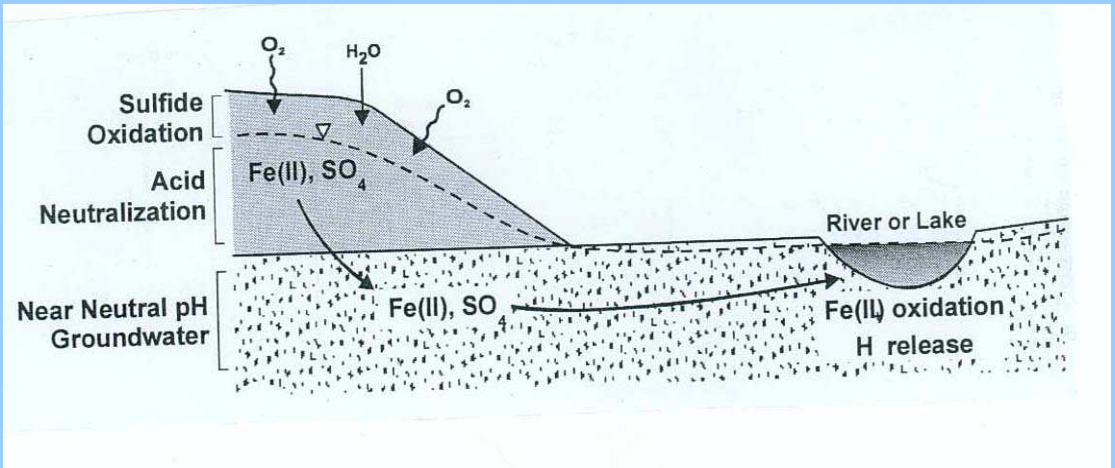
where D_{O2} is effective diffusion coefficient for oxygen, which depends on water saturation of mine tailings:



Elberling, Nicholson, 1996

There are several geochemical zones in and around mine tailings:

(1) pyrite oxidation zone, (2) neutralization zone in mine tailings, (3) plume out of mine tailings and (4) discharge of the plume to surface water bodies (lakes, creeks etc.):



Blowes, Ptacek, 2003

Neutralization reactions:

(1) Calcite dissolution

$CaCO_3(s) + H^+ = Ca^{2+} + HCO_3^-$

(2) Siderite dissolution

$FeCO_3(s) + H^+ = Fe^{2+} + HCO_3^-$

(3) Aluminium hydroxide dissolution

$Al(OH)_3(s) + 3H^+ = Al^{3+} + 3H_2O$

(4) Ferric hydroxide dissolution

$Fe(OH)_3(s) + 3H^+ = Fe^{3+} + 3H_2O$

(5) Dissolution of silicates

$Silicate(s) + 4H^+ = Na^+ \text{ etc.} + Al^{3+} + H_4SiO_4$

- calcite dissolution is fast and buffers pH around 6.0

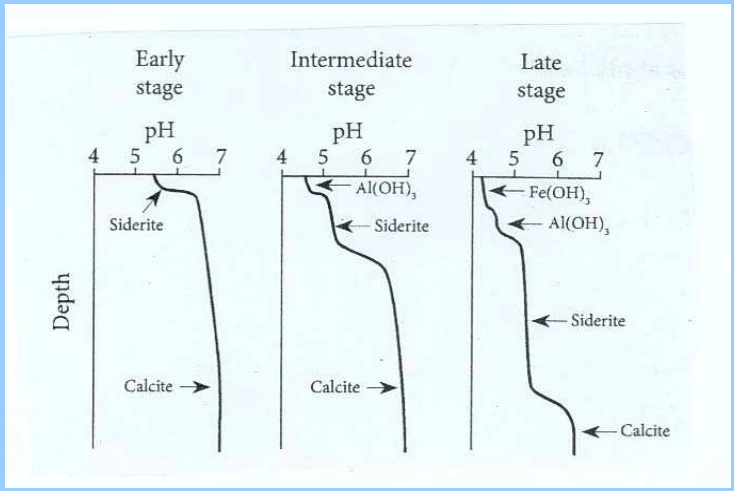
- dissolution of siderite is slower and buffers pH around 5.0

- dissolution of $Al(OH)_3$ is slow, buffers pH around 4.0 and produces Al

- dissolution of $Fe(OH)_3$ is slow and buffers pH around 3.0

- dissolution of silicates is very slow and produces Al

Neutralization zones are moving with time:



Blowes, Ptacek, 1994

Reactions in discharge zone:

(a) Precipitation of aluminium hydroxide:

$Al^{3+} + 3H_2O = Al(OH)_3(s) + 3H^+$

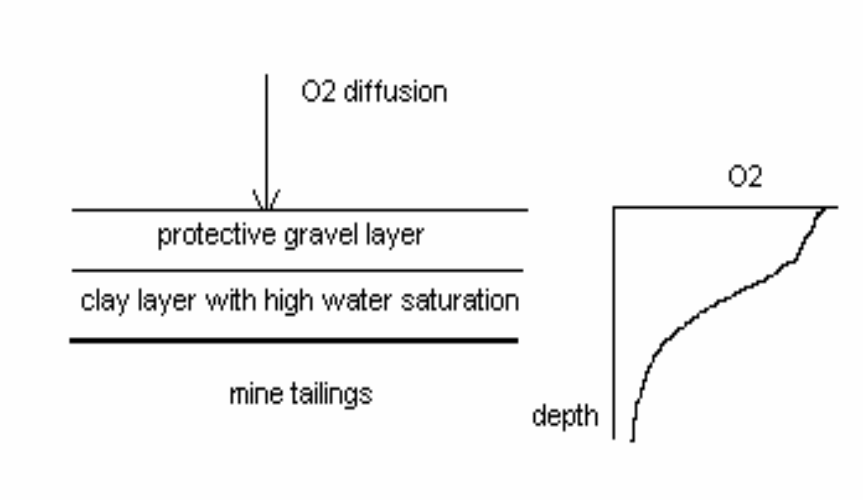
(b) Oxidation of Fe(II) and precipitation of ferric hydroxide:

$Fe^{2+} + 0.25O_2 + 2.5H_2O = Fe(OH)_3(s) + 2H^+$

Both reactions produce acidity, but hydroxides are adsorbents of contaminants like Pb, Zn, Cd etc.

Prevention of acid mine drainage:

(1) Aplication of clay layers as oxygen penetration barriers



(2) Aplication of surface layers with organic matter for oxygen consumption

(3) Complete flooding of mine tailings

CONCLUSIONS

- There are 2 principal types of mining wastes: mine tailings and waste rock, in mine tailings oxygen is transported by diffusion, in waste rock by diffusion and by convection;

- transport of oxygen by diffusion depends on effective diffusion coefficient for oxygen which depends on water saturation of mine tailings;

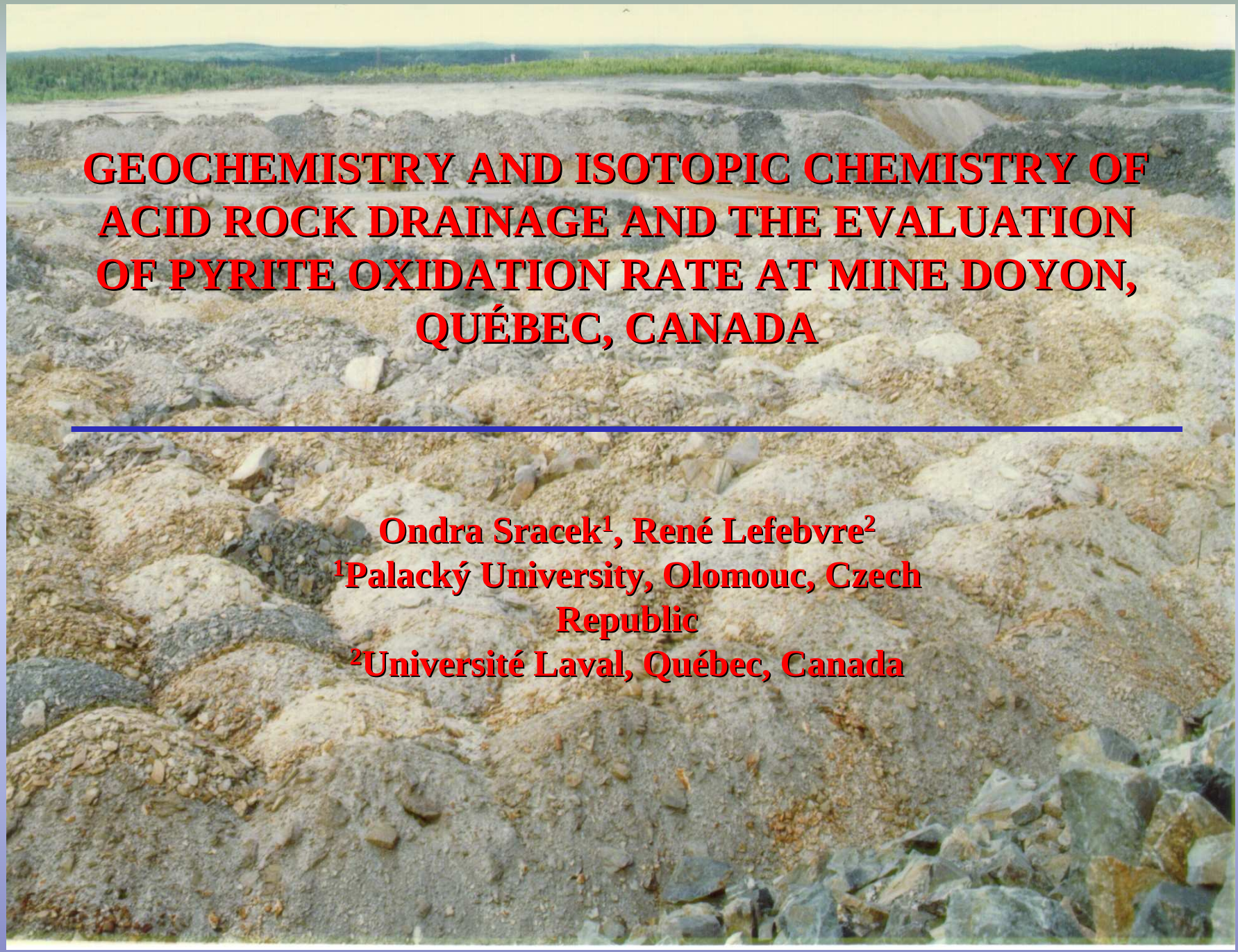
- principal geochemical zones in mining wastes are: - pyrite oxidation zone, - neutralization zone, - plume out of mining wastes, and – zone of plume discharge into surface water;

- neutralization reactions sequence is: calcite, siderite, aluminium hydroxide and ferric hydroxide;

CONCLUSIONS (continuation)

- in discharge zone reactions like aluminium hydroxide precipitation and ferric hydroxide precipitation produce acidity;

- principal method of acid mine drainage prevention is the installation of oxygen penetration barriers on the surface of mining wastes (clay layers with high water saturation and organic matter layers, where oxygen is consumed); prevention is always better than remediation;



GEOCHEMISTRY AND ISOTOPIC CHEMISTRY OF ACID ROCK DRAINAGE AND THE EVALUATION OF PYRITE OXIDATION RATE AT MINE DOYON, QUÉBEC, CANADA

Ondra Sracek[1], René Lefebvre[2]

[1]Palacký University, Olomouc, Czech Republic

[2]Université Laval, Québec, Canada

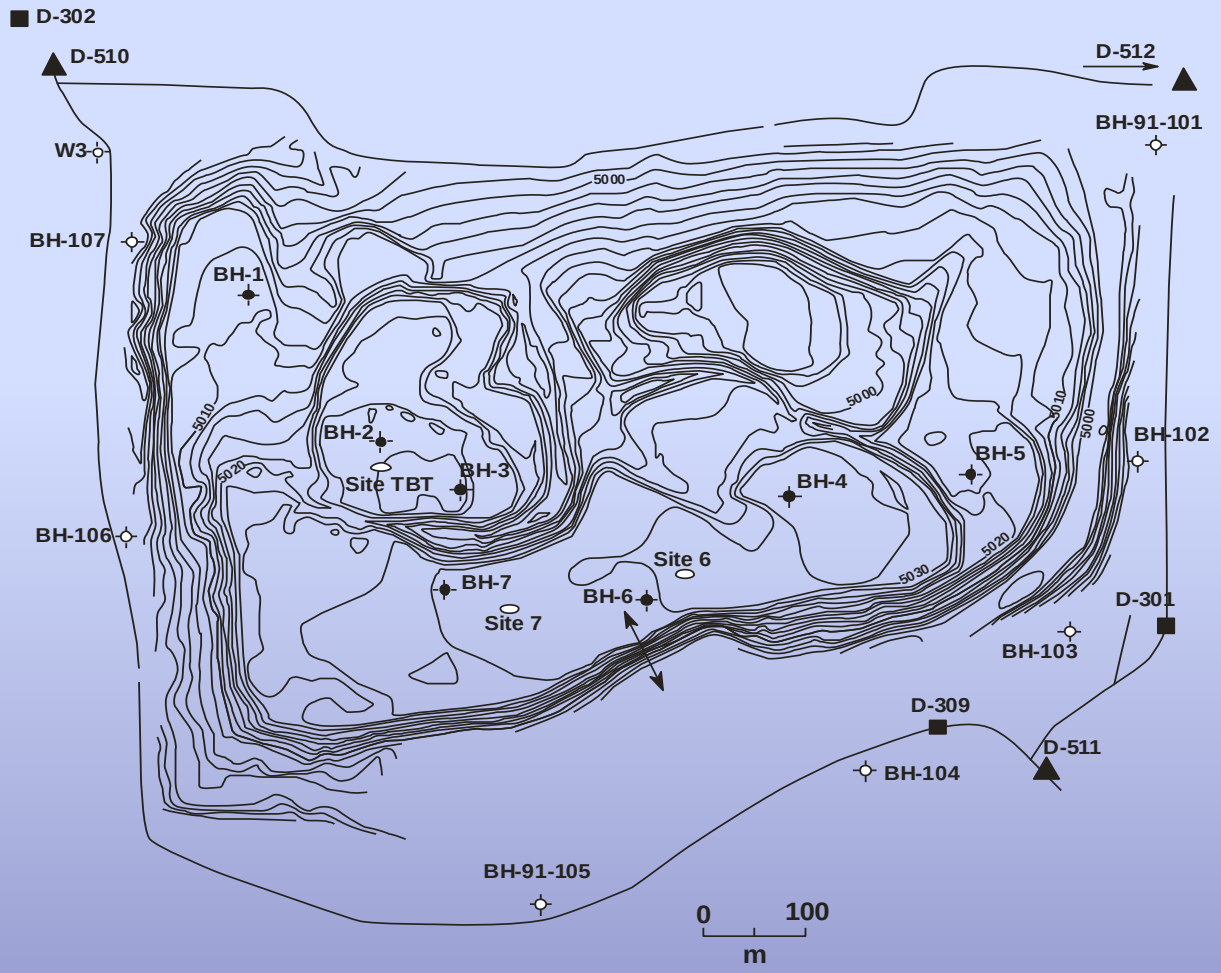
Mine Doyon pile - description(1)

- Mine Doyon is a gold mine, located north of Montreal, in Abitibi region,
- Average height of south pile is 30-35 m, rocks are sericite schists with pyrite content up to 7.0 wt % (locally 9.0 wt %), initial calcite content about 2.0 wt % has been generally depleted,
- AMD appeared 2 years after construction of pile and reached steady-state in 1988; typical pH values are about 2,0 and concentrations of sulfate in pore water are > 200 g/L; under such low pH conditions, behavior of Al and Mg can be considered conservative in long term.

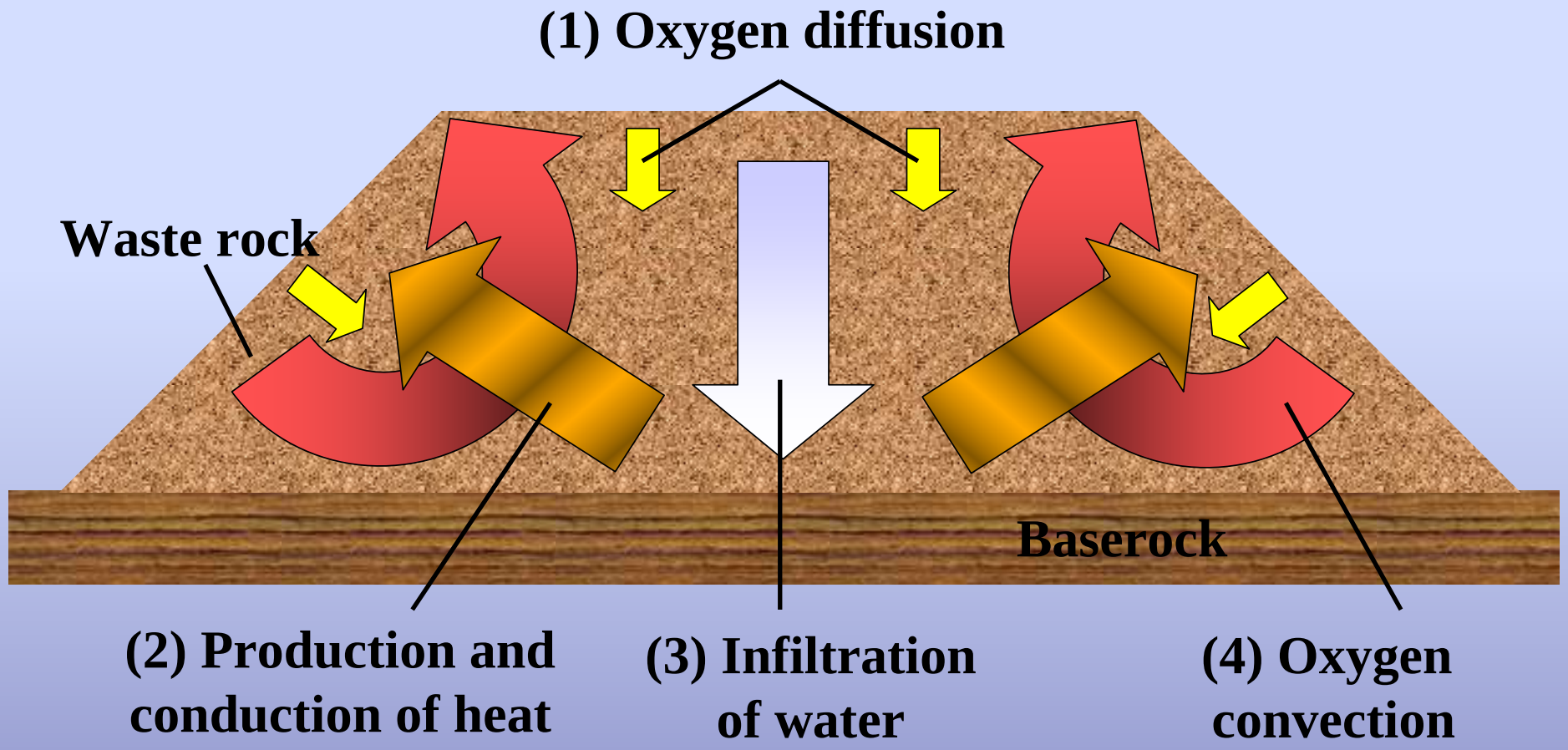
Mine Doyon pile – description (2)

- Behavior of sulfate in the pile is not conservative due to the precipitation of gypsum ($CaSO_4*2H_2O$) and K-jarosite ($KFe_3(SO_4)_2(OH)_6$),
- Precipitation of these minerals occurs within metamorphic foliation, with resulting decomposition of rocks and increased access of oxidants to unoxidized pyrite; this process increases greatly pyrite oxidation rate;

Mine Doyon pile: sampling and mesurement sites

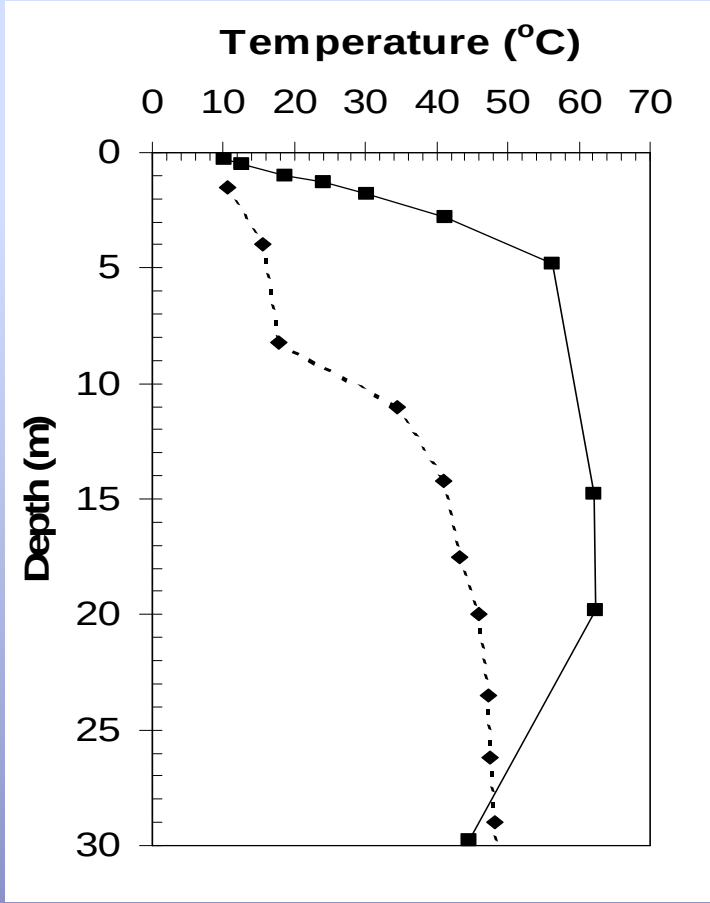


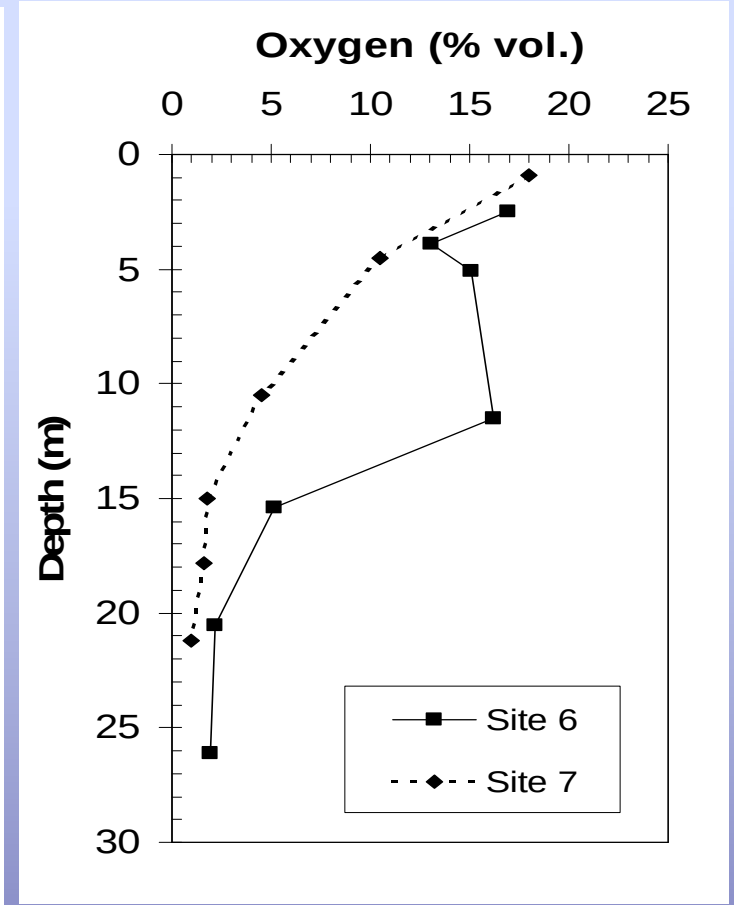
Conceptual model of processes in Mine Doyon pile



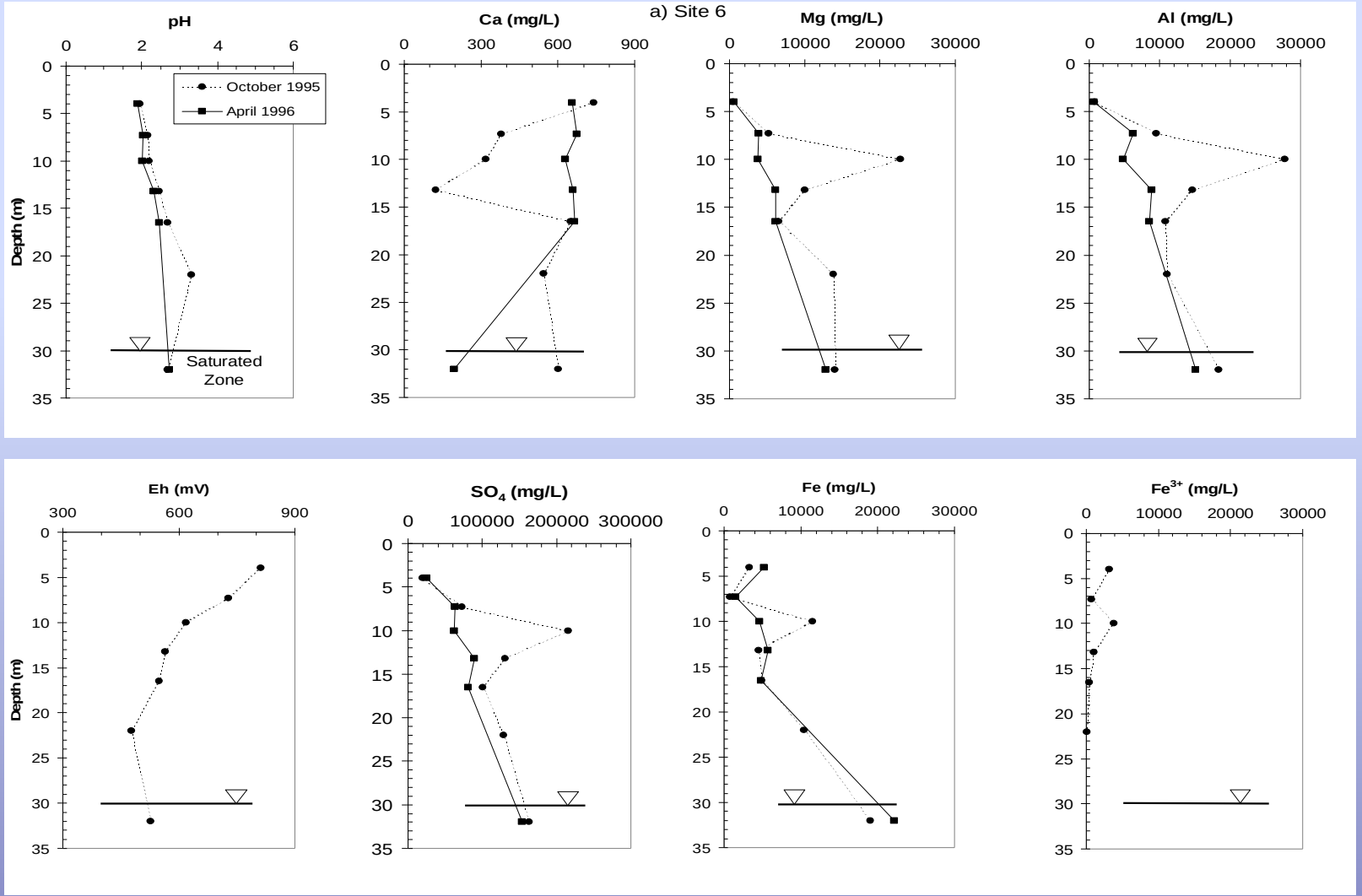
Two types of oxygen transport are evident in temperature and O_2 profiles

- Convection oxygen transport close to slope (Site 6)
- Diffusion oxygen transport in the core (Site 7)

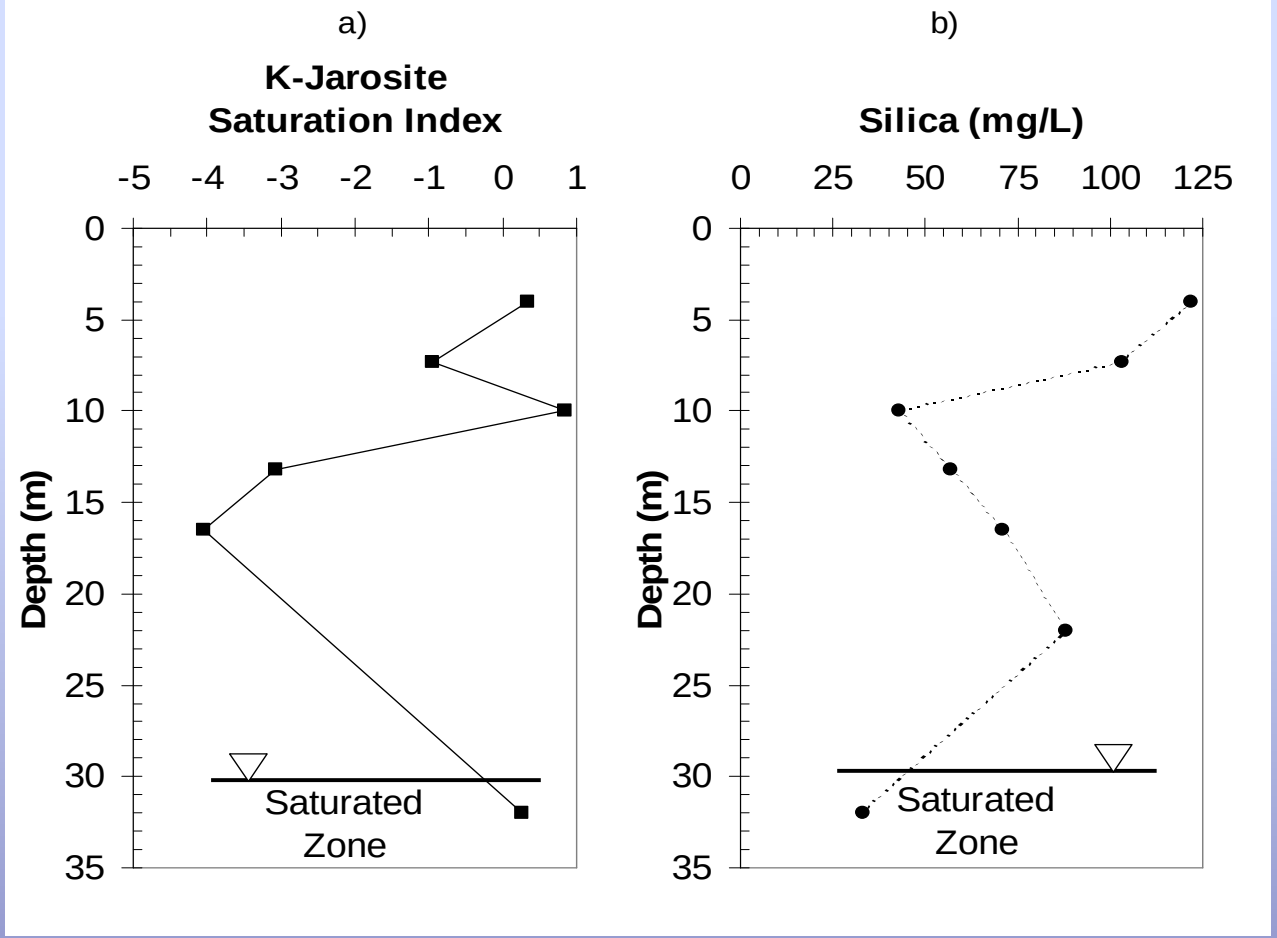




Profiles of dissolved species concentrations



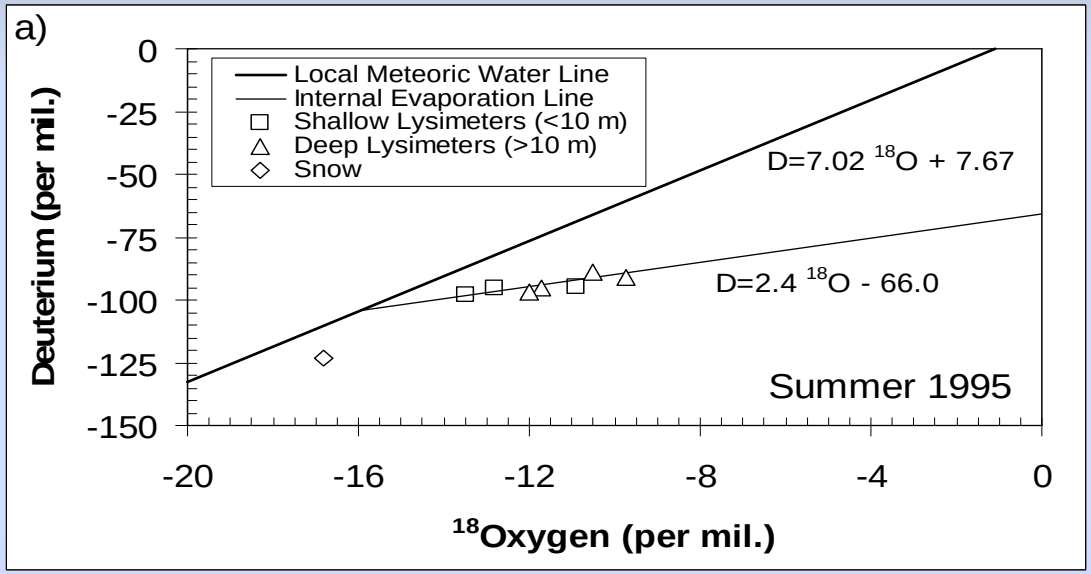
SI values for K-jarosite and Si concentrations



Isotopes D and ^{18}O

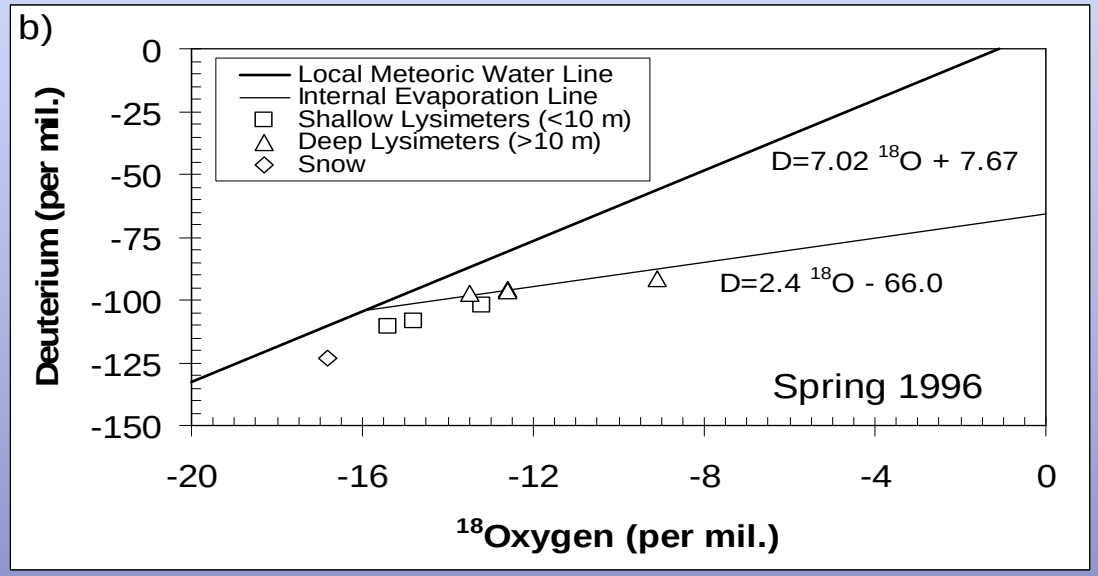
a) Dry period

(Summer 1995)



b) Recharge period

(Spring 1996)



Determination pyrite oxidation rate (POR)

There are 3 principal possibilities in waste rock piles:

(1) Interpretation of temperature and oxygen profiles (TOP)

(2) Mass balance for sulfate/pyrite (SMB/PMB)

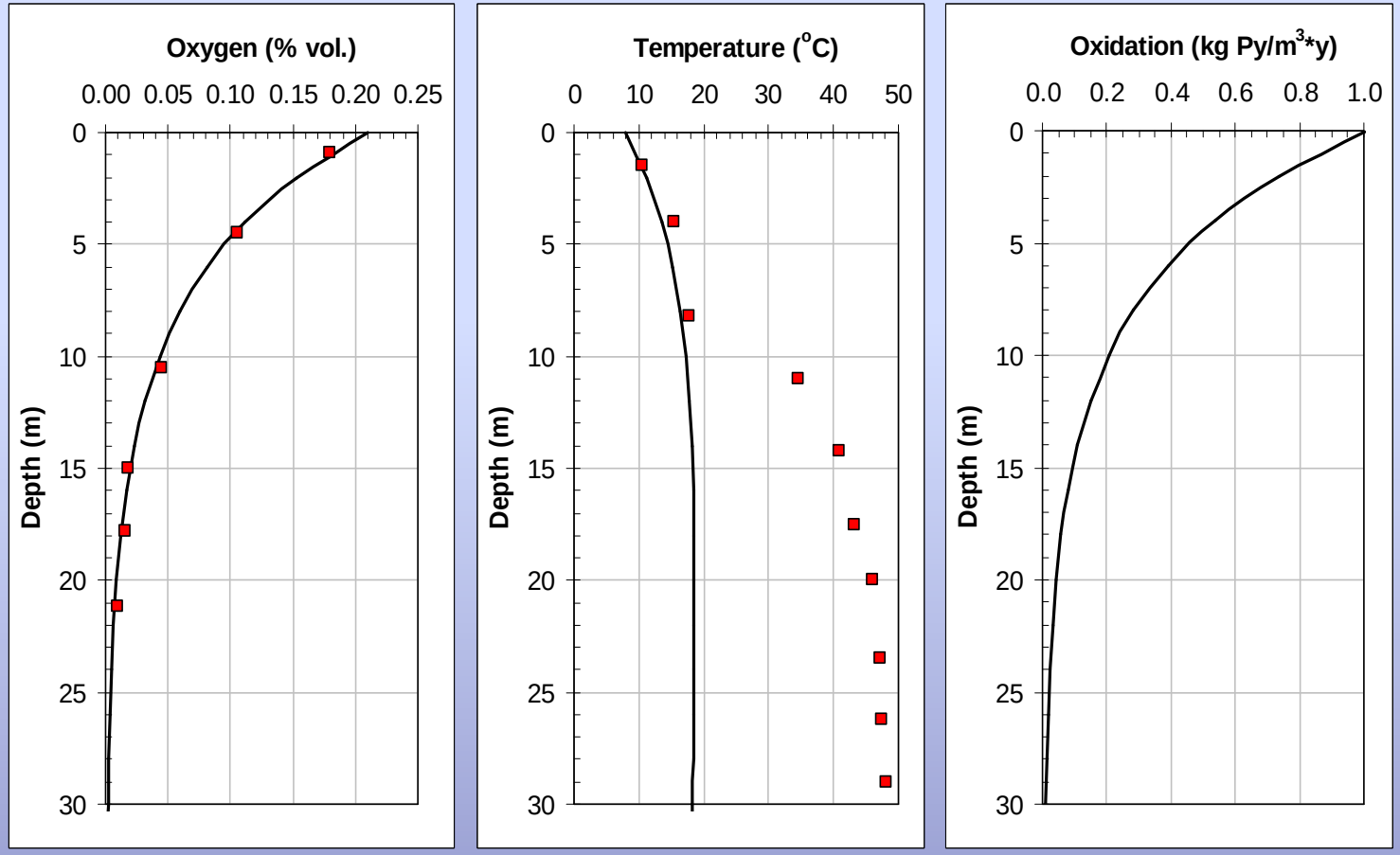
(3) Oxygen consumption method in laboratory (OCM)

Experiments in different scales generally produce different results (Malmström et al., 2000).

(1) POR from T and O_2 profiles (TOP)

- When O_2 is dominated by diffusion, O_2 concentration profile is more or less exponential,
- Analytical solution of Crank can be applied to determine transport parameters,
- In Mine Doyon pile, O_2 profile at Site 7 indicates O_2 transport by diffusion,
- At this site analytical solution works for O_2 profile, but not for T profile - there probably is lateral heat transport,
- Calculated POR at Site 7 is 4.4×10^{-10} $mol(O_2) \cdot kg^{-1} \cdot s^{-1}$,

A comparison between calculated and measured profiles of T and O_2 – Site 7



(2) POR from mass balance for sulfate/pyrite (SMB/PMB)

- Oxidation of pyrite for pH < 3.0 is described as:

$$FeS_2 + 3.5O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+$$

(oxidation of 1 mol of pyrite produces 2 moles of sulfate),

- When behavior of sulfate is conservative, the amount of sulfate flushed out of the pile can be converted to oxidized pyrite, e.g. sulfate mass balance (SMB),

- As an alternative, pyrite mass balance (PMB) can be used, assuming known initial pyrite content and pyrite content at time zero; calculated POR is an average value for whole oxidation period.

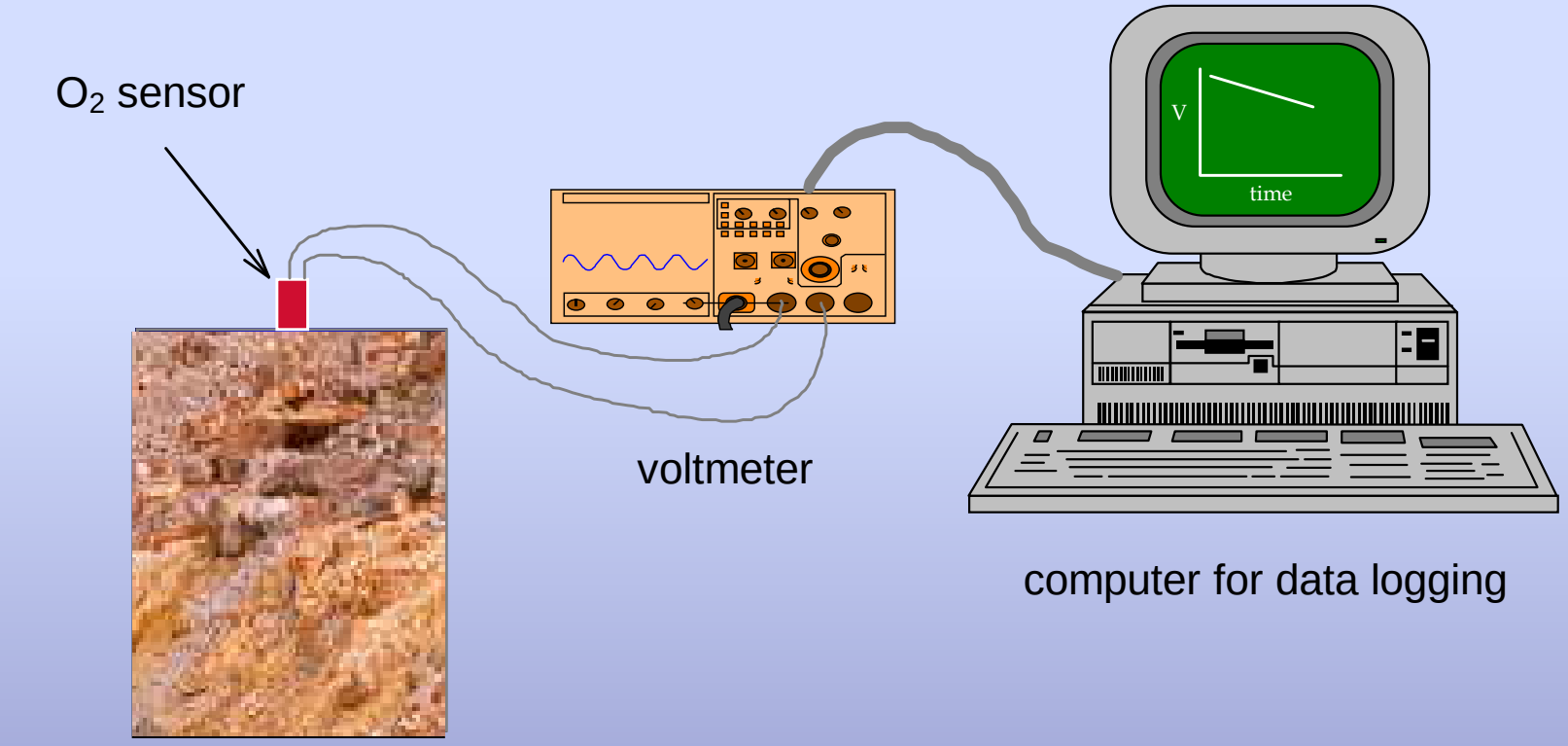
Role of secondary minerals in mass balance calculations

- At Mine Doyon, precipitation of gypsum, $CaSO_4.2H_2O$, and jarosite, $KFe_3(SO_4)_2(OH)_6$, in the pile affects mass balance for sulfate (SMB) and values of POR are underestimated,
- For this reason, pyrite mass balance (PMB) was a better option.

(3) POR from oxygen consumption method (OCM)

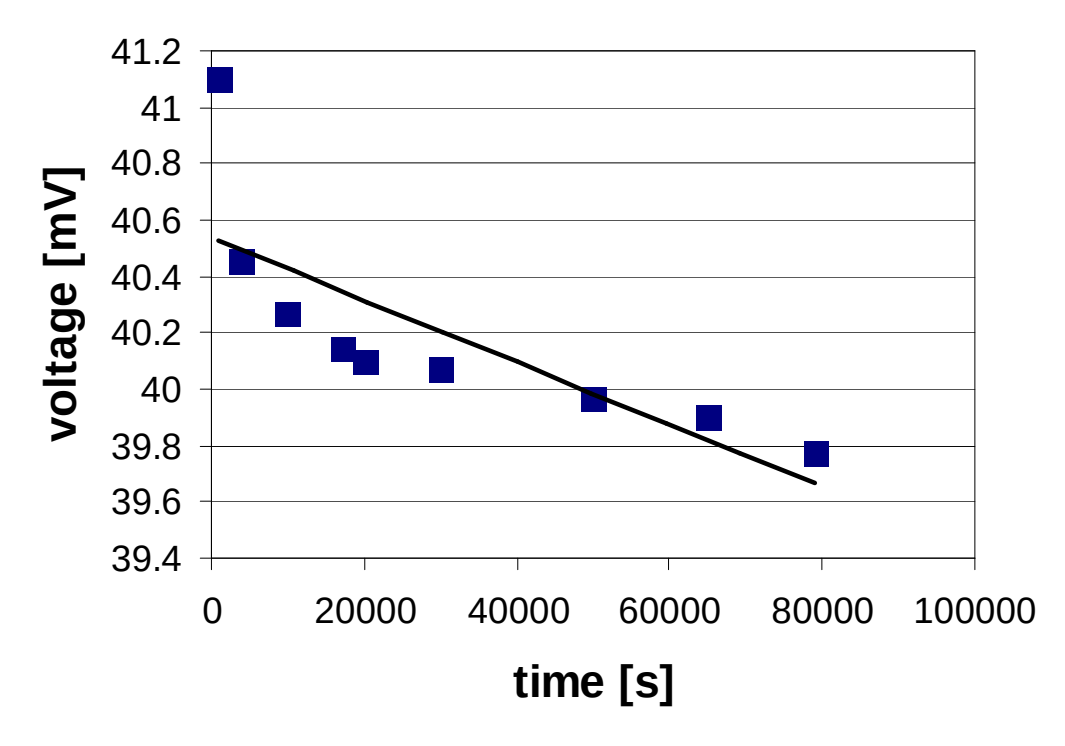
- Sample of a broken waste rock is placed into a closed chamber, sprinkled with water and changes in headspace oxygen concentration are recorded,
- A graph of voltage as a function of time is plotted and straight line in the graph is used to calculate POR in $mol(O_2) \cdot kg^{-1} \cdot s^{-1}$,
- Scale of the test is small compared to field and POR values are generally high (oxygen transport limitations are not present);

Mesurement of oxygen consumption



Voltage vs. time plot

- Fresh material from Mine Doyon, size of particles 4.5 cm:



Comparison of various methods of POR [$mol(O_2) \cdot kg^{-1} \cdot s^{-1}$] determination

Site/method	Temperature and O_2 profiles (TOP)	Pyrite mass balance (PMB)[&]	Oxygen consumption method (OCM)
Site 6 (slope)	3.9×10^{-9}	2.2×10^{-9}	n.a.
Site TBT (core)	n.a.	1.8×10^{-9}	n.a.
Site 7 (core)	4.4×10^{-10}	2.0×10^{-9}	n.a.
Pile average	1.5×10^{-9}	2.0×10^{-9}	6.6×10^{-8}** 3.4×10^{-9}*

[&] - based on 5 maximum values of pyrite content in deep unoxidized zone, n.a.-not available, **- fresh material, 5 runs, *- weathered slope material, 4 runs

CONCLUSIONS

• In Mine Doyon waste rock pile oxygen convection plays an important role,temperature and oxygen concentration profiles indicate convection close to slope and diffusion in the pile core,

• Concentrations of contaminants in pore water (sulfate, iron, aluminum etc.) are extremely high close to slope an in dry period and decrease in recharge, high concentrations are linked to internal evaporation of pore water in the pile due to high temperature (up to 67º C),

• Internal evaporation is also confirmed by enriched values of isotopes D and ^{18}O,

• Principal secondary minerals are gypsum and jarosite, their precipitation within metamorphic foliation breaks rocks and facilitates the access of oxidants to the surface of unoxidized pyrite,

CONCLUSIONS (continuation)

- POR values obtained by different methods are comparable,
- PMB method with a minimum precision can still distinguish between POR values close to slope (Site 6) from central zone (Sites 7 and TBT),
- When oxidized material from the slope is used, results obtained by OCM are consistent with TOP results from Site 6 close to slope,
- This means that when transport of O_2 is not a limiting factor, values of POR obtained from small scale experiments may give representative results; this is different from sites like Aitik in Sweden with oxygen transport dominated by diffusion, where POR values depend very much on the scale of experiments.

LIST OF ACRONYMS

A	Contaminated area (hectares)
ADAF	Age-dependent Adjustment Factor
ADD	Average daily dose of a substance from all exposure pathways (mg/kg-day)
ADD_D	Dermally-absorbed average daily dose of a substance from water, including personal cleaning and washing of clothes
ADD_j	Average daily dose of contaminant j (mg/kg-day)
ADD_F	Average daily dose of the substance from food sources (mg/kg-day)
ADD_I	Average daily dose of a substance due to inhalation of air (mg/kg-day)
ADD_O	Average daily dose of a substance due to oral intake of water (µg/kg-day)
ADD_W	Average daily dose of the substance from intake of water (mg/kg-day)
ADD_S	Average daily dose of the substance from intake of soil (mg/kg-day)
ADD_{SD}	Average daily dose of the substance from intake of sediment (mg/kg-day)
AEC	Area of Environmental Concern
AF	The attributable fraction of mortalities or morbidities due to exposure to the pollutant
AT	Averaging time (days or years)
ATSDR	Agency for Toxic Substances and Disease Registry
B	The population incidence of mortality or morbidity (e.g., deaths or hospitalisation rates per 1 000 people)
BAF	Bioavailability factor for substances in air (default 1)
BGR	Bundesanstalt für Geowissenschaften und Rohstoffe. Federal Institute for Geosciences and Natural Resources
BMDL	Benchmark Dose Limit
BW	Body weight of endpoint species (kg)
C	Concentration of substance in air (mg/m3), soil (mg/kg) or water (mg/litre)
C_{ij}	Concentration of contaminant j in medium (mg/kg or mg/litre)
CCME	Canadian Council of Ministers of the Environment
CF	Unit conversion factor
CHS	Contamination Hazard Scenario

CoM	Chamber of Mines
CPT	Cone Penetration Tests
CRA	Cumulative Risk Assessment
CSF	Cancer Slope Factor
CTE	Central Tendency Exposure
Δ_{deaths}	Potential proportion change in mortality associated with a change in the pollutant concentration of 1 µg/m^3
Δ_p	The modelled change in the mean pollutant concentration in µg/m^3
DA_{event}	Absorbed dose per unit skin area per event (mg/cm^2-event)
DME	Department of Minerals and Energy (South Africa)
DWA	Department of Water Affairs (Namibia)
DRA	Detailed Risk Assessment
E	Potential mortalities or morbidities per day or per year due to exposure to the pollutant
ED	Exposure duration (years)
EDGM	Earthquake Design Ground Motion
EEC	Estimated Environmental Concentration on site (mg contaminant/l of water, mg contaminant/kg of soil, mg contaminant/kg of food)
EF	Exposure frequency (days/year)
ERA	Ecological Risk Assessment
EV	Event frequency (events/day)
FAO	Food and Agriculture Organization
FIR	The total food ingestion rate (kg/day)
FIR_i	Intake rate of food type i (kg/day)
FMEA	Failure Mode Effect Analysis
FMECA	Failure Modes Effects Criticality Analysis
Fs	Factor of Safety
GHS	Globally Harmonized System
GPS	Global Positioning System
GSN	Geological Survey of Namibia
HDPE	High Density Polyethylene
HHRA	Human Health Risk Assessment

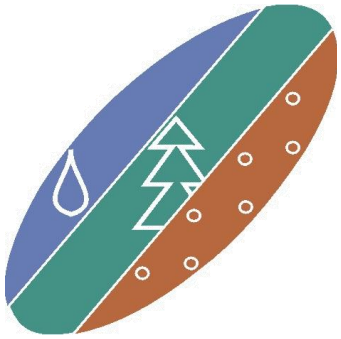
HI	Hazard Index.
HQ	Hazard Quotient.
HR	Home range size (hectares)
IARC	International Agency for Research on Cancer.
ICOLD	International Commission on Large Dams.
ILCRs	Increment Lifetime Cancer Risk.
IMDG	International Marine Dangerous Goods (Code)
IPEP	Institute of Professional Environmental Practice
IR	Daily intake rate of air (m^3/day), soil (mg/day) or water (litres/day)
IR_i	Consumption rate of medium i (kg/day or litre/day)
IRIS	USEPA Integrated Risk Information System.
IRS	Intact Rock Strength
ISO	International Organization for Standardization
ITER	International Toxicity Estimates of Risk
JICA	Japan International Cooperation Agency
LDPE	Low Density Polyethylene
LOAEL	Lowest-Observed-Adverse-Effect Limit
MAC	Maximum Allowable Concentrations
mamsl	metres above mean sea level
MEL	Mining Environmental Liability
MET	Ministry of Environment and Tourism
MIDS	Mine Inventory Data Sheet
MME	Ministry of Mines and Energy
MRLGH	Ministry of Regional and Local Government and Housing
NOAEL	No-observed-adverse-effect-level
NRC	National Research Council (USA)
OEHHA	(California) Office of Environmental Health Hazard Assessment
P	Size of the exposed population (number)
P_i	Proportion of the i^{th} food type in the diet
PCB	Polychlorinated biphenyl
Pf	Probability of Failure

PI	Probability Index
PLPS	Leaching test by synthetic precipitation
PMF	Probable Maximum Flood
Q*	Cancer slope factor $(mg/kg\text{-}day)^{-1}$
QA/QC	Quality Assurance / Quality Control
QEP	Qualified Environmental Professional
RABM	Risk Assessment Base Map
RARF	Risk Assessment Record Form
RBC	Risk Based Concentration
RfD	Reference Dose. Measured in mg/kg-day
RME	Reasonable Maximum Exposure
RR	Risk Ratio
SA	Total skin surface area (cm^2)
SANS	South African National Standards
SD/AMS	Shut Down / Abandoned Mine Site
SHS	Safety Hazard Scenario
SPT	Standard Penetration Test
SRA	Simplified Risk Assessment
SSTL	Site-specific target level
SWCC	Soil Water Characteristic Curve
TDI	Tolerable Daily Intake (has same meaning as RfD)
TSF	Tailings Storage Facility
UCLM	Upper Confidence Limit of the Mean
UNEP	United Nations Environment Programme
URF	Unit Risk Factor
USEPA	United States Environmental Protection Agency
UTM	Universal Transverse Mercator System
UV	Ultra Violet
WHO	World Health Organization

EGG – Environmental Geochemistry Group

Application of extraction and leaching methods and their interpretations





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Presentation outline

- introduction – what is leaching?
- single extractions
- sequential extraction procedures (SEP)
- leaching tests for wastes

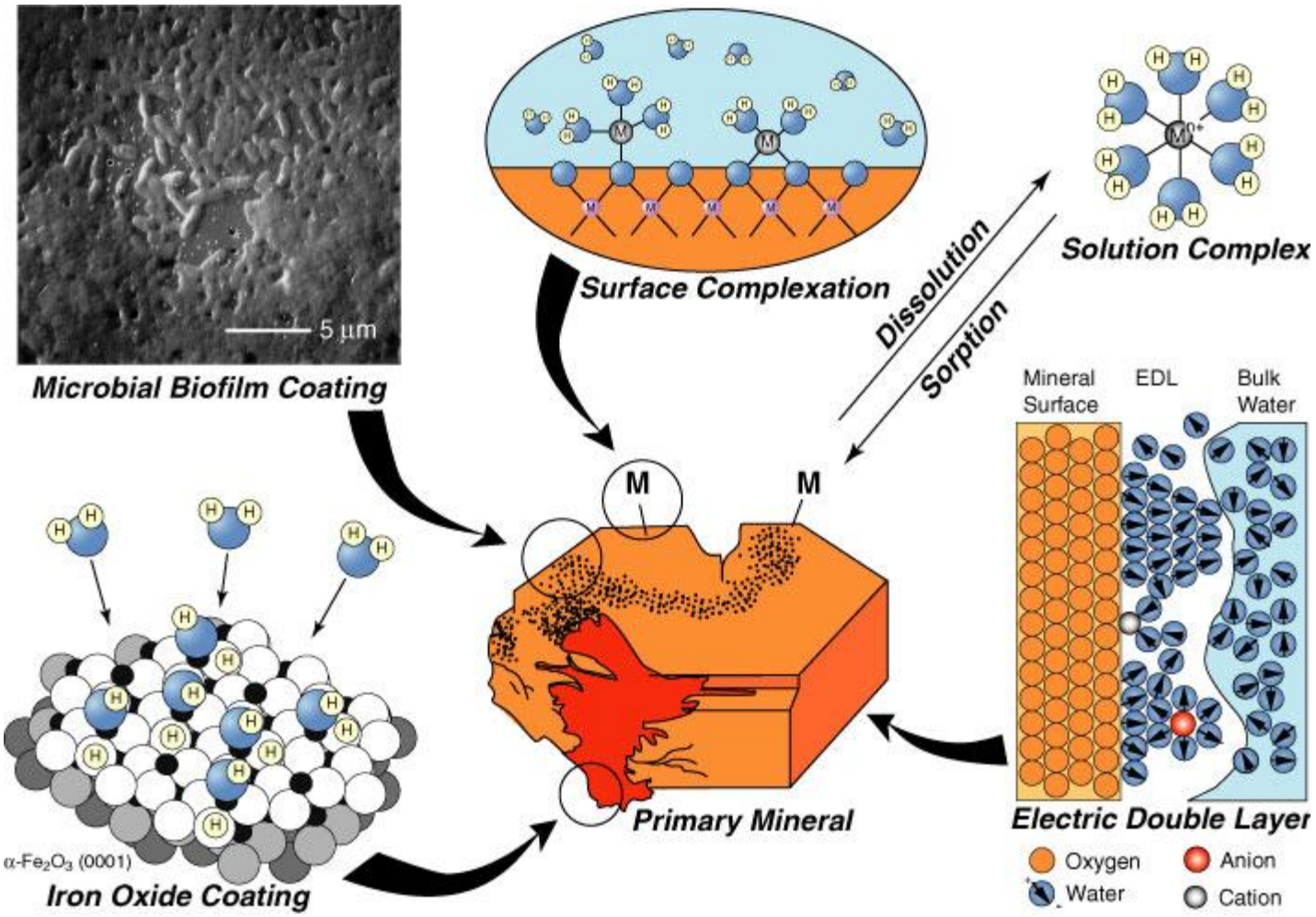
methods and their applicability
problems
certified reference materials

Introduction – why and how?

- *leaching/extraction tests*
- interaction between solution and solid
- analysis of compounds in solution

- application for *contaminants*
- determination of their mobility & bioavailability
- environmental sciences (geochemistry, agrochemistry, waste management)

Leaching process - interactions



Part 1

Single extractions

Methods and their applications

- experimentally simple, easy and quick
- determination of leachability of a given element from the solid to the
- **soils and sediments**

- „bioavailability“, mainly for plants
- „(bio)available“ – leachable in the root zone of plants - rhizosphere

Experimental protocols



- solid sample
- PE bottle
- leaching solution
- liquid-to-solid ratio (L/S)
  L/S = 2 to 10
- time of shaking 1-24 h
- centrifugation – filtration
- solution analysis, recalculation mg/l ➔ mg/kg
- expressed as % element leachability

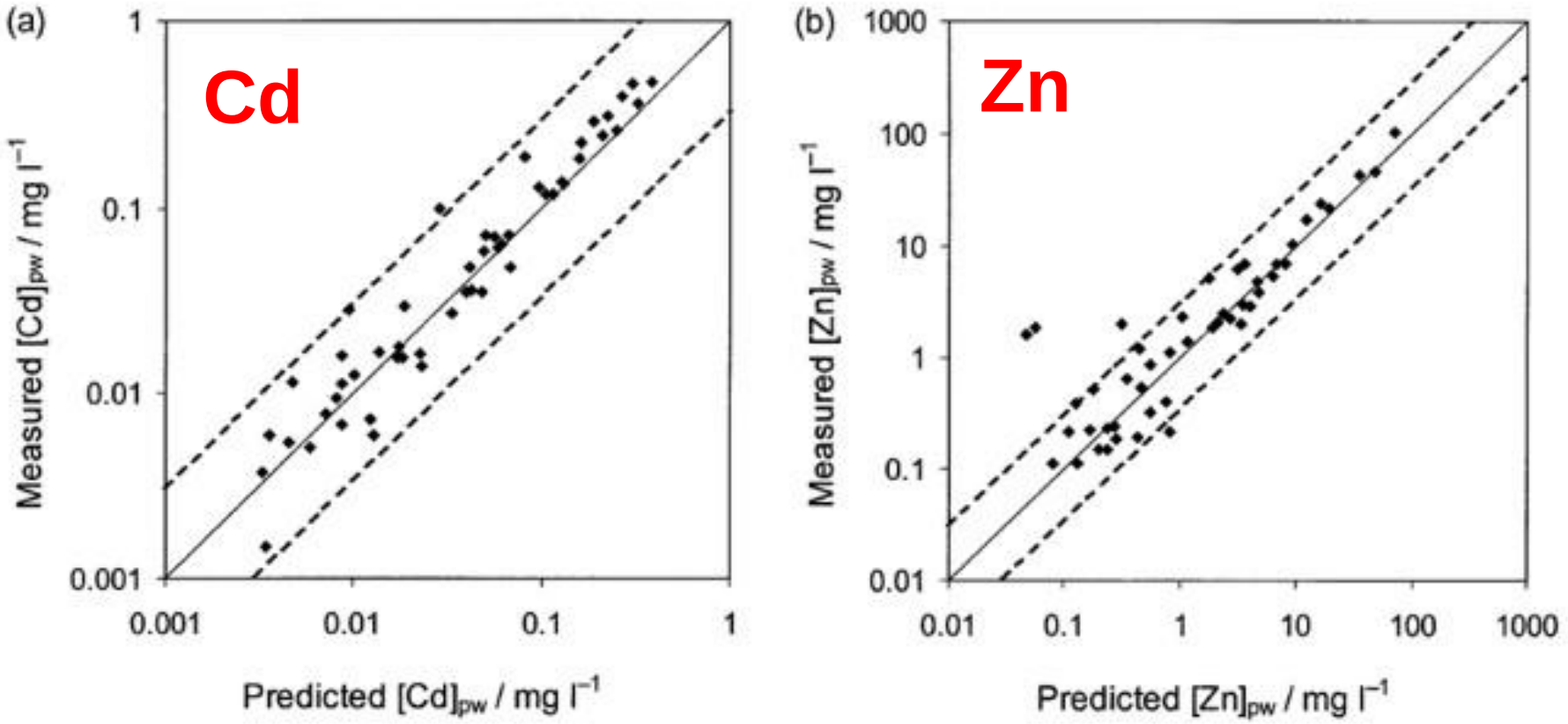
Inorganic extracting solutions

- deionized water
- „exchangeable“ fraction
- 0.01-1 M solutions of inorganic salts

- 0.01 M $CaCl_2$
  composition and ionic strength as a soil solution
- 1 M NH_4NO_3
  standard method (Germany), agrochemistry

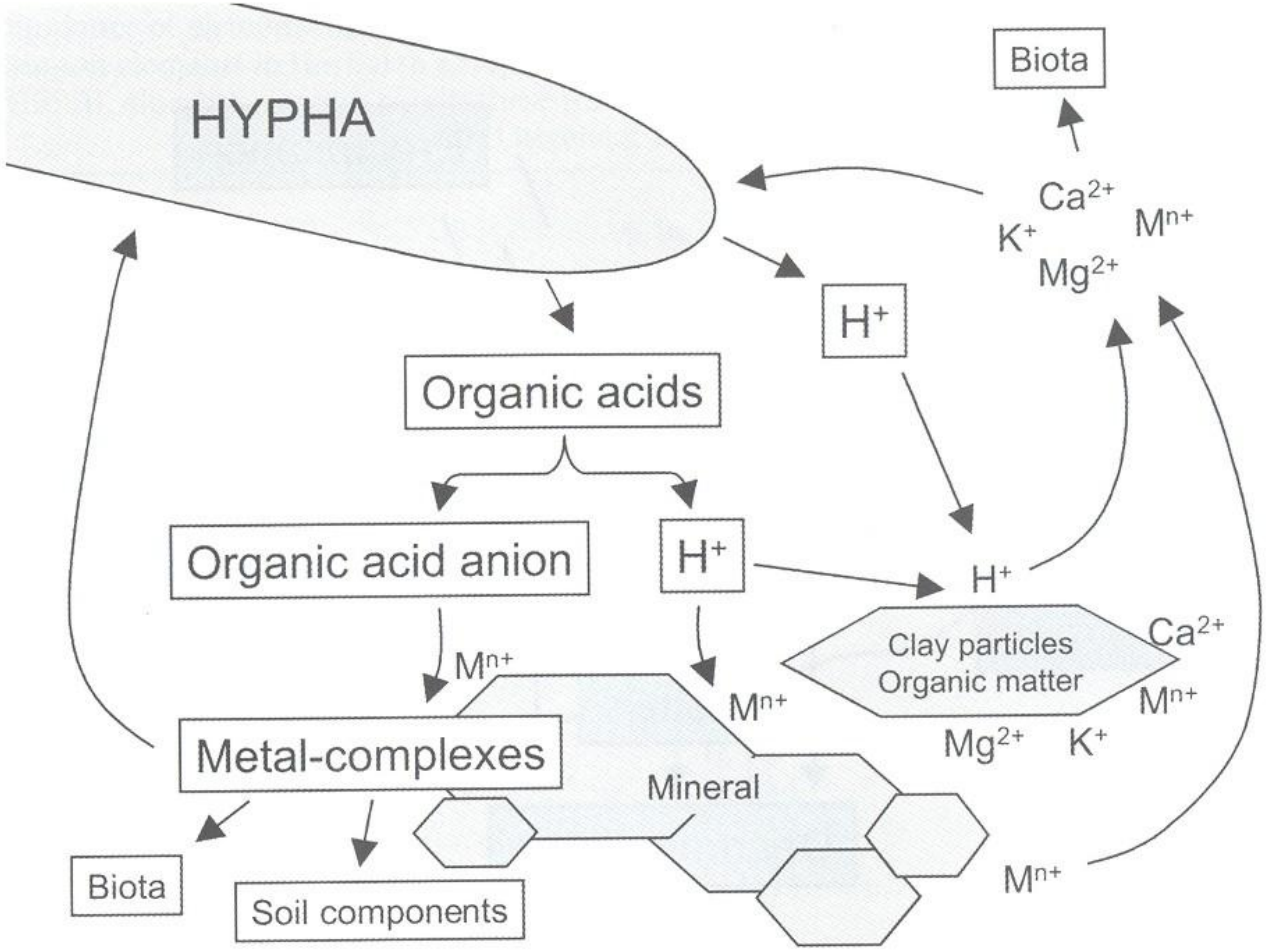
0.01 M $CaCl_2$ extraction - Cd & Zn

Element measured in soil water from lysimeters *versus* in 0.01 M $CaCl_2$



Degryse et al. (2003) *Eur. J. Soil. Sci.* **54**, 149

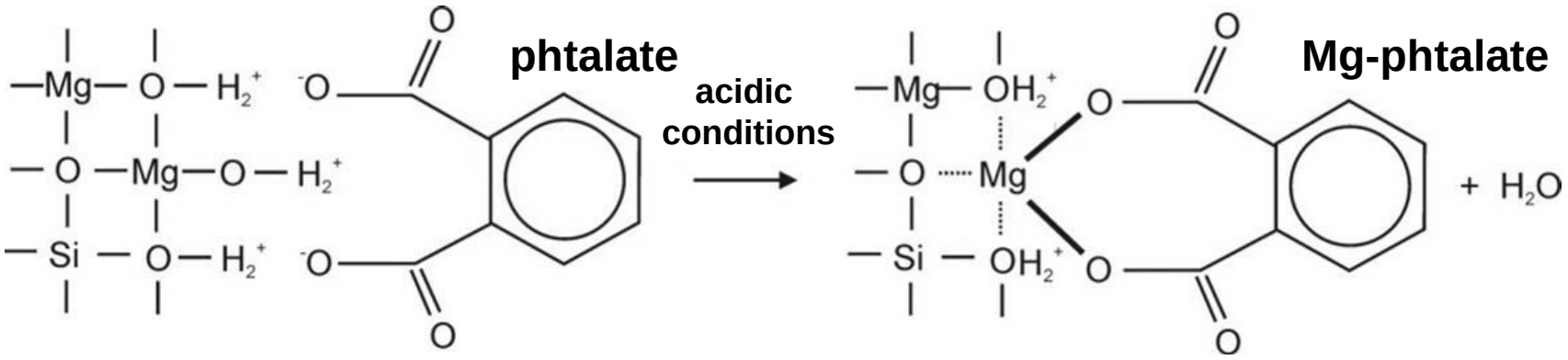
Organic extractants – why?



- acidification
- complexation

fungi hyphae
plant roots

Organic extractants – why?



hydrated surface of a silicate mineral

- chelating reactions
- promoting dissolution of primary minerals



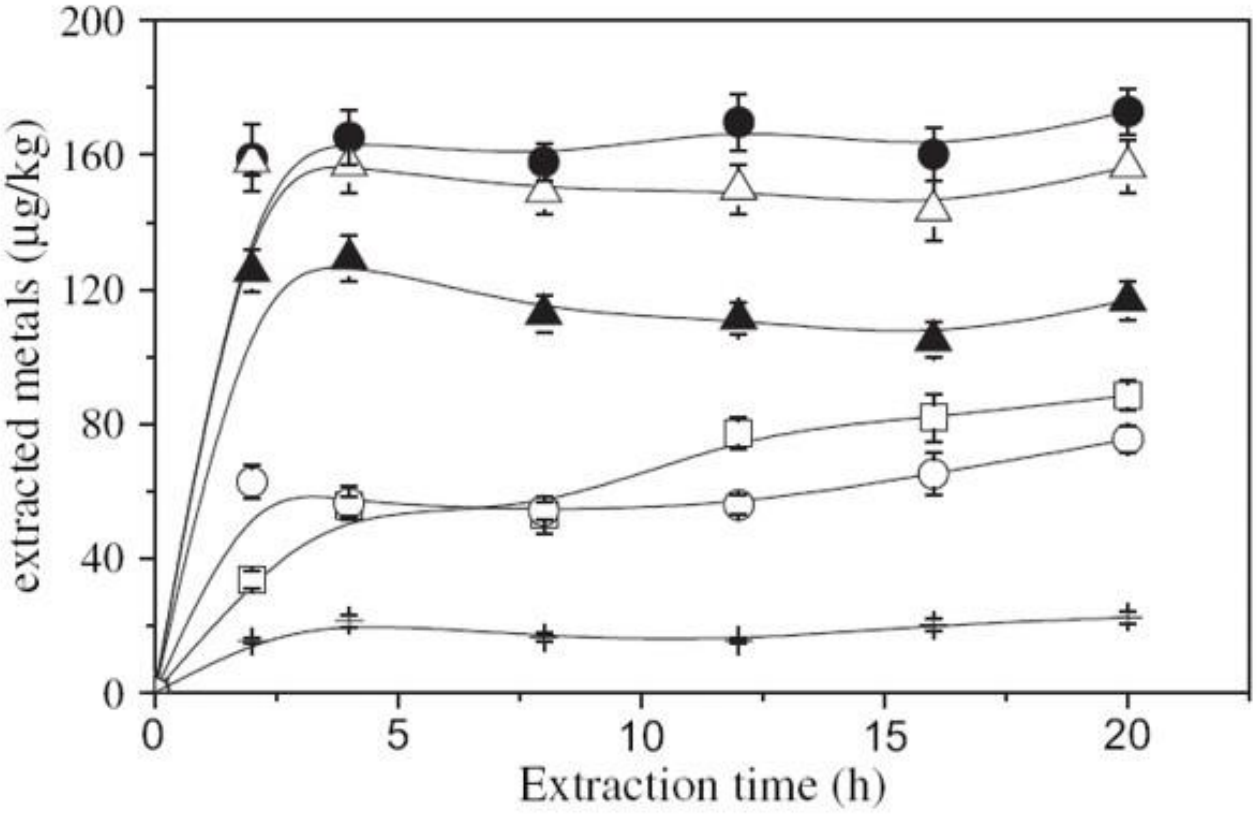
Organic extractants - methods

- acetic acid (0.11-0.43 M)
- EDTA – ethylendiaminetetraacetic a.(0.05 M)
- DTPA – diethylentriaminepentaacetic a. (0.005 M + 0.01 M TEA a $CaCl_2$)

- used in standardized protocols
- often buffered solutions or pH adjusted to the value of 7
- time of extraction 1-2 h

Problem #1 – kinetics of the extraction

Leachability in the mixture of low-molecular-weight organic acids [10 mM]



Feng et al. (2005) *Environ. Pollut.* **137**, 231.

Problem #2 – buffering capacity

- the buffering capacity of extractant can be exhausted during the interaction with soil
- DTPA buffered to pH 7.3
- for highly organic acidic soil >>> lowering the pH of the extract

Eg. Polluted forest soil (37-46% TOC, pH 3.5-3.7). During extraction with DTPA buffered to pH 7.3 the final pH of the extract is 3.4-3.9. Resulting mobile concntration of a given element is a combination of effects related to complexating reactions and pH.

Ettler et al. (2007) *Anal. Chim. Acta* **602**, 131.

Problem #3 - oxyanions

- some contaminant are present as anions
- **As:** [As(III)] **AsO_3^{3-}** & [As(V)] **AsO_4^{3-}**
- **Sb:** [Sb(III)] **$Sb(OH)_3^0$** & [Sb(V)] **$Sb(OH)_6^-$**

- easy binding to ⊕ charged surfaces
  Fe oxyhydroxides at low pH and humic substances *via* aminogroups

$HA\text{-}NH_2 + HX \text{ (weak acid)} = HA\text{-}NH_3^+X^-$

$HA\text{-}NH_3{+}Sb(OH)_6^- + OH^- = HA\text{-}NH_3^+OH^- + Sb(OH)_6^-$

Problem #3 - oxyanions

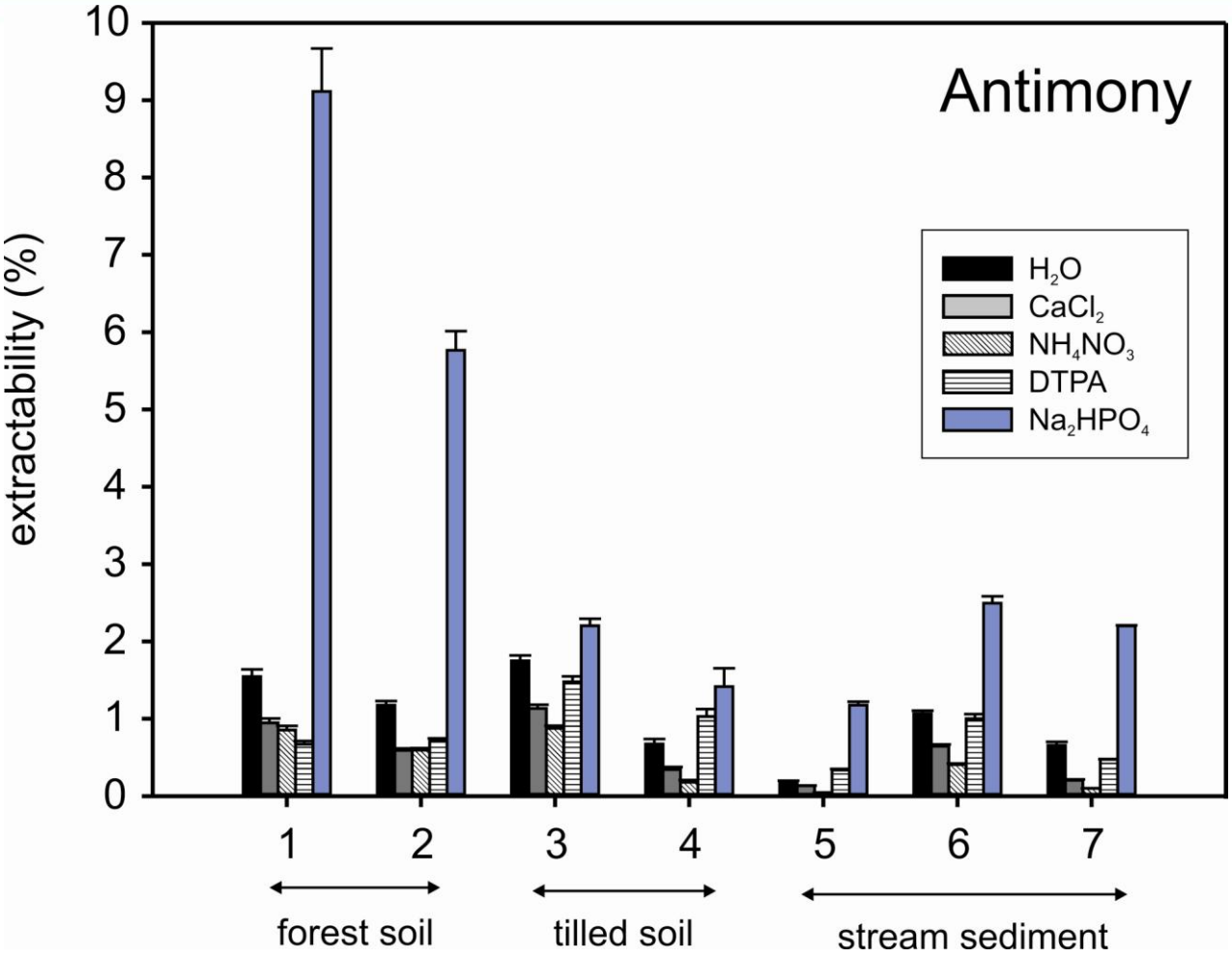
Ion exchange

$Sb(OH)_6^- \leftrightarrow Cl^-$

$Sb(OH)_6^- \leftrightarrow NO_3^-$

Specific sorption

$Sb(OH)_6^- \leftrightarrow PO_4^{3-}$



Ettler et al. (2007) *Chemosphere* **68**, 455.

Certified reference materials (CRM)

- European Commission´s Measurement and Testing Program (IRMM, Belgium)

- EDTA & acetic acid (Cd, Cr, Cu, Ni, Pb a Zn)
  BCR-483 (sewage sludge amended soil)
  BCR-484 (sewage slunge amended terra rosa soil)
  BCR-700 (organic rich soil)

- $CaCl_2$, $NaNO_3$, NH_4NO_3 (indicative values)
  BCR-483

Part 2

Sequential extraction procedures (SEP)

Basic facts

- „selective“ or „sequential“ extraction
- higher number of extracting solutions
- 1 g of sample (sediment, soil)
- successive leaching using extracting solutions with increasing extractability

- based on SEP proposed in 1979 by André Tessier et al.

SEP applications 1970-2006

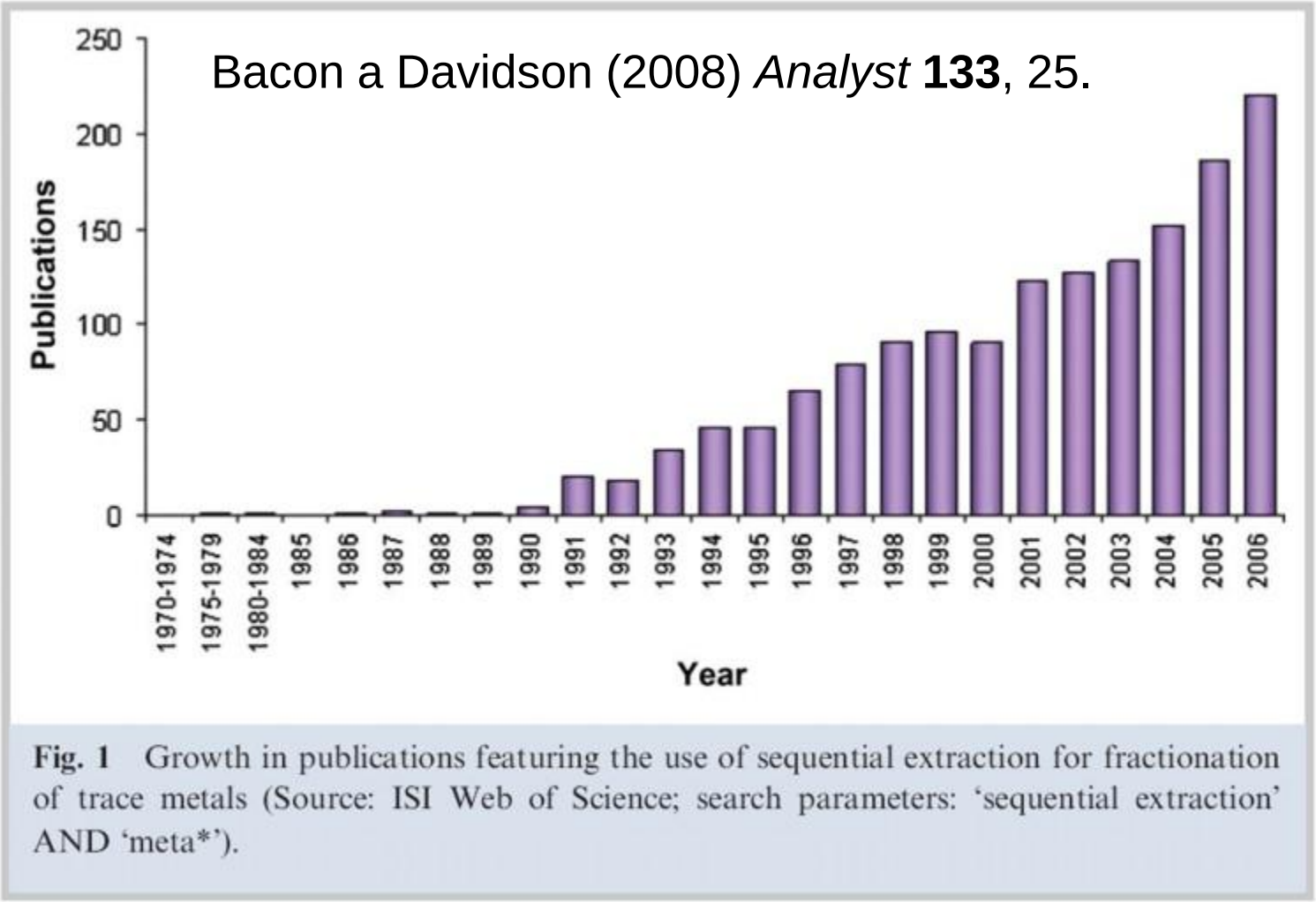


Fig. 1 Growth in publications featuring the use of sequential extraction for fractionation of trace metals (Source: ISI Web of Science; search parameters: 'sequential extraction' AND 'meta*').

SEP according to Tessier et al. (1979)

1. Exchangeable fraction

1 mol/l $MgCl_2$ (pH 7)

2. Fraction bound to carbonates

1 mol/l Na-acetate with acetic acid (pH 5)

3. Fraction bound to Fe & Mn oxides

0.04 mol/l hydroxylamine hydrochloride ($NH_2OH \cdot HCl$) in 25% acetic acid (96°C)

4. Fraction bound to organic matter and sulphides

HNO_3/H_2O_2 (85°C) then ammonium acetate in 20% HNO_3

5. Residual fraction

total digestion in mineral acids ($HClO_4$/HF)

Interpretation of the Tessier´s SEP

1. Exchangeable fraction

sorption to soil sorption complex

2. Fraction bound to carbonates

dissolution under slightly acidic conditions

mobile fractions

3. Fraction bound to Fe and Mn oxides

release during the dissolution of Fe and Mn oxides

4. Fraction bound to organic matter and sulphides

digestion of organic matter and sulphides under highly oxidizing conditions

5. Residual fraction

bound to „residuum“, in silicates and less soluble oxides (e.g. spinels)

SEP according to BCR

- simplified methodology
- **Exchangeable + acid-extractable fraction**
  (0.11 mol/l acetic acid)
- **Reducible fraction**
  (0.5 mol/l hydroxylamine hydrochloride at pH 1.5)
- **Oxidisable fraction**
  (H_2O_2 at 85°C, then 1 mol/l ammonium acetate)

Sum of these fraction substracted from the pseudo--total *aqua regia* digest (HNO_3/HCl = 1/3)
~ residual fraction

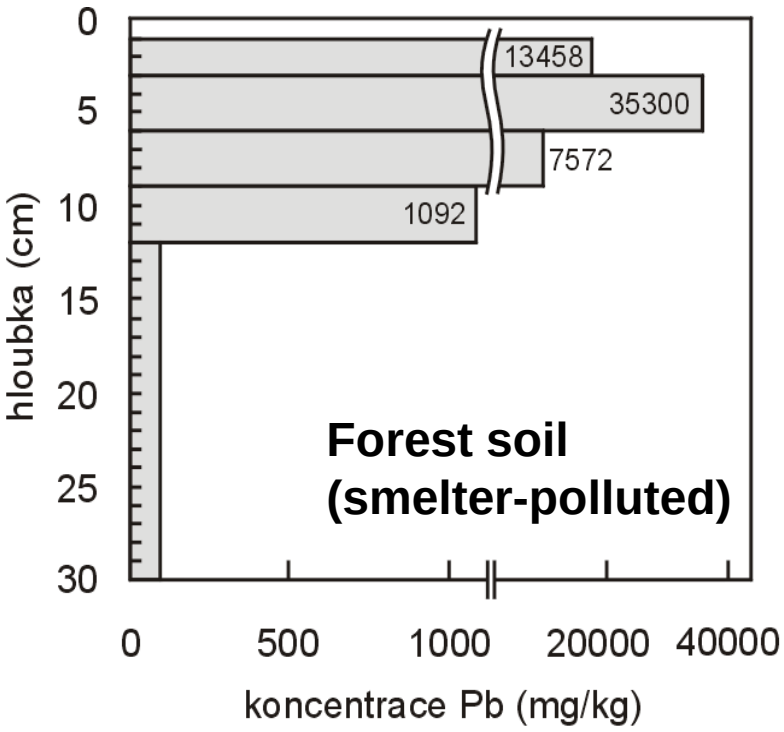
Problem #1 – selectivity of extractants

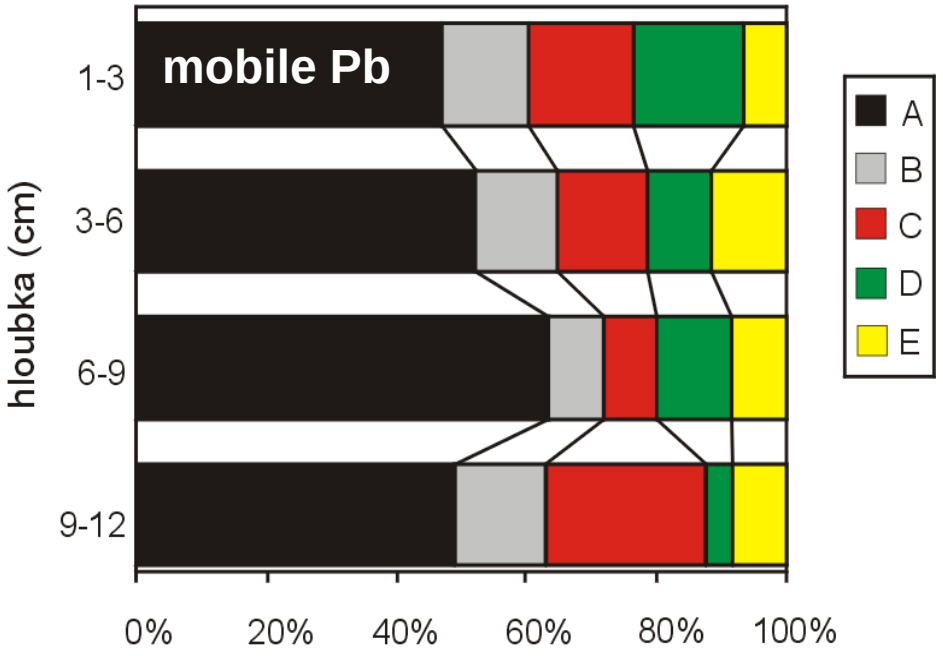
Is the element bound to fraction 3 (Fe and Mn oxides) in the Tessier´s methodology really bound to these oxides?

COULD NOT BE!

- Extracting solutions should be considered as „operationally defined“, in terms of chemical reactivity
- It is important to verify the presence/absence of a given phase using some independent method (XRD, VMP, EXAFS, SEM)

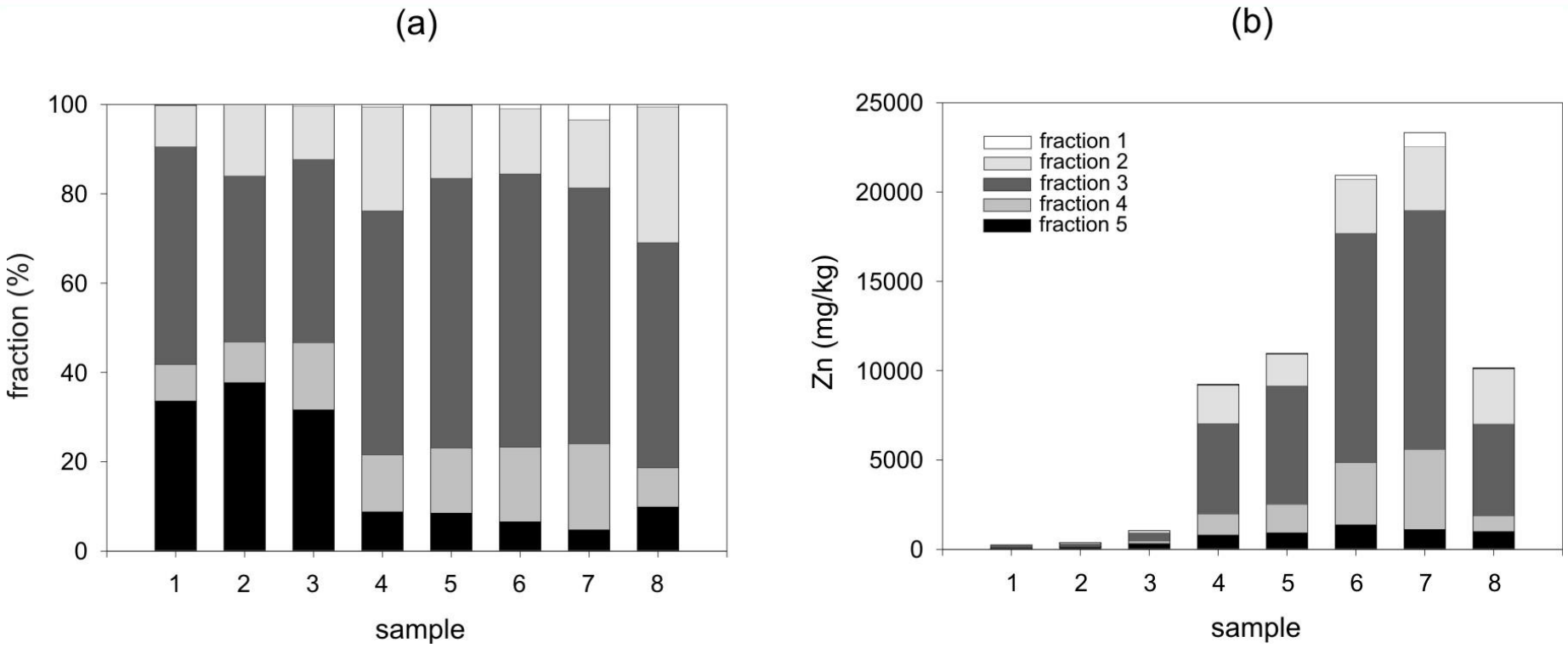
Problem #1 – selectivity of extractants





- Pb bound in mobile (exchangeable fraction), although bound to OM
- OM is also an adsorbing material, to which metals are bound to!!!

Problem #2 – data visualization



- better visualize the data in real concentration than in %
- not misleading!

Problem #3 - oxyanions

- similar problem as for single extractions
- in literature you can find a number of comparative studies and new procedures better suited for oxyanions (mainly As)

Certified reference materials (CRM)

- CRM for standard SEP according to BCR
  BCR-601 (lake sediment, no more available)
  BCR-701 (lake sediment)
  BCR-483 (sewage sludge amended soil)

  values for Cd, Cr, Cu, Ni, Pb, Zn

  in the literature also NIST 2711 (Montana soil) etc

- **application of BCR SEP is the most practical**

Part 3

Bioaccessibility extractions

Human health implications

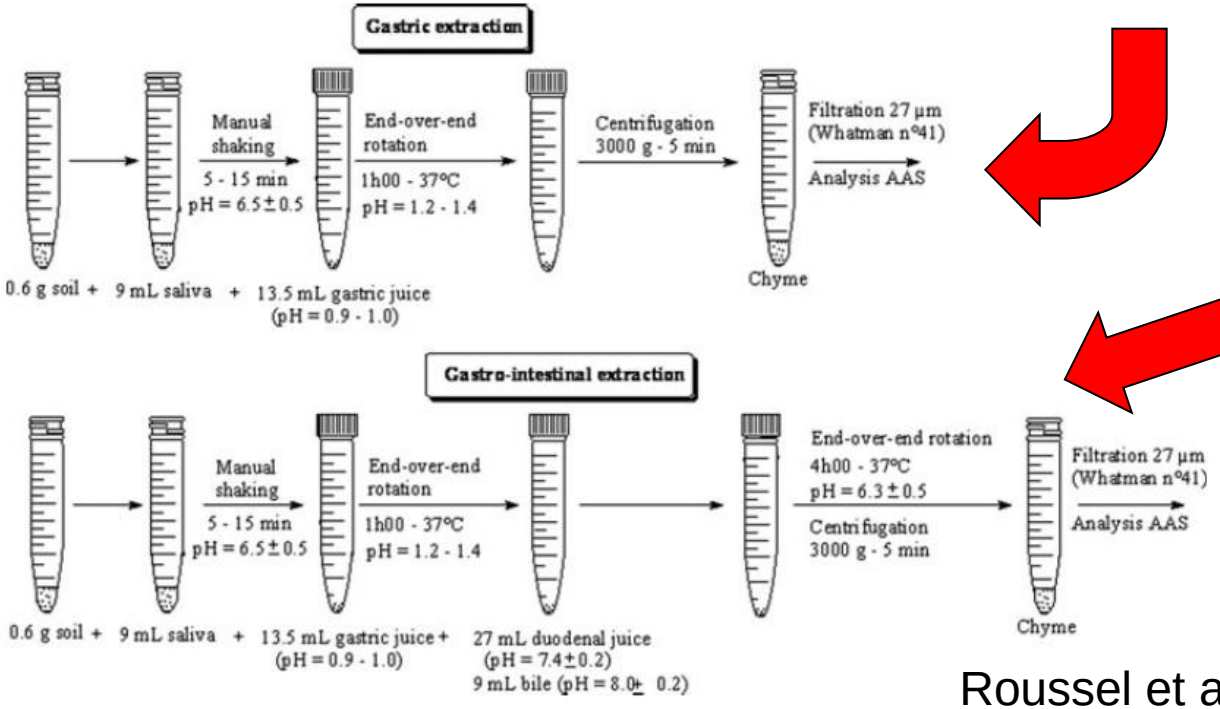
- extraction test *in vitro*

- how contaminants are leached from a given material (soil, dust) in simulated human body fluids?

- gastric bioaccessibility (ingestion)
- lung bioaccessibility (inhalation)

Gastric bioaccessibility

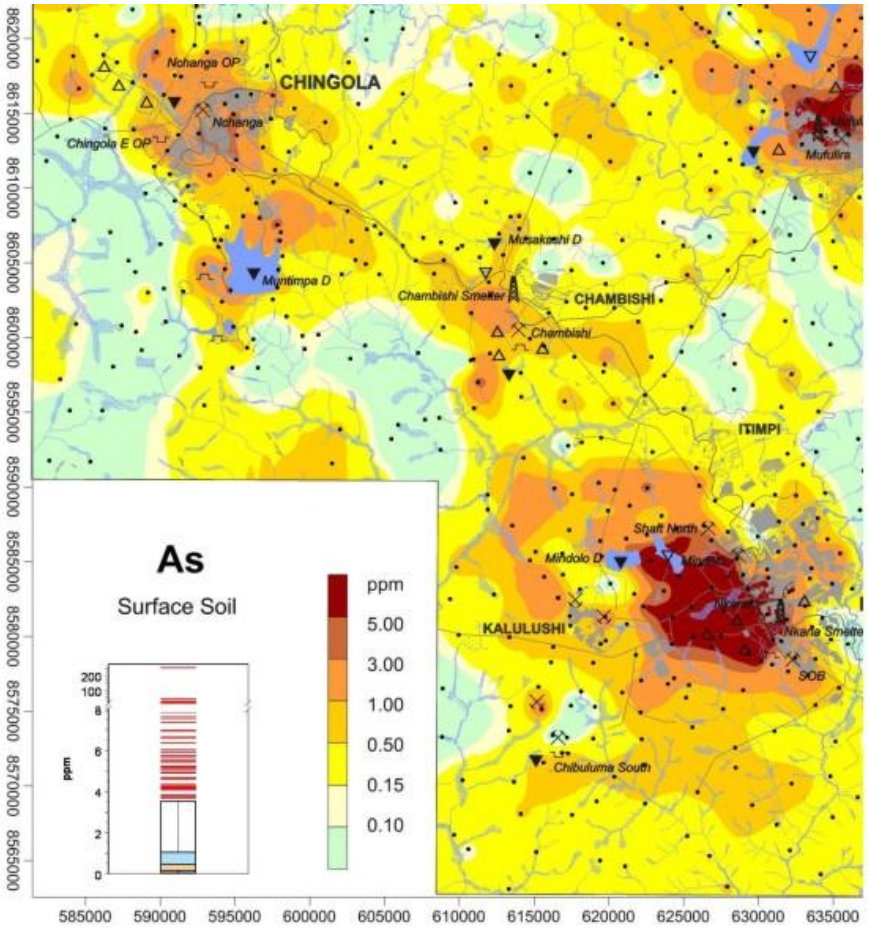
- soil ingestion (pica behaviour)
- Simple Bioaccessibility Extraction Test (SBET) – US EPA
- gastric fluid simulation
- 0.4 M glycine, pH 1.5 (HCl), L/S = 100, 2 h extraction at 37°C

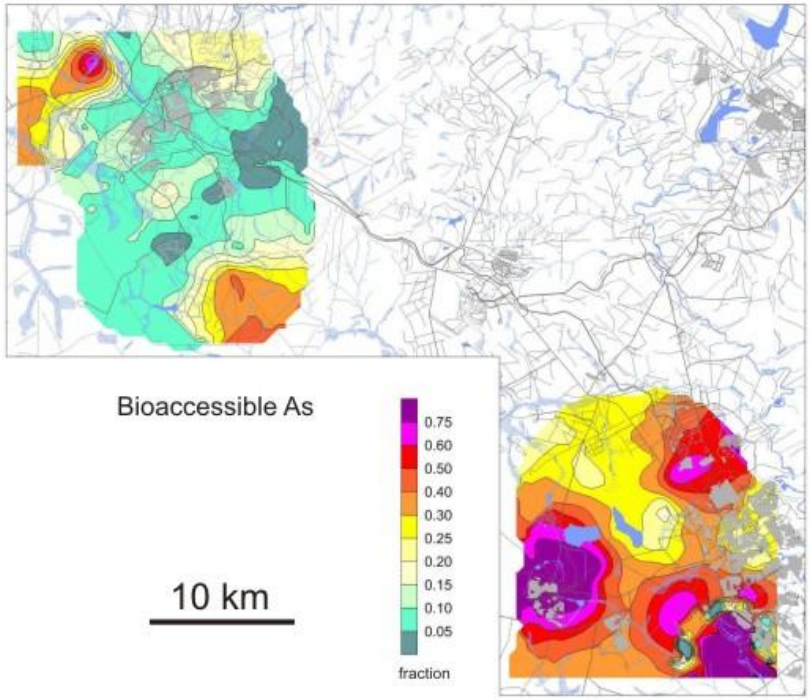


Gastro-intestinal Extraction
Step 1. pH ~ 1
Step 2. pH = 7

Roussel et al. (2010): *AECT* **58**, 945.

Example: mining/smelting soils in Zambia





Bioaccessibility:
As, Pb (81-100%)
Co, Cu, Zn (58-83 %)

Ettler et al. (2012) *J. Geochem. Explor.* **113**, 68.

Lung bioaccessibility

- only solid of grain size < 10 μm should be taken
- fraction accessible for inhalation
- simulated lung fluid:

  NaCl (110 mM), $NaHCO_3$ (31 mM), Ca acetate (2.5 mM)
  $CaCl_2$ (2.5 mM), Mg acetate (1 mM), $MgCl_2$ (1 mM)
  KH_2PO4 (2 mM), K_2SO_4 (1 mM), citric acid (1 mM)
  albumin (0.2 g/l)

- L/S = 20, 37°C, 6 days leaching to attain equilibrium

Twining et al. (2005) *Environ. Sci. Technol.* **39**, 7749.

Part 4

Leaching tests for mineral wastes

Why?

- determination of hazardous properties (**contaminant release/leaching**)
- standardized leaching tests
- defined by legislation at national and at international level

E.g.
*Germany (norms DIN, **www.din.de**)*
*France (norms AFNOR, **www.afnor.fr**)*
*Netherlands (norms NEN, **www.nen.nl**)*

EU framework – www.leaching.net

Network on Harmonization of Leaching/Extraction Tests

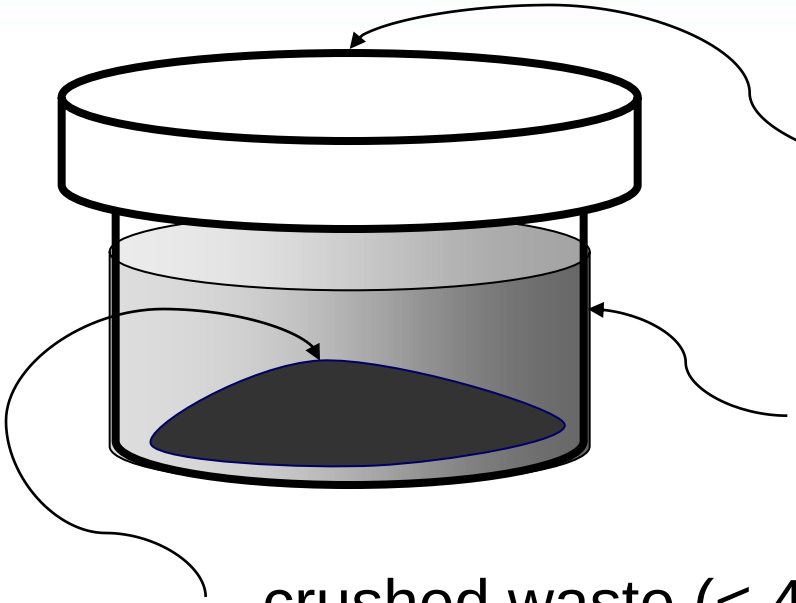
- definition of EU testing methods under CEN (Comité Européen de Normalisation)
- norms **CEN TC 292 WG6 - Characterization of waste** (partly validated, some tests under construction)
- based on national tests applied for waste testing and international ISO norms

EN 12457

- first part ” Characterization of waste” validated in EU states as **EN 12457 (parts 1-4)**

Characterisation of waste - Leaching -Compliance test for leaching of granular waste materials and sludges

Batch leaching test EN 12457



- shaked on a table shaker for 24 h
- filtration (0.45 µm) and analysis of leachate
- limit criteria (inert, non-hazardous, hazardous)

Limit criteria (test EN 12437-2, L/S = 10)

mg/kg	NH/N non-hazardous	H hazardous
As	2	25
Cd	1	5
Cr	10	70
Cu	50	100
Hg	0,2	2
Pb	10	50
Sb	0,7	5
Zn	50	200

If the limit for hazardous waste is exceeded, the material must be stabilized/solidified and test repeated before being landfilled.

Problem #1

Advantages of the batch test:

- simple experimental protocol
- quick and cheap

Drawbacks of the batch test:

- only short-term interaction (24 h)
- solid sample and liquid may not be in equilibrium
- no long-term predictions can be done using this batch test

pH-static leaching test

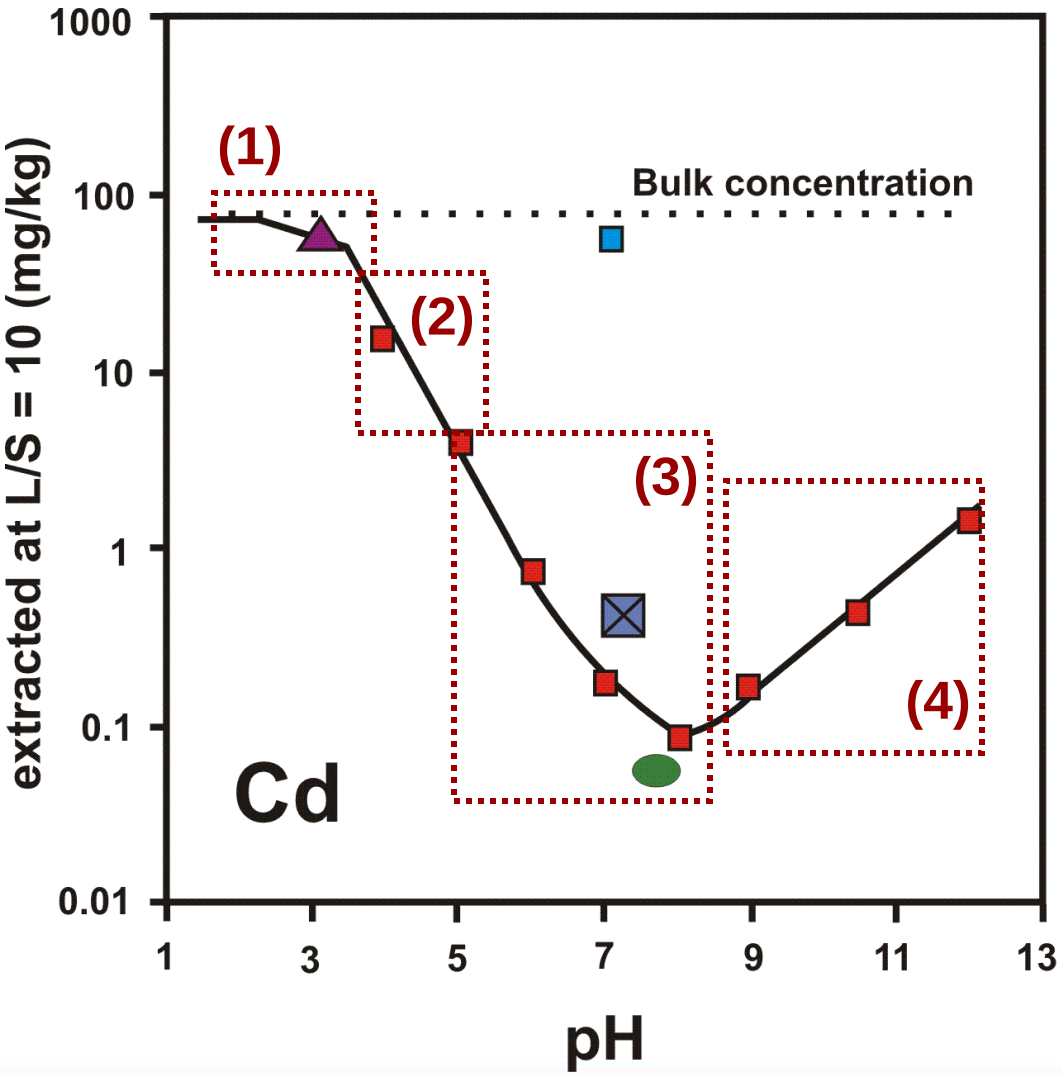
- paralel extractions at L/S = 10 (for 48 h) at a range of pH (at least 8 values of pH)
- pH controlled by addition of HNO_3 or NaOH

- **CEN/TS 14429 – pH dependence leaching test (initial acid/base addition) – published 2005**
- **CEN/TS 14997 – pH dependence leaching test (continuous pH control) – published 2006**

Experimental setup of pH-stat test



Output of the pH-stat test



(1) ingestion

(2) acidic soils

(3) neutral soils

(4) stabilized soils (cementation)

Problem #2

Advantages of the pH-stat test:

- information useful for geochemical modelling
- pH is a key parameter influencing the leachability
- material behaviour in extreme conditions (worse-case scenario)

Drawbacks of the pH-stat test:

- interaction process may not be in equilibrium even after 48 hours of leaching
- installation of natural steady-state pH not possible

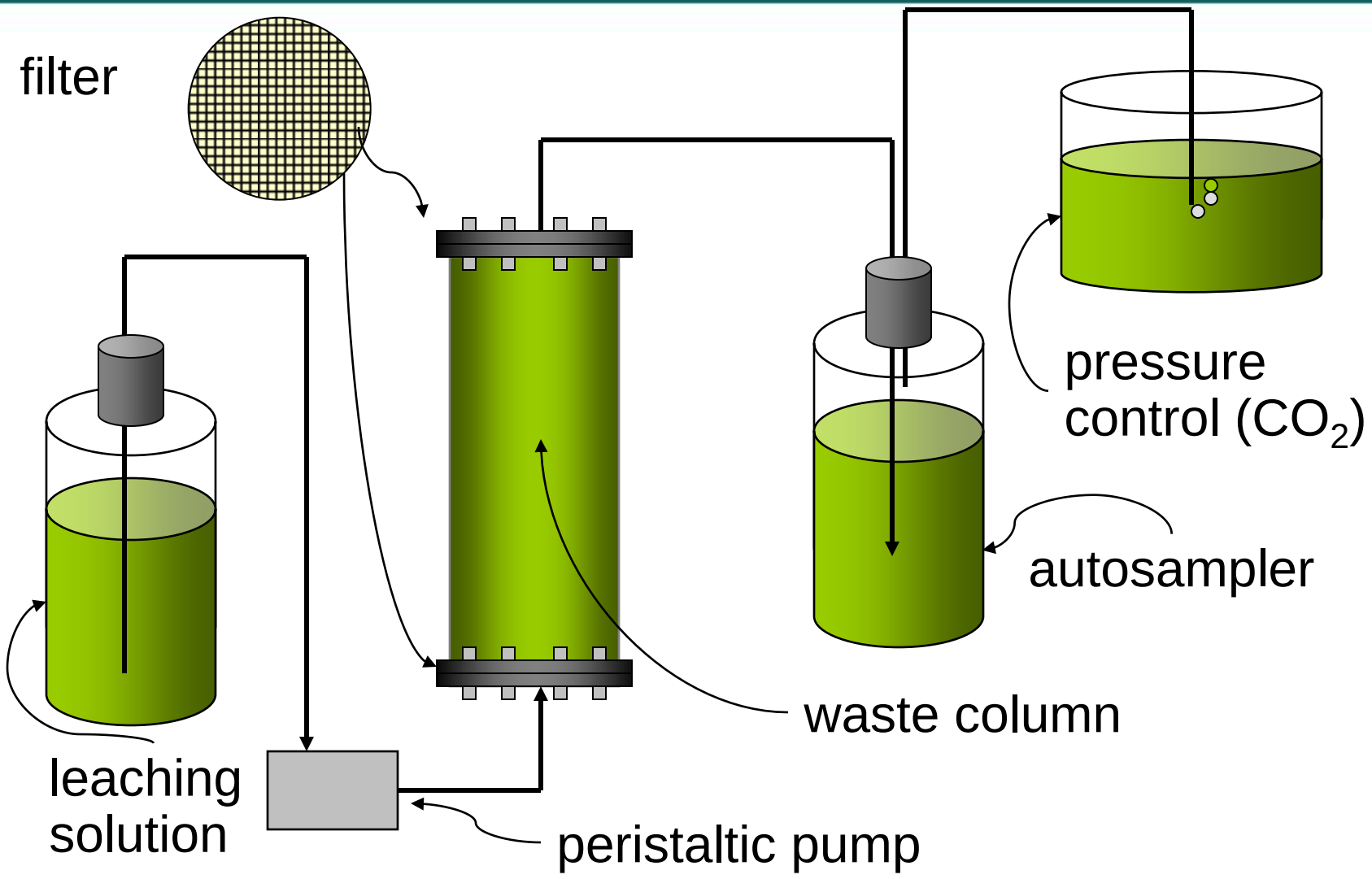
Column leaching test (percolation)

Percolation test (CEN/TS 14405 - column test) with up-flow setup
- published 2004

- based on Dutch test NEN 7343 crushed sample, 95% of grains
- must be < 4 mm
- 0,8 l of sample is leached (ca. 3 kg)
- procedure of sample insertion in the column is strictly defined in the norm



Experimental setup



Experimental setup

- flow in the column is ca. 15 cm/day
  (12 ml/h for column ∅ 5 cm, 48 ml/h for ∅ 10 cm)
- sampling of leachate fractions

cumulative ratio L/S (liquid-to-solid in l/kg)
- volume of solution interacting with waste solid
- total of 7 fractions
  L/S = 0,1; 0,2; 0,5; 1,0; 2,0; 5,0; 10,0

- filtration and subsequent analysis of the leachate
- experiment duration ca. 30 days

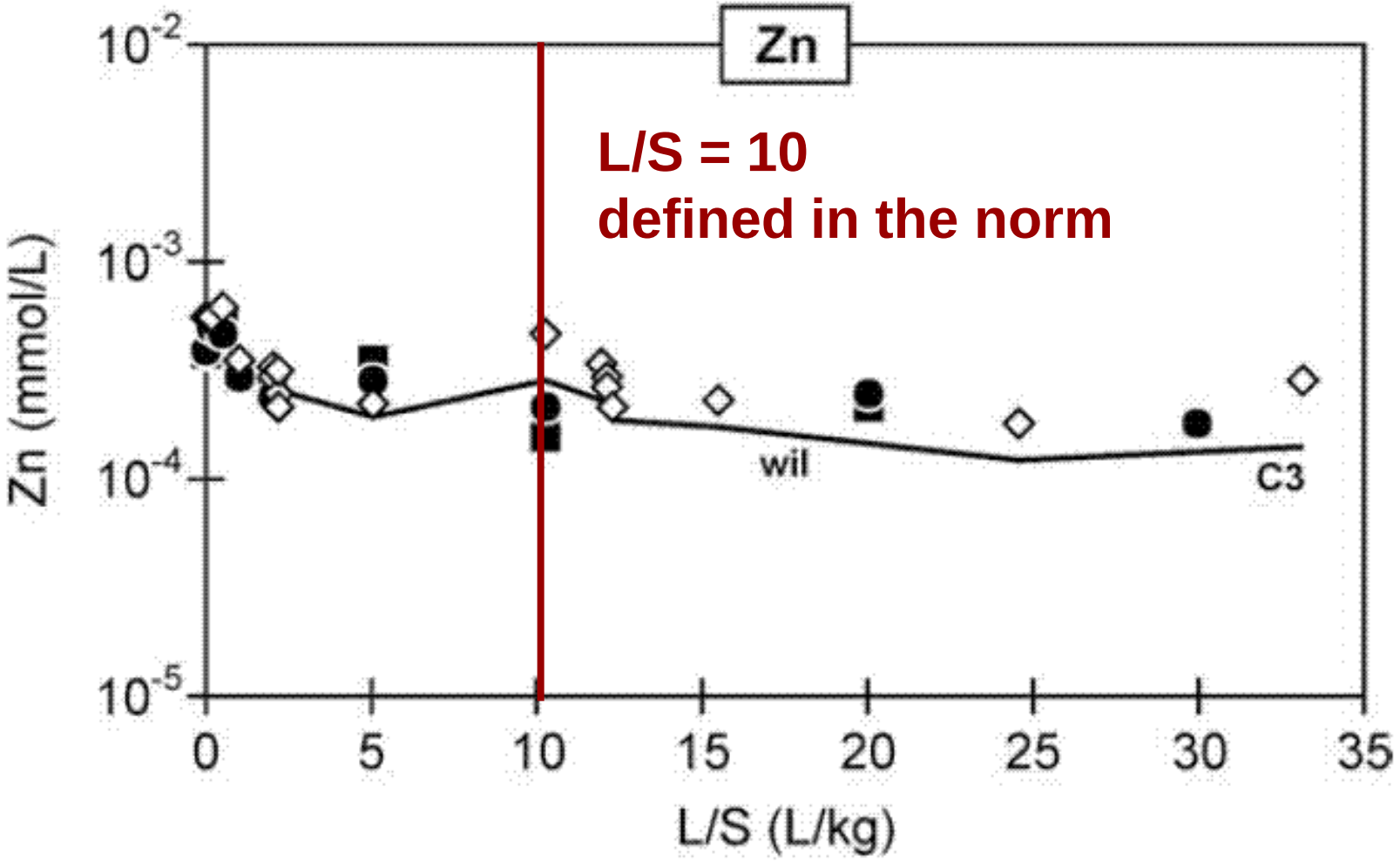
Experimental setup of column test



Replication of experimental columns

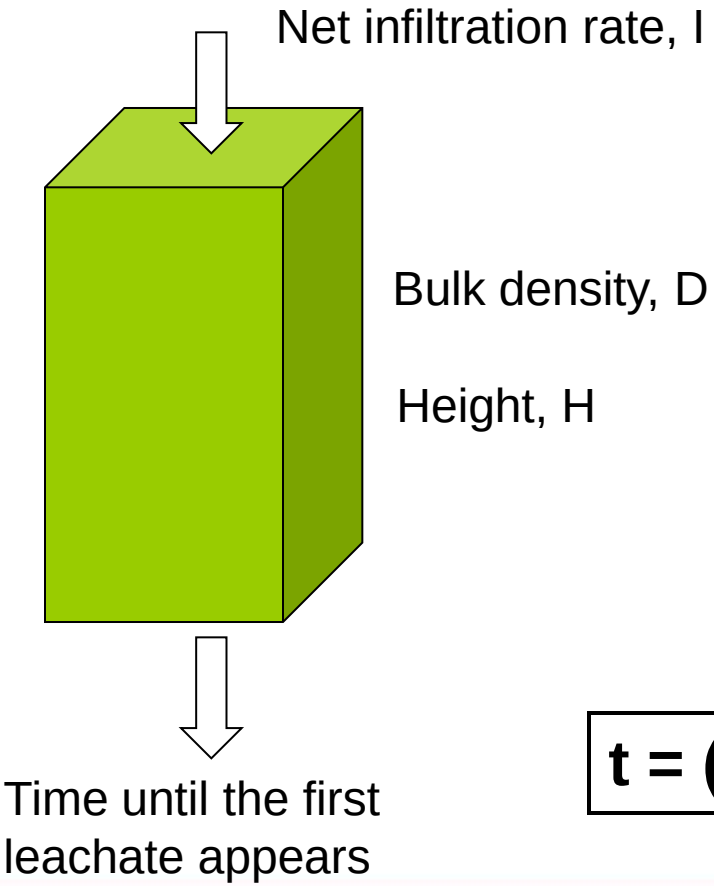


Output of the column leaching test



L/S concept – what the L/S ratio says?

Liquid to solid ratio defines the volume of water that has been in contact with one kilogram of solid material



L/S = (I * t) / (D * H)
t = (L/S * D * H) / I

Example:
L/S = 2 L/kg
D = 1 kg/dm^3
H = 10 m
I = 200 mm/yr

t = (2 * 1 * 10)/0.2 = 100 years

Problem #3

Advantages of the column test:

- better simulates real-life conditions (scenarios) such as dumping in a disposal site
- longer-term test

Drawbacks of the column test:

- sometimes difficult interpretation
- preferential path of water percolation through the column

Leaching results - interpretations

- **availability** (combination with *in situ* experiments)
- **geochemical behaviour**
  (combination with geochemical models:
  PHREEQC-2, ORCHESTRA - speciation, sorption,
  ionic exchange, precipitation of solids)
- **mobility in a disposal site**
  (combination with speciation/transport modelling
  PHAST)
- **mineralogical studies** (speciation in solid phase)

Concluding remarks

- *extraction/leaching methods*
- routinely used in environmental sciences *s.l.*
- relatively cheap tools in comparison with e.g. biological techniques
- studies on contaminant mobility and various geochemical interactions between solid and solutions
- CRM available for some extraction (QC/QA feasible)

Literature – see for example:

Journals:

Analytica Chimica Acta
TrAC-Trends in Analytical Chemistry
Analyst
Environmental Science & Technology

Internet:

www.leaching.net

Thanks for your attention!

Questions?

ettler@natur.cuni.cz

IGCP/SIDA 594 Training course, University of the Witwatersrand, Johannesburg, July 13-15, 2013

Methods of environmental monitoring in mining areas: The Zambian Copperbelt Case Story

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One of the tools enabling to assess the effect of mining and mineral processing on the environment and human health is **environmental-geochemical monitoring**

Regional environmental-geochemical mapping and monitoring involve in particular:

- The **localization and identification** of the sources of contamination
- The **elucidation of the mode of contaminants spreading**
- The determination of **areal extent and intensity of contamination**
- The estimation of **harmful properties and biotoxicity** of contaminants
- The **proposal for application of the most efficient methods** to improve land remediation and land-use planning

SOURCES OF ANTHROPOGENIC CONTAMINATION IN MINING AREAS

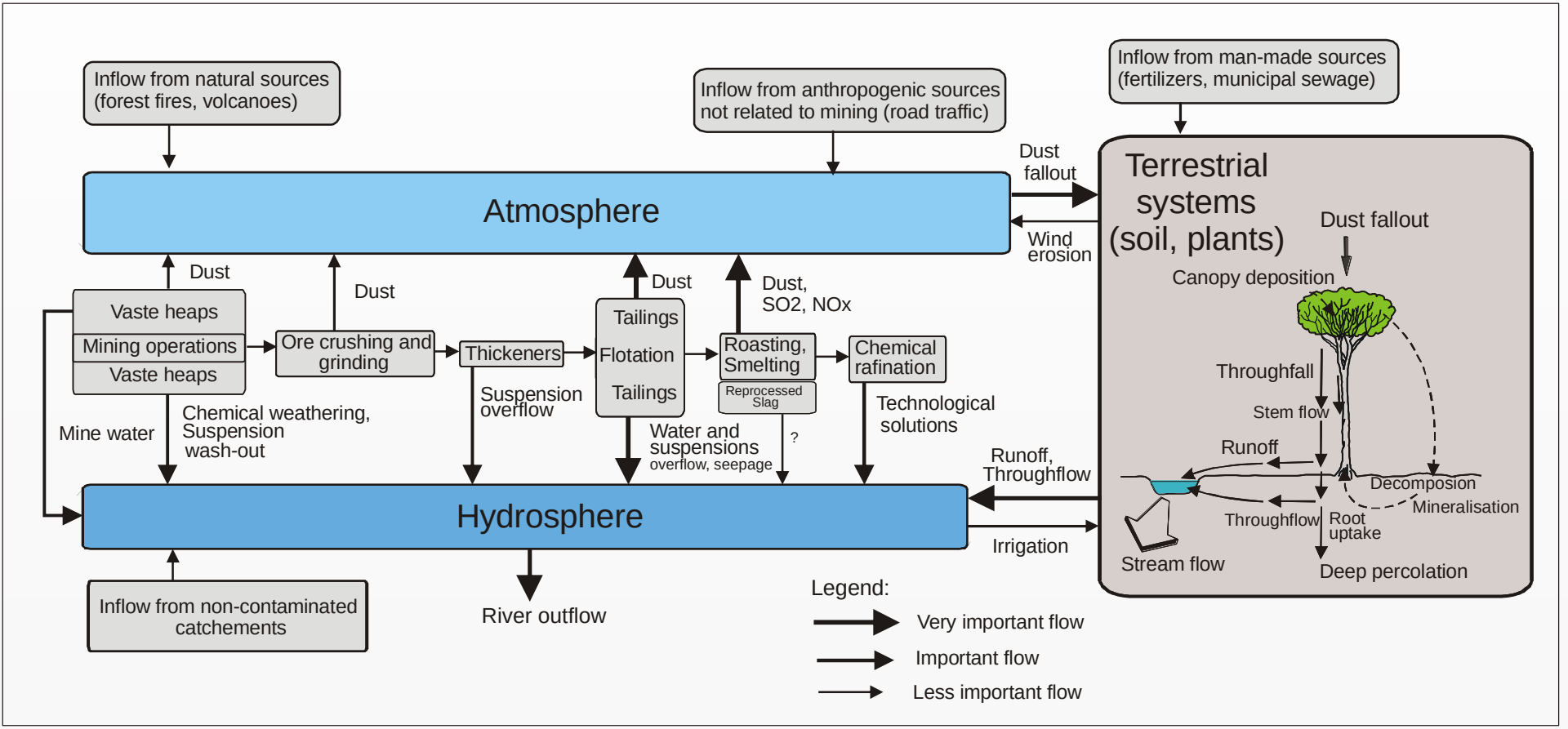
Soils and Plants:

- Gaseous and solid emissions from smelters
- Dust from dry parts of tailing impoundments
- Dust from mining operations, processing plants and slag deposits
- Transport of concentrate and products

Surface Waters and Stream Sediments

- Industrial water discharged into the watercourse
- Seepage and owerflow from tailing impoundments
- Erosion and washout of fine-grained particles from spoil banks and tailing impoundments (siltation)

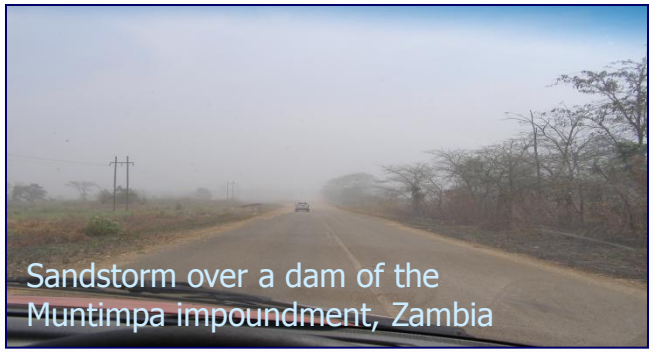
ROUTES OF POLLUTANTS INTO ENVIRONMENT IN MINING DISTRICTS



SOURCES OF ANTHROPOGENIC CONTAMINATION IN MINING AREAS - DUST



Sandstorm over a dry beach of the Mindolo impoundment, Copperbelt, Zambia, Zambia



Sandstorm over a dam of the Muntimpa impoundment, Zambia

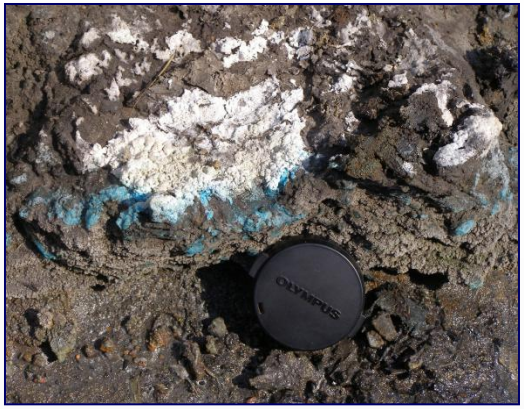


Sandstorm over the Mufulira impoundment

SOURCES OF ANTHROPOGENIC CONTAMINATION IN MINING AREAS - SEEPAGE



Chambishi tailing pond seepage, Chambishi, Zambia



Chalcantite and gypsum precipitates, the Uchi River, Kitwe, Zambia



Muntimpa tailings pond seepage, Zambia

SOURCES OF ANTHROPOGENIC CONTAMINATION IN MINING AREAS - SILTATION



Collapse of the Luanshya tailings dam, Copperbelt, Zambia



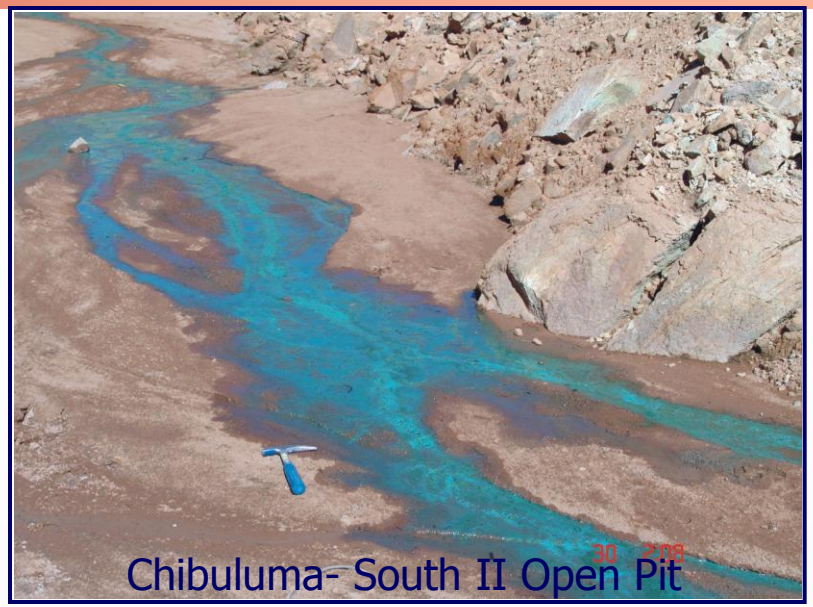


Siltation of the Chingola River, Chingola, Zambia

SOURCES OF ANTHROPOGENIC CONTAMINATION IN MINING AREAS – TECHNOLOGICAL WATERS FROM CHEMICAL LEACHING PLANTS



Chambeshi River, whitish precipitates of carbonates and gypsum, efluents from the Chambishi Chemical Plant



Chibuluma- South II Open Pit



Technological water from the Nkana Smelter and Processing Plant

BOX 1 Soil sampling

- **Each soil sample is a composite of 3-5 sub-samples collected from sampling sites located at the distance of 10-20 m from each other. Soil samples may be collected from soil pits or using soil auger.**
- **Two different depth-related samples should be collected:**

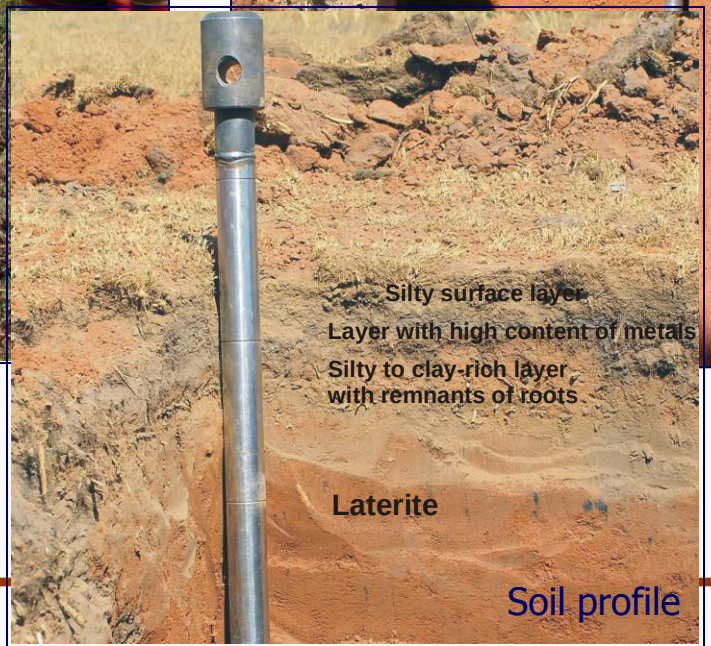
  (1) A topsoil sample from the 0 to 25 cm depth (excluding material from the organic-rich layers where present) and,

  (2) lower soil (subsoil) sample from a 25 cm thick section within a depth range of 50-100 cm.
- **Comparison of topsoil and subsoil data gives information about enrichment or depletion processes between soil layers.**
- **Topsoil and subsoil samples (0.5-1 kg) have to be dried on paper or plastic dishes and sieved using plastic sieving set equipped with nylon mesh (2 mm). The < 2mm fraction (50-100 g) is recommended to homogenize in agate ball mill to analytical fineness (< 0.063 mm)**
- **Recommended soil sampling density for local phase of survey: 1 – 10 samples for km^2**
- **Recommended soil sampling density for detailed phase of survey: 10 – 100 samples for km^2**

SOIL SAMPLING



Sampling of subsurface soil with soil auger



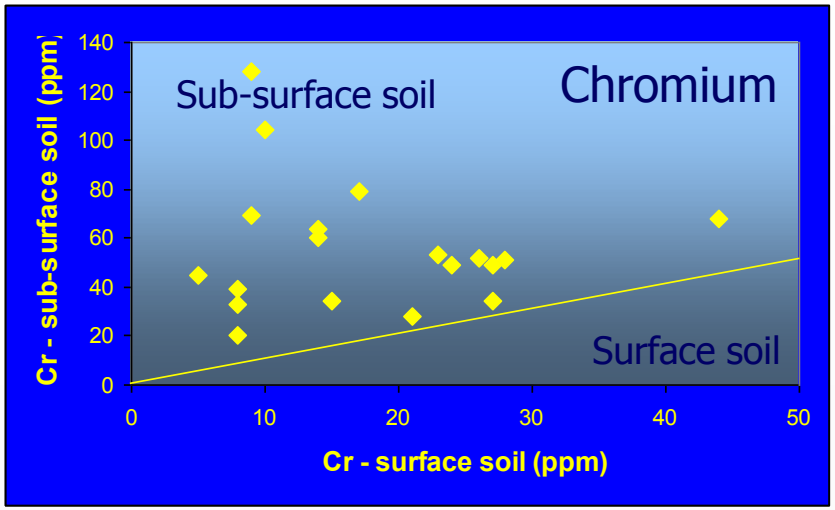
Soil profile

SOIL SAMPLING

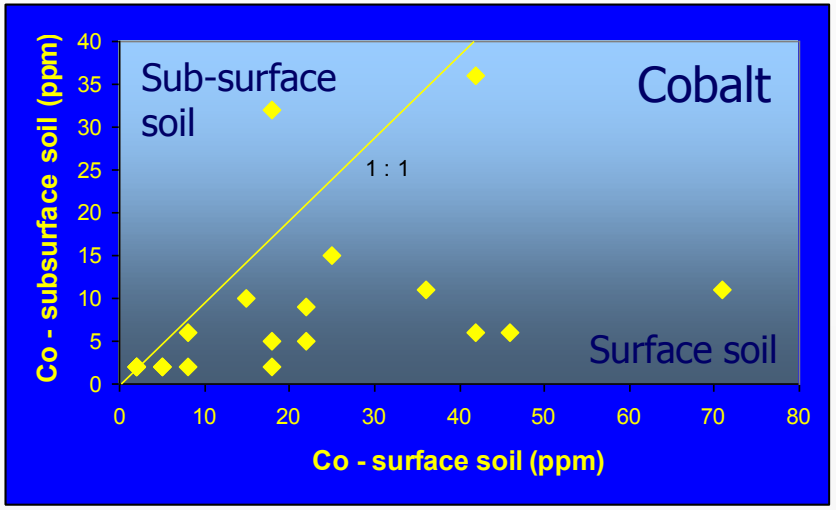
Distribution of metals in soils

– Surface *vs.* sub-surface soil concept

Higher concentration of chemical element in sub-surface soil compared to its concentration in surface soil indicates its geogenic origin. This is typical for Cr, Ni and V.

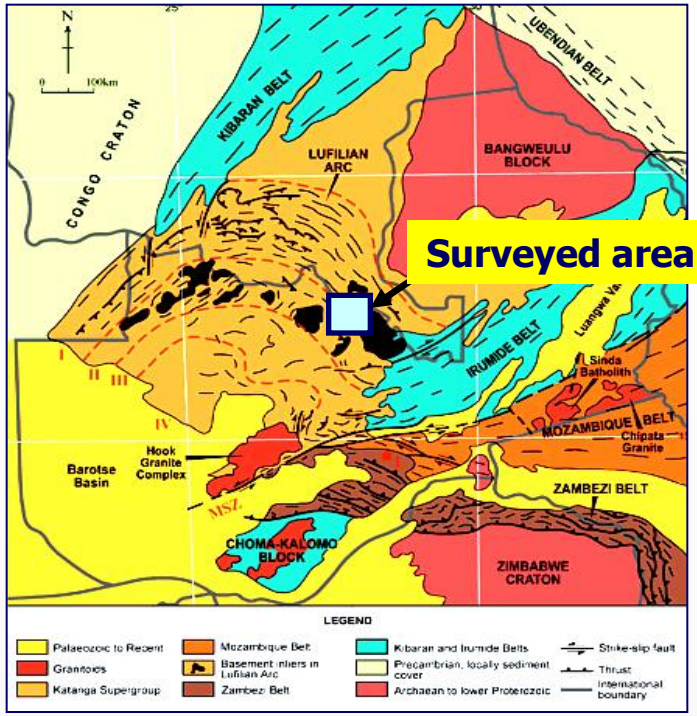


Higher concentration of chemical element in surface soil compared to its concentration in sub-soil indicates an anthropogenic contamination. This is characteristic for As, Co, Pb, Zn, Hg and S.



Straight lines in graphs correspond to the $Metal_{(surface\ soil)}$ /$Metal_{(sub\text{-}surface\ soil)}$ concentration ratio=1

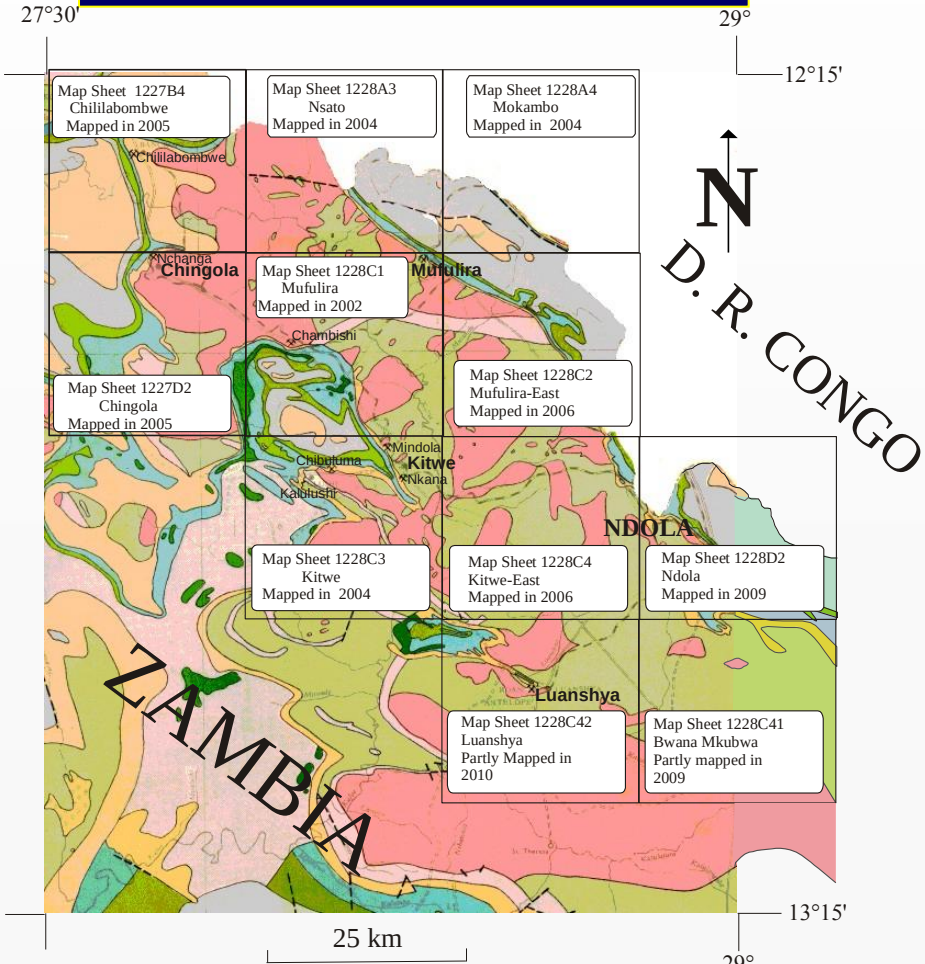
GEOLOGICAL MAP OF ZAMBIA



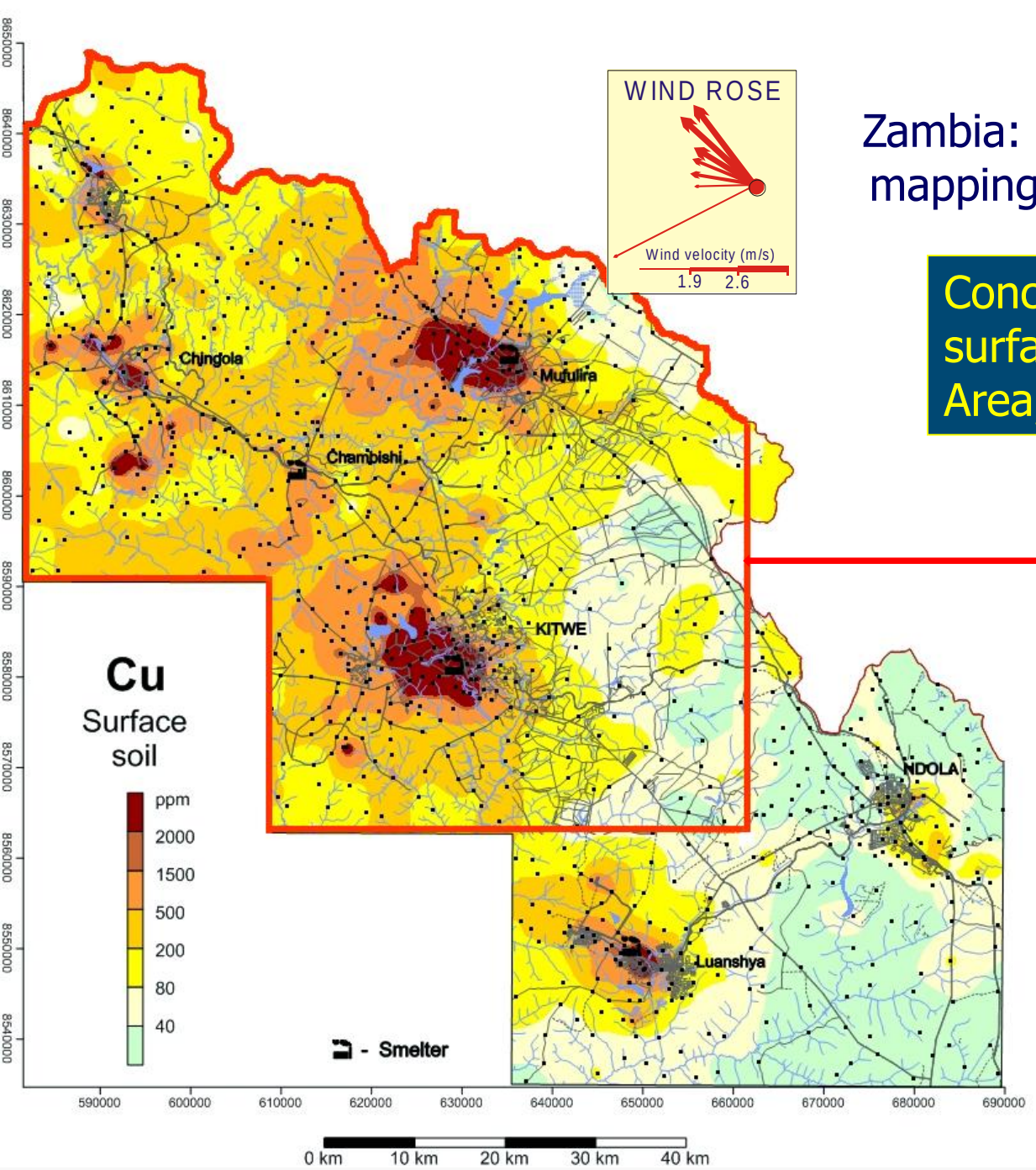
Total area: 4700 km^2

- 760 composite samples of surface soil
- 264 samples of subsurface soils
- 270 samples of stream sediments
- 120 samples of surface waters
- 60 special samples (slag, tailings, ochres)

Geological sketch map of Zambian Copperbelt and the extent of the environmental-geochemical survey



Zambia: Geochemical-environmental mapping in the Copperbelt Province



Concentration of copper in surface soil, the Copperbelt Area, Zambia

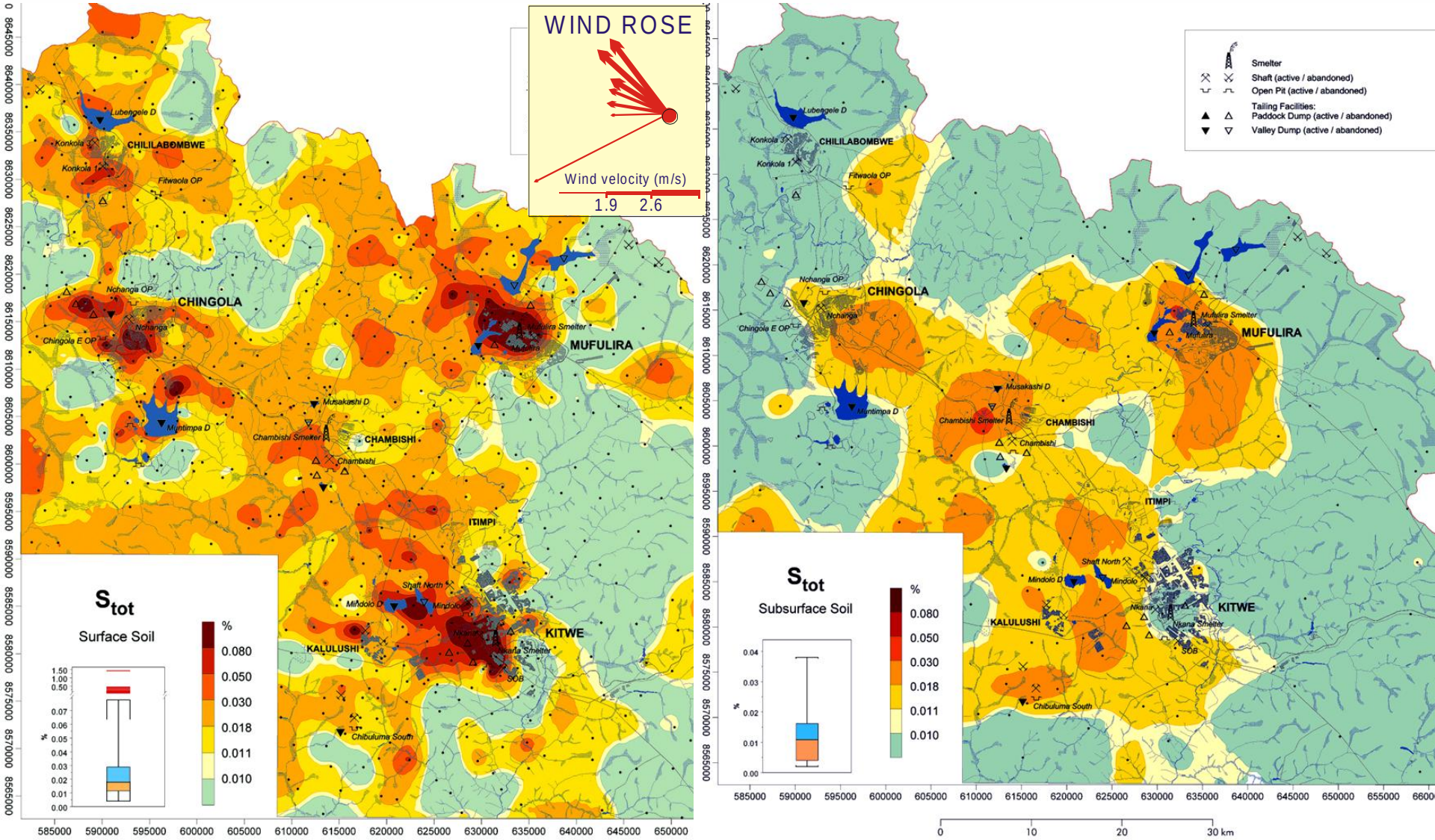
Central-northern part of the Zambian Copperbelt (Kitwe, Mufulira, Chambishi, Chingola, Chililabombwe Mining Districts)

CZECH GEOLOGICAL SURVEY 1919

TOTAL SULFUR IN SOILS

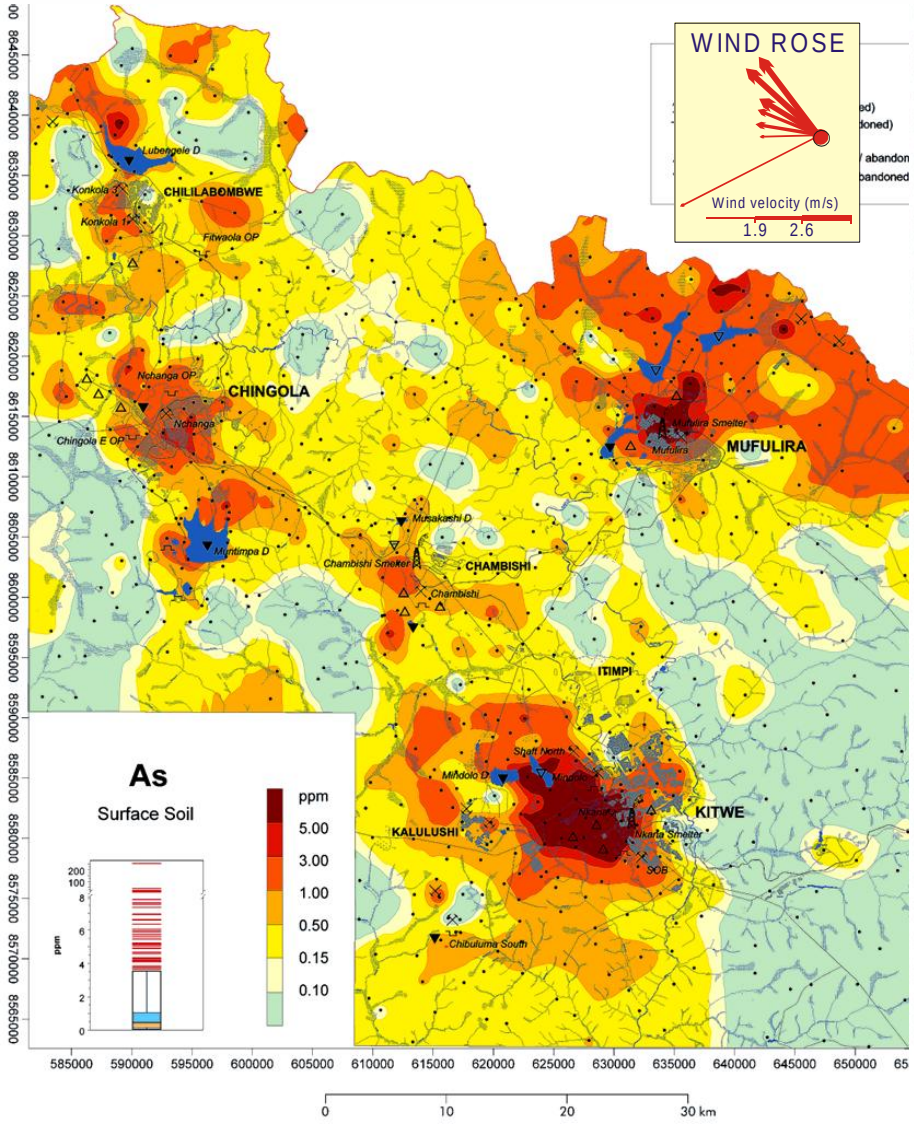
SURFACE SOIL (0-3 cm)

SUBSURFACE SOIL (80-90 cm)

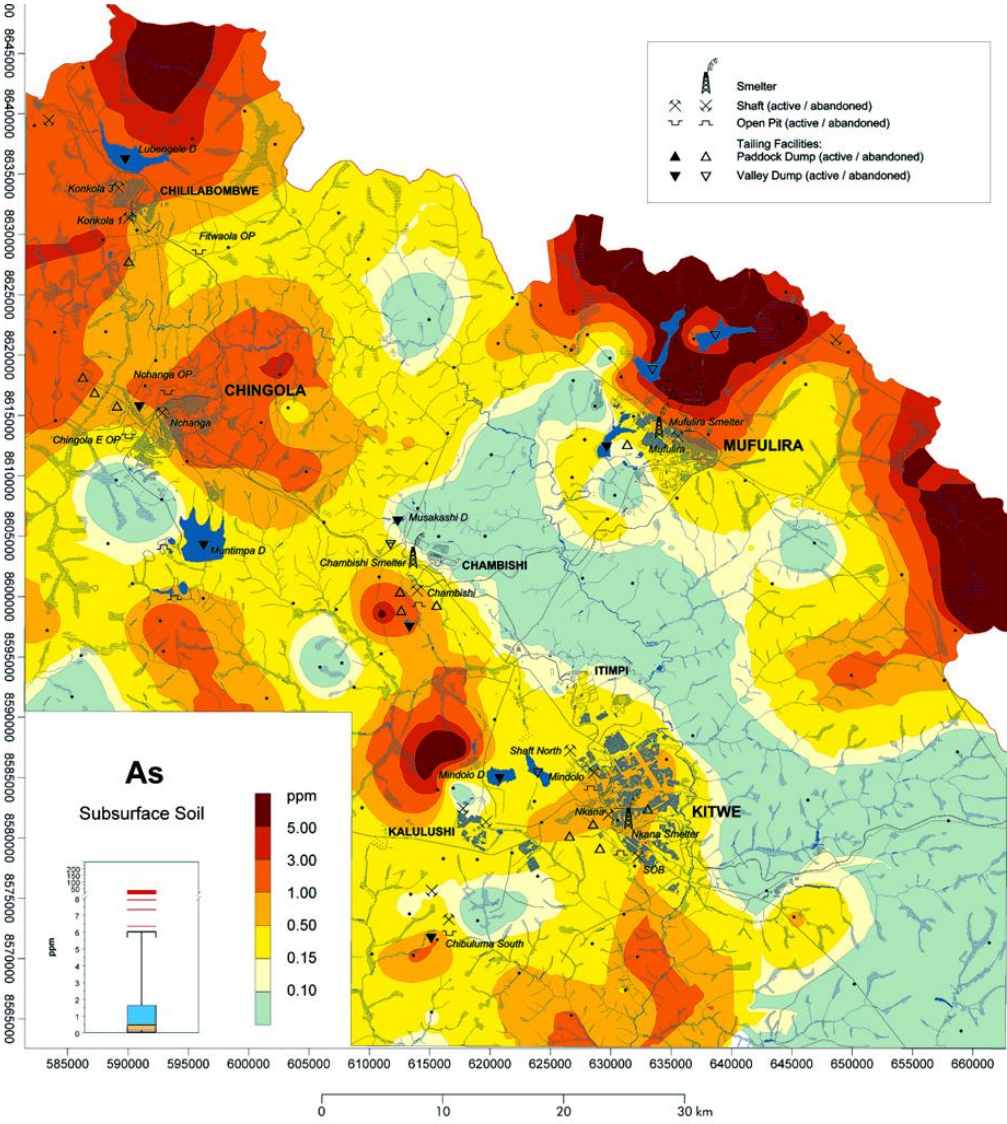


ARSENIC IN SOILS

ARSENIC IN SURFACE SOIL

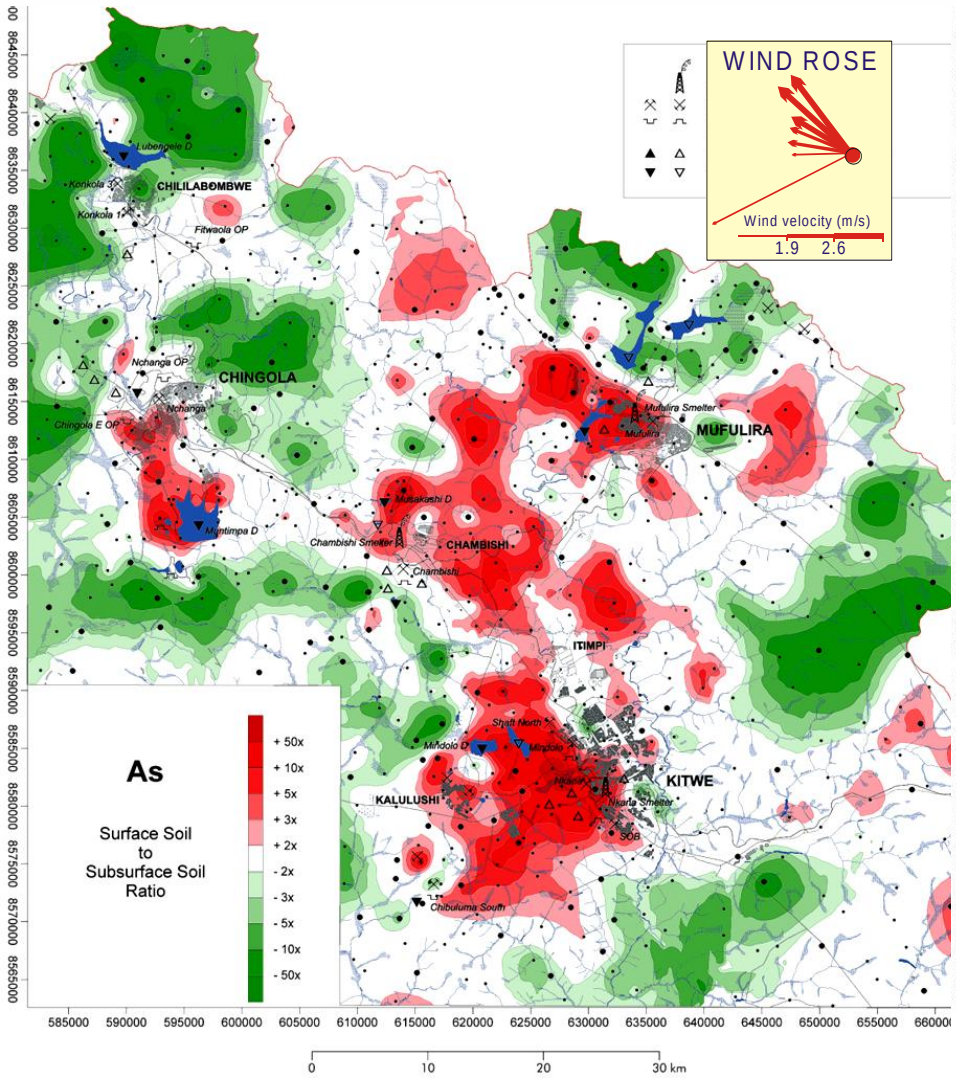


ARSENIC IN SUBSURFACE SOIL

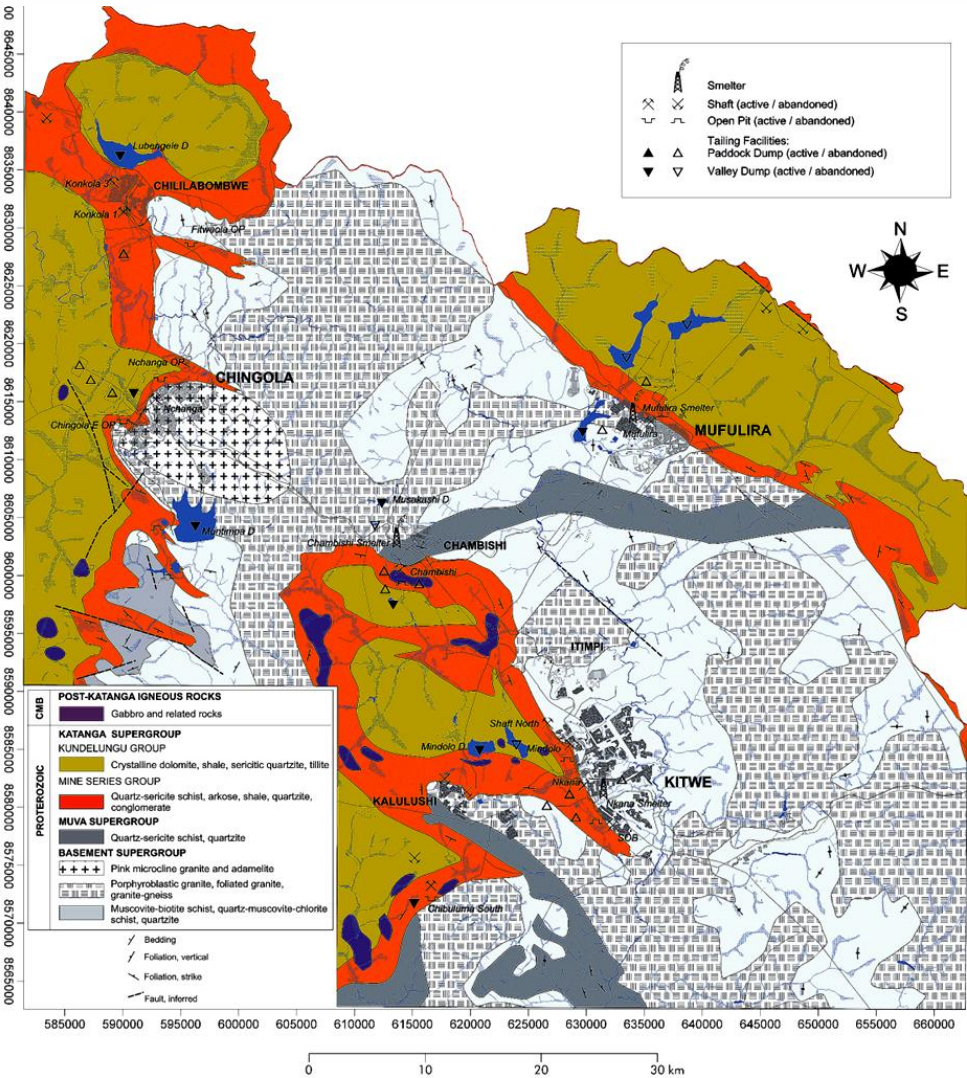


ARSENIC IN SOILS

DIFERENCE: SURFACE TO SUBSURFACE SOIL

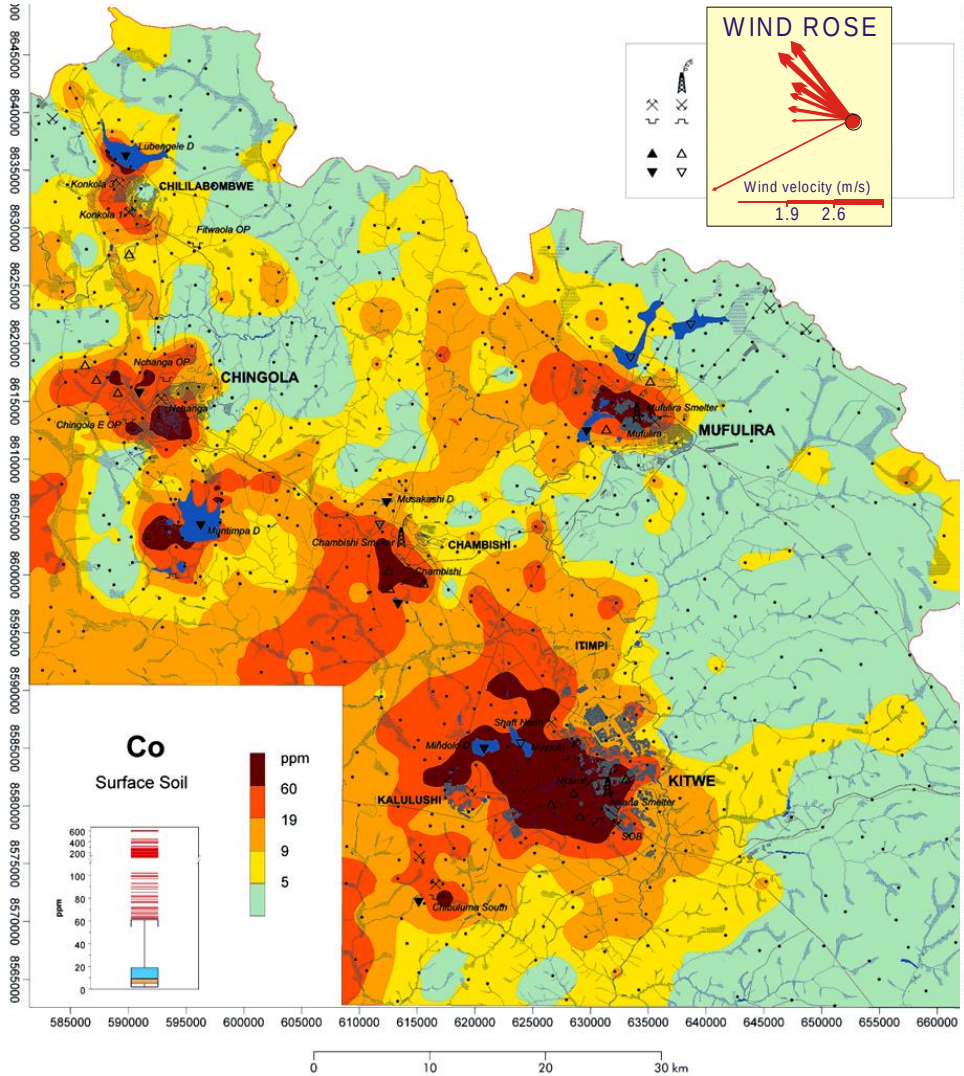


GEOLOGICAL MAP

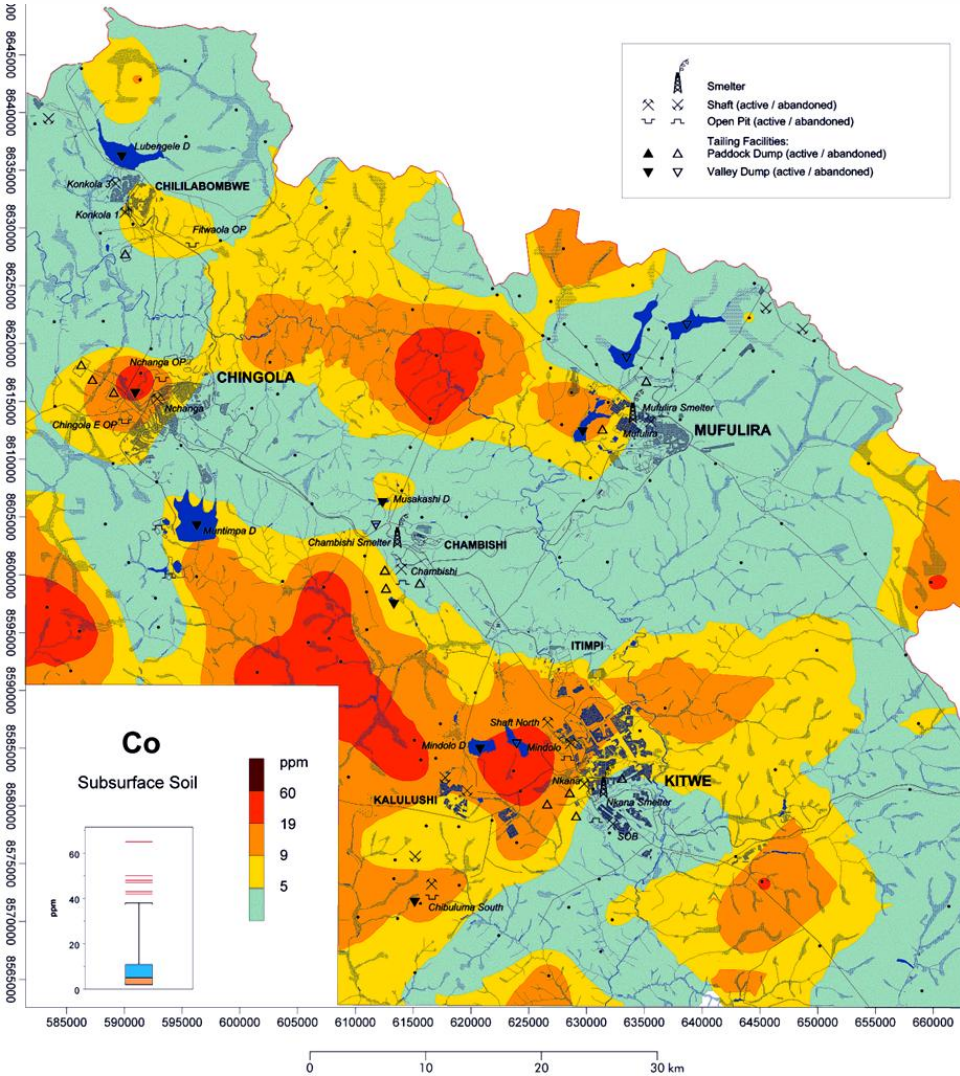


COBALT IN SOILS

COBALT IN SURFACE SOIL

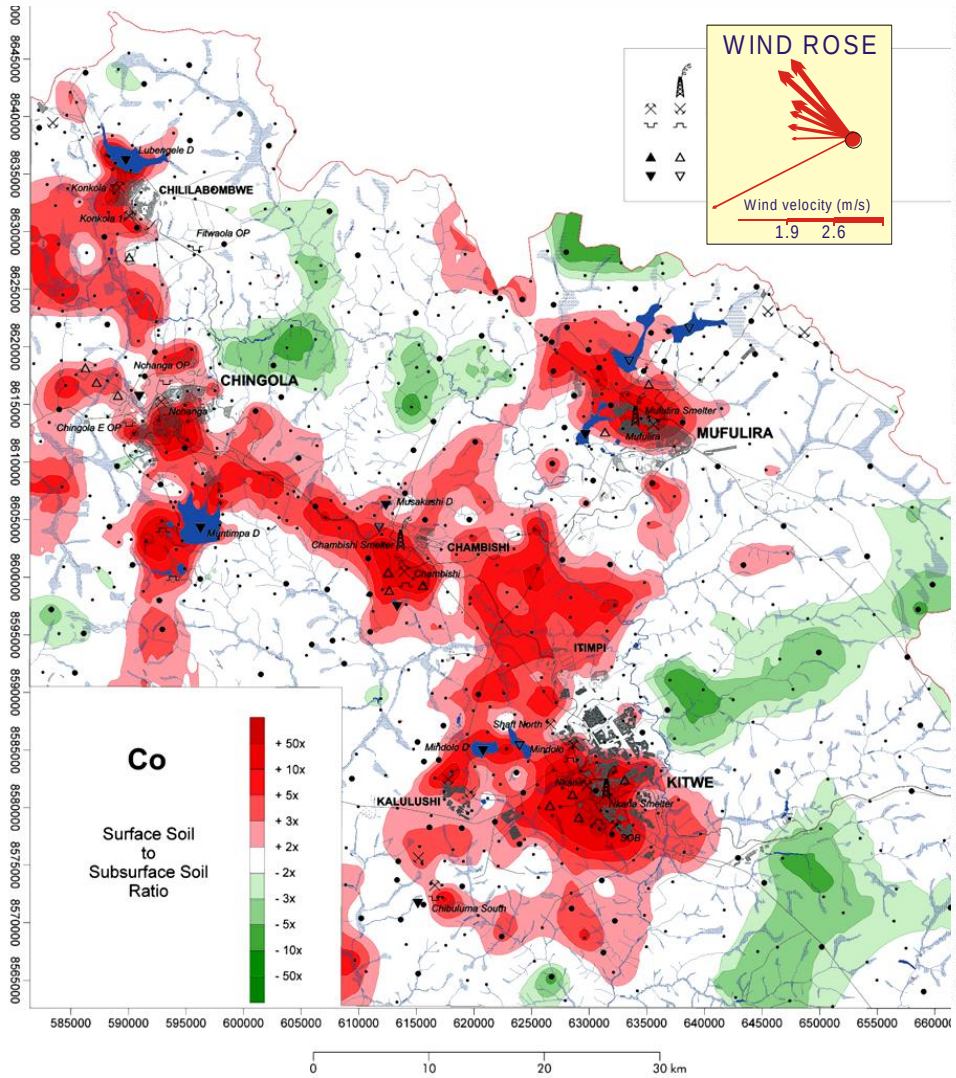


COBALT IN SUBSURFACE SOIL

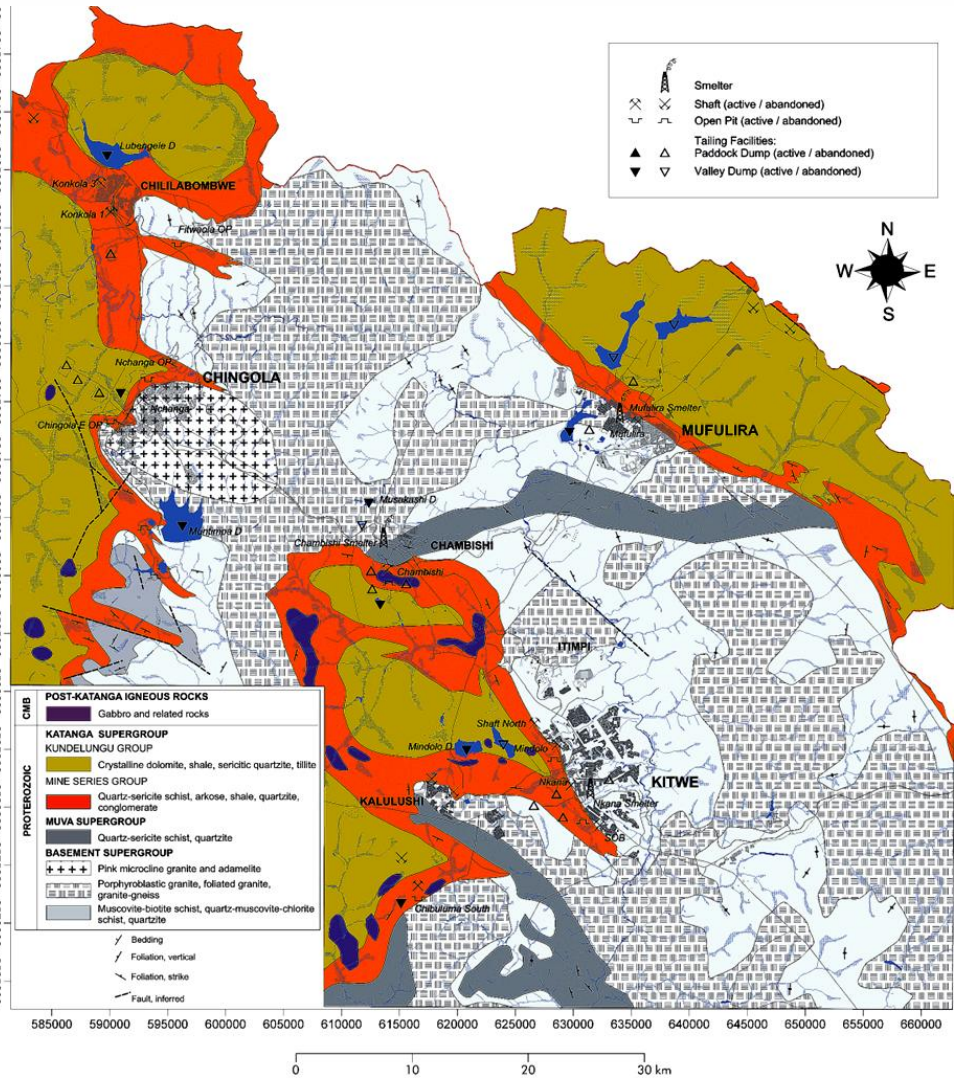


COBALT IN SOILS

DIFERENCE: SURFACE TO SUBSURFACE SOIL

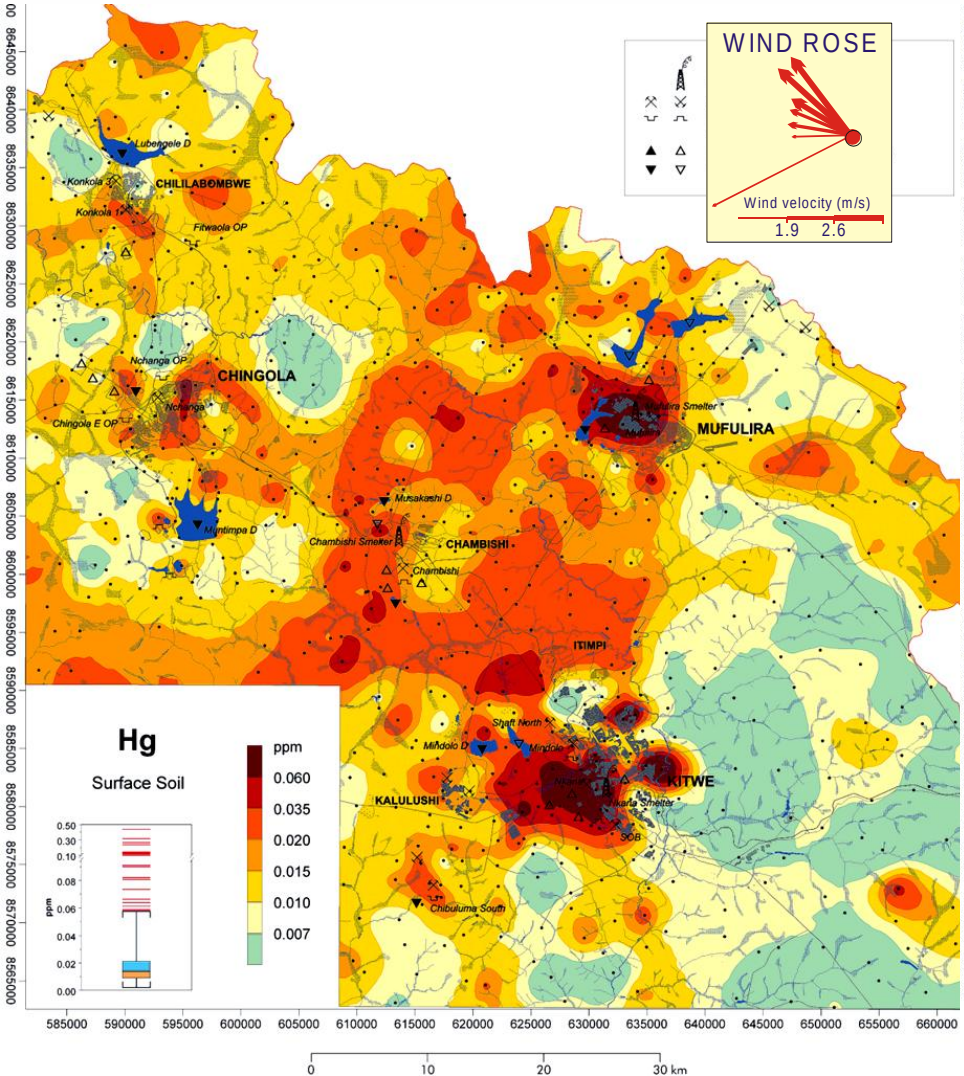


GEOLOGICAL MAP

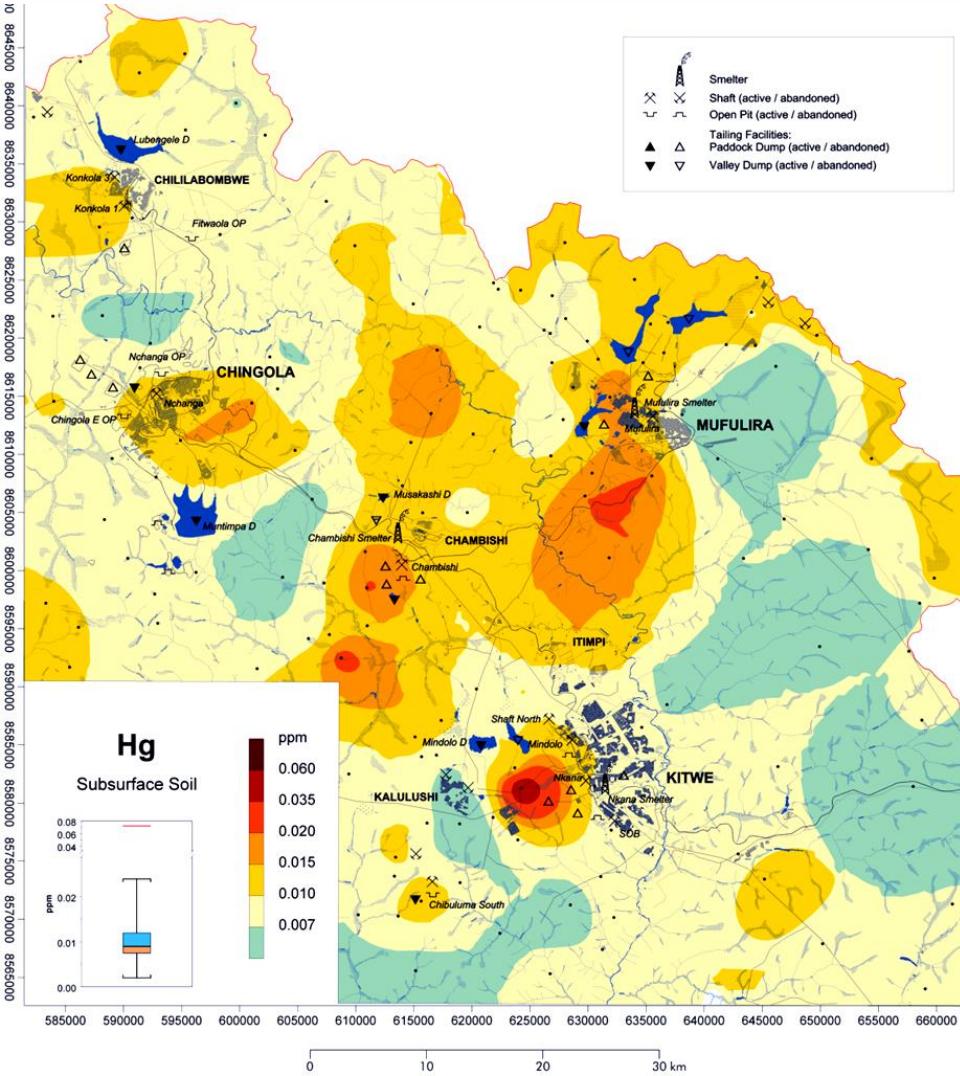


MERCURY IN SOILS

MERCURY IN SURFACE SOIL

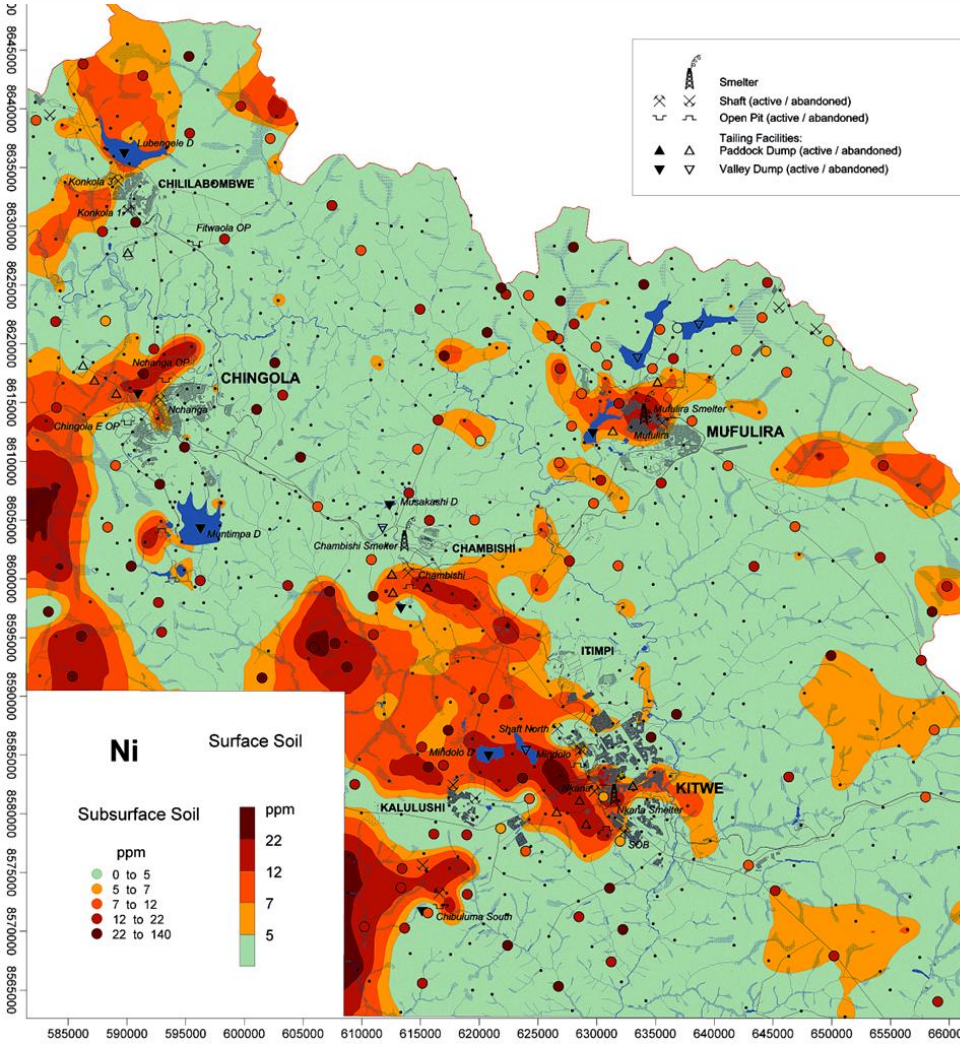


MERCURY IN SUBSURFACE SOIL

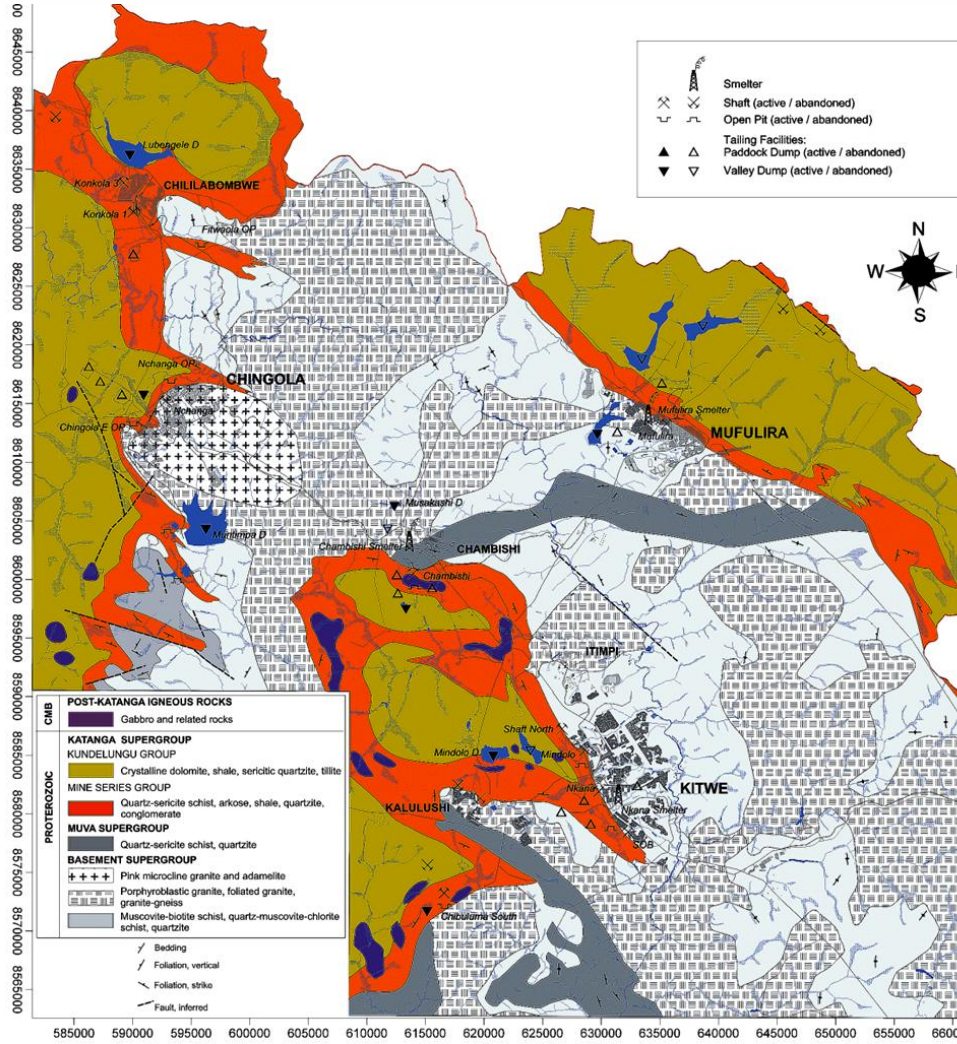


NICKEL IN SOILS

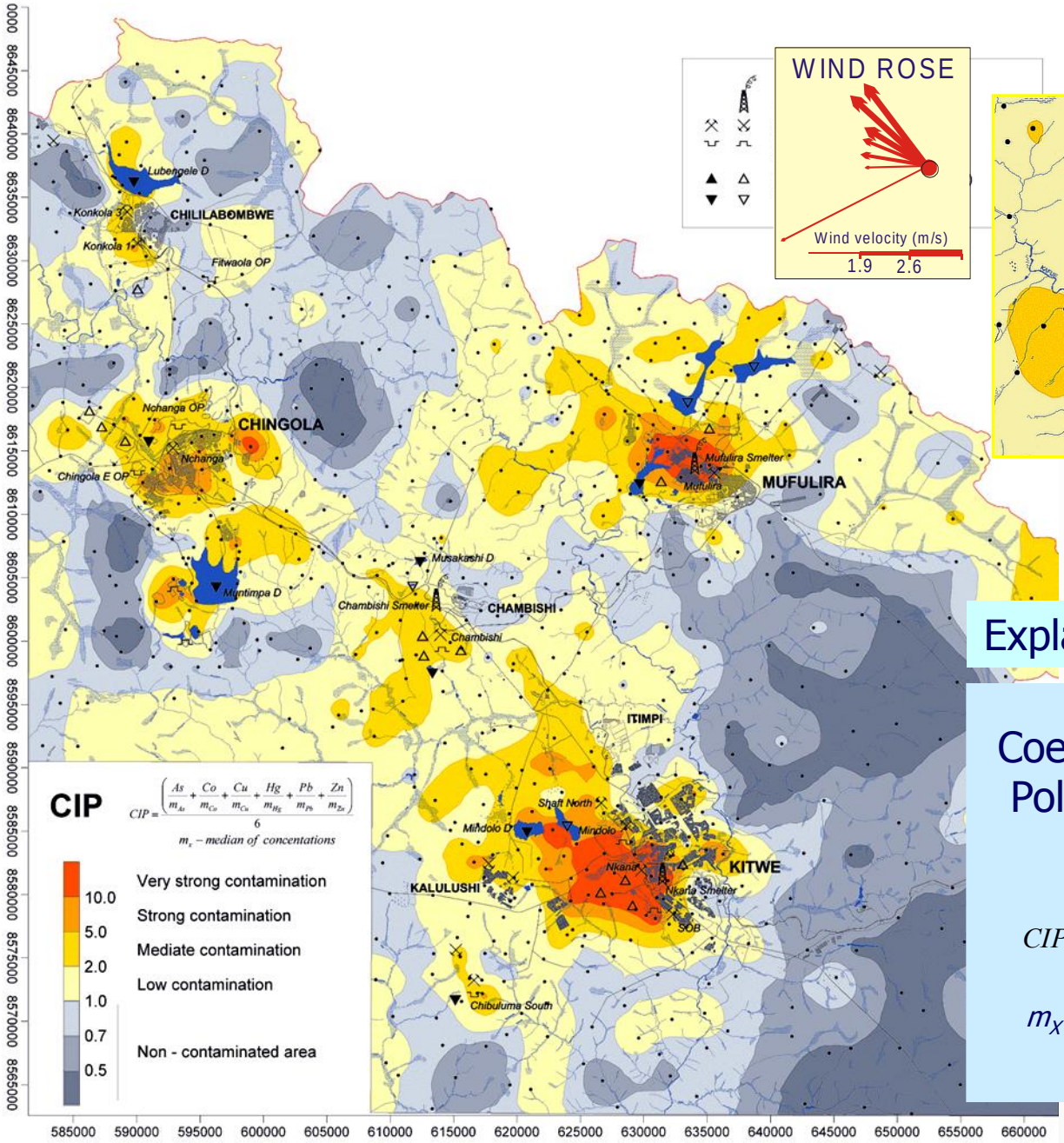
NICKEL IN SURFACE AND SUBSURFACE SOIL

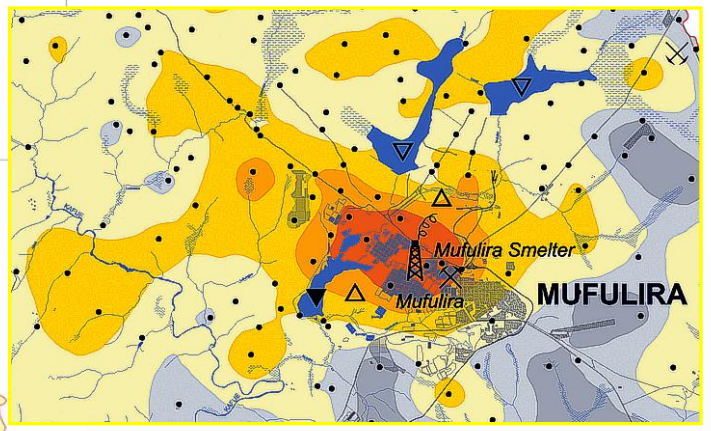


GEOLOGICAL MAP



COEFICIENT OF INDUSTRIAL POLLUTION (SURFACE SOIL)





Close-up: Mufulira area

Explanation:

Coeficient of Industrial Pollution

$$CIP = \frac{\left(\frac{As}{m_{As}} + \frac{Co}{m_{Co}} + \frac{Cu}{m_{Cu}} + \frac{Hg}{m_{Hg}} + \frac{Pb}{m_{Pb}} + \frac{Zn}{m_{Zn}}\right)}{6}$$

m_X – *value of the metal concentration*

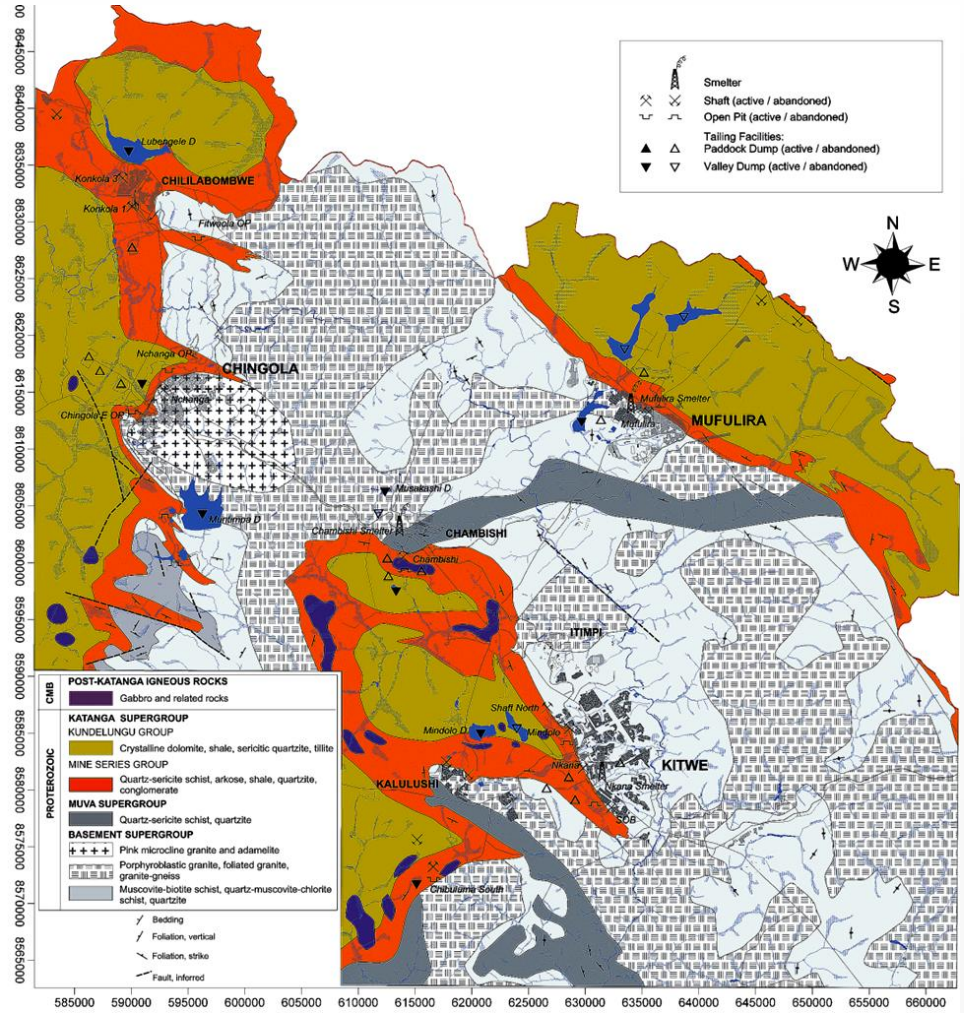
RESULTS OF THE ENVIRONMENTAL GEOCHEMICAL MAPPING

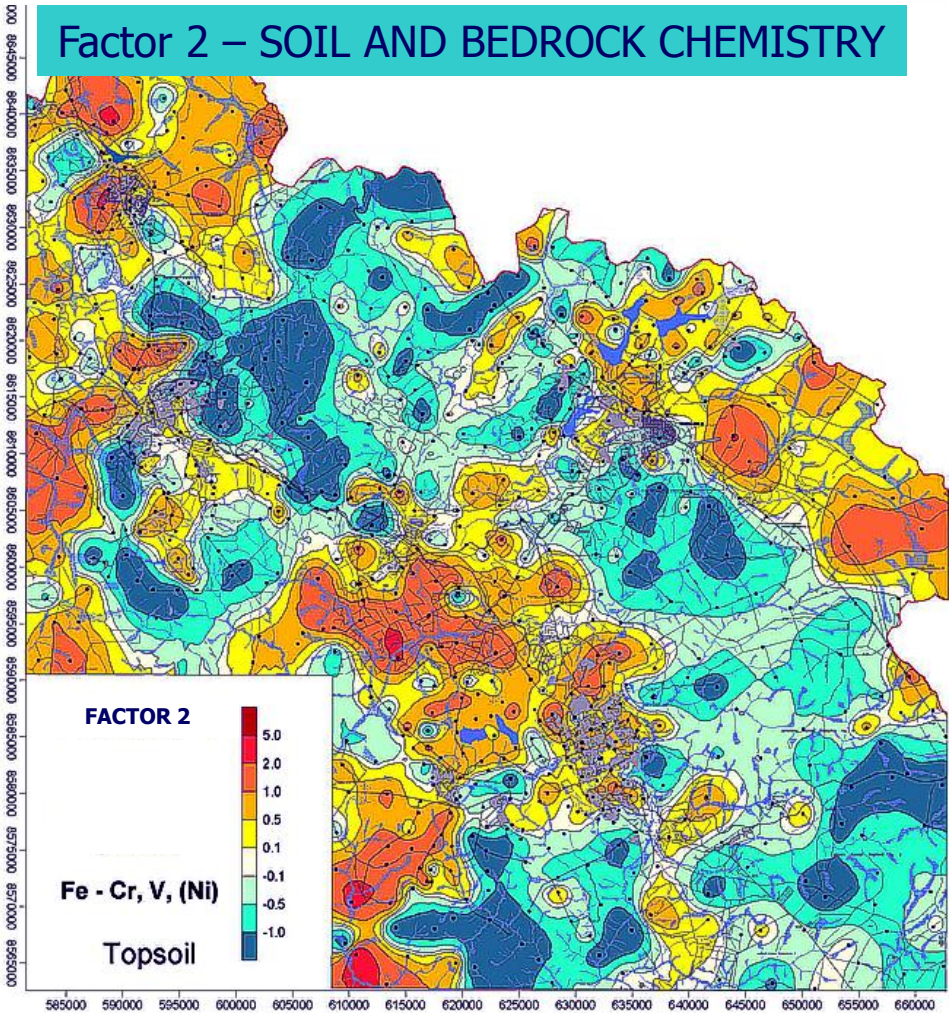
Factor analysis – trace elements in surface soils

Factor No.	Factor Loading	Interpretation
Factor 1: Explains the variability of Co, Cu, Ni, Pb, Zn Hg, Se As, and S_{tot}	19.1%	Contamination of soils by trace elements transported by air in form of sulphide or sulfate particles from smelters, tailing ponds and mining operations
Factor 2: Explains the variability of Co, Cr, Ni, V, Zn and Fe_{tot}	22.7%	This association reflects geochemical characteristics of soils and bedrock in the mapped region (This factor not related to mining)
Factor 3: Explains the variability of Zn, Hg S_{tot} and C_{org}	13.0 %	This factor reflects geochemical characteristics (content of C_{org} Corg) in soils (This factor is not related to mining)

RESULTS OF THE ENVIRONMENTAL GEOCHEMICAL MAPPING

Factor analysis – Maps of Factor Scores (topsoils)

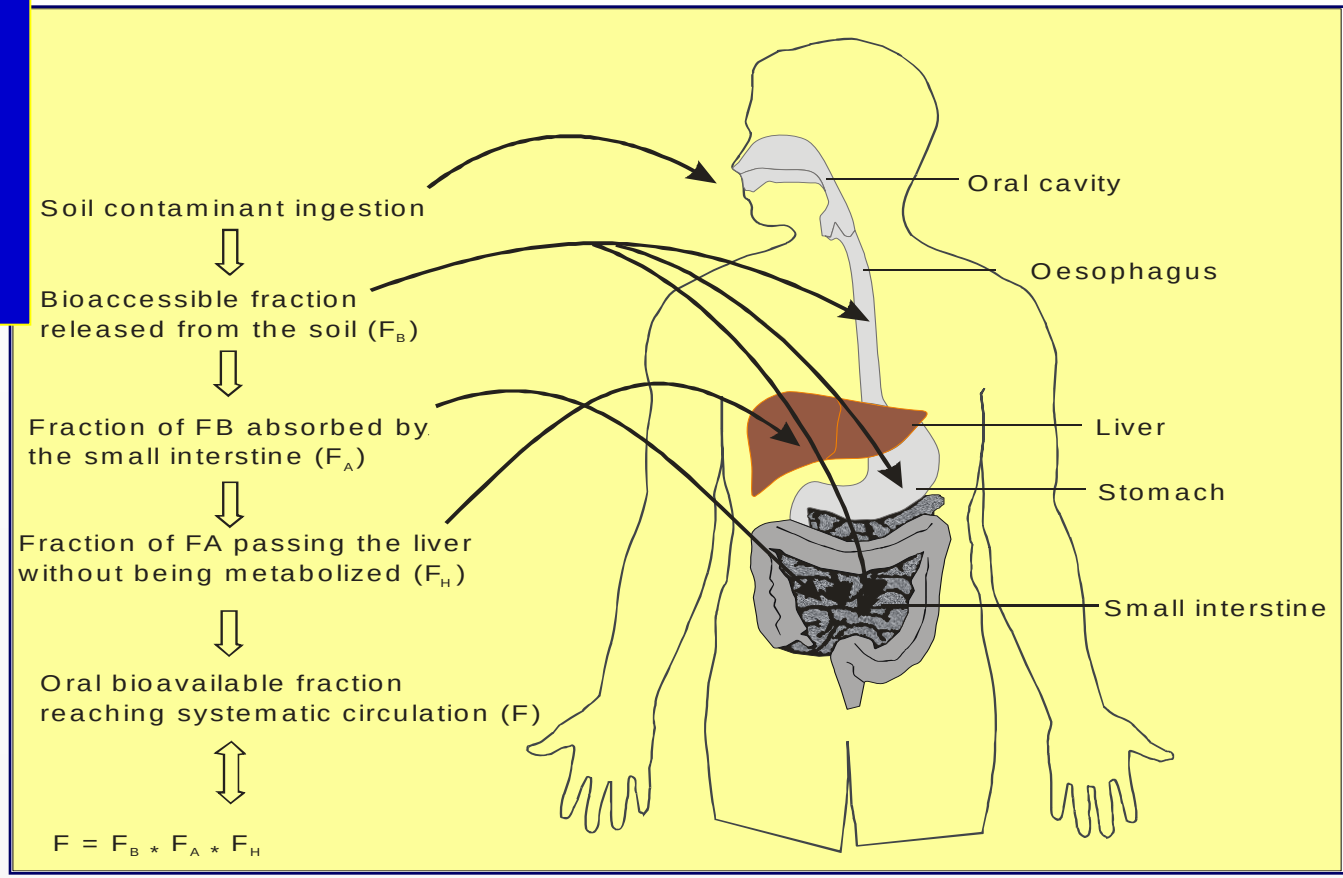




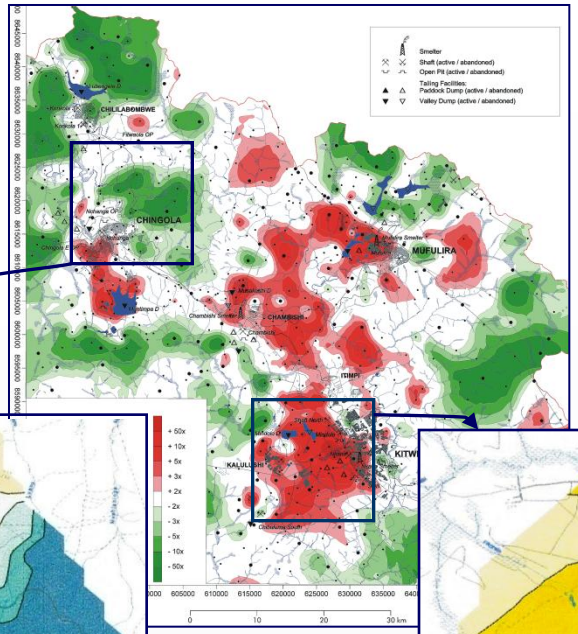
Total *vs.* gastric-available metals is surface soil

Total metal
(Aqua regia extraction)

Gastric-available metal
(extraction to glycine
at pH 2.2, T= 38 °C).
Extraction simulate
solubility of metals
in human stomach

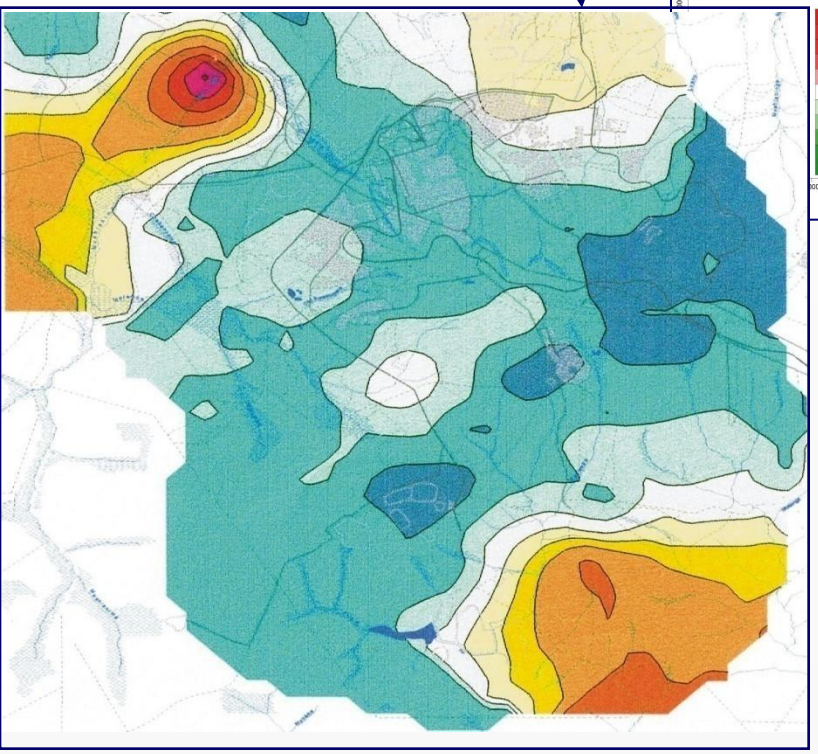


Gastric-available lead



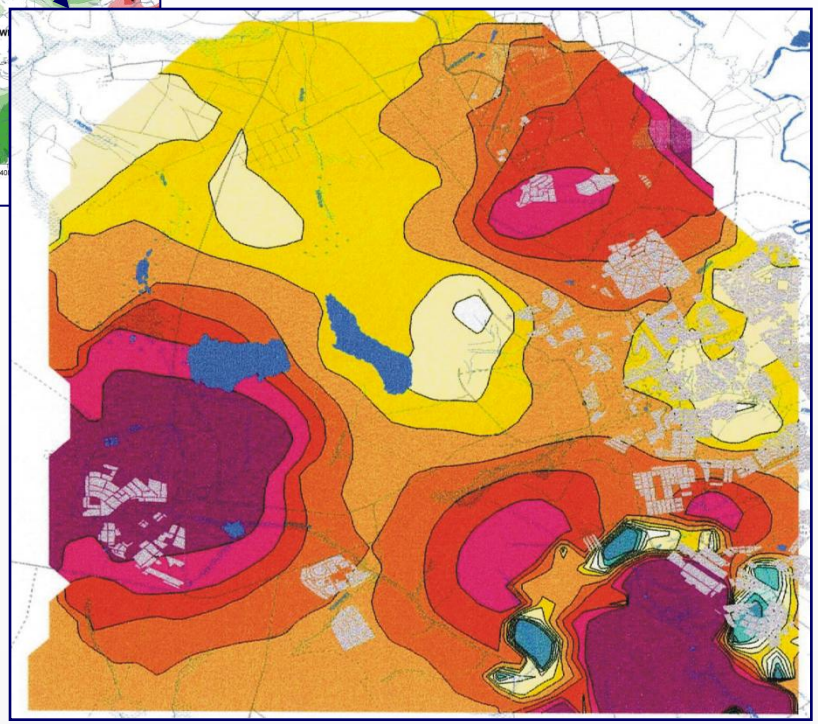
Chingola Mining Area

Gastic-available lead: 20% of TOTAL lead

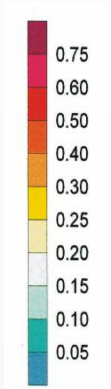


Nkana Smelter Area

Gastric-available lead: 80% of TOTAL lead

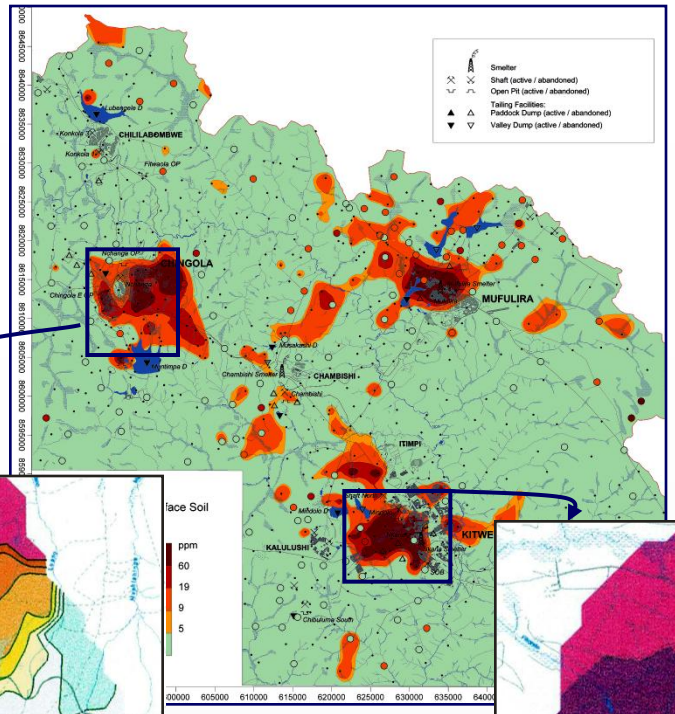


Total Pb/ Available Pb



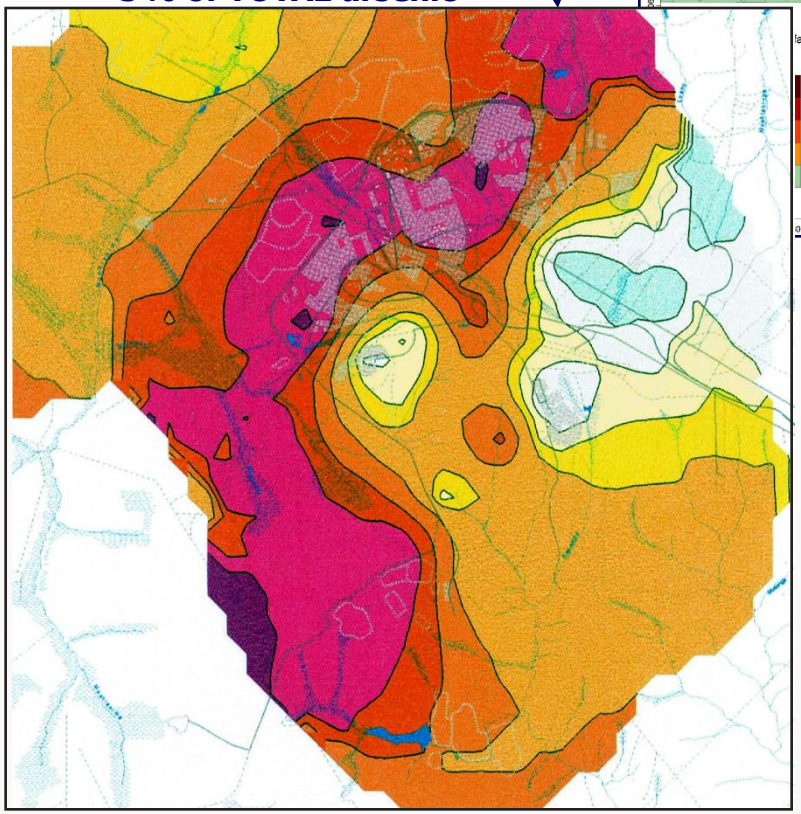
Lead in soils is more grastric-available in the smelter contaminated areas compared with mining areas

Gastric-available arsenic



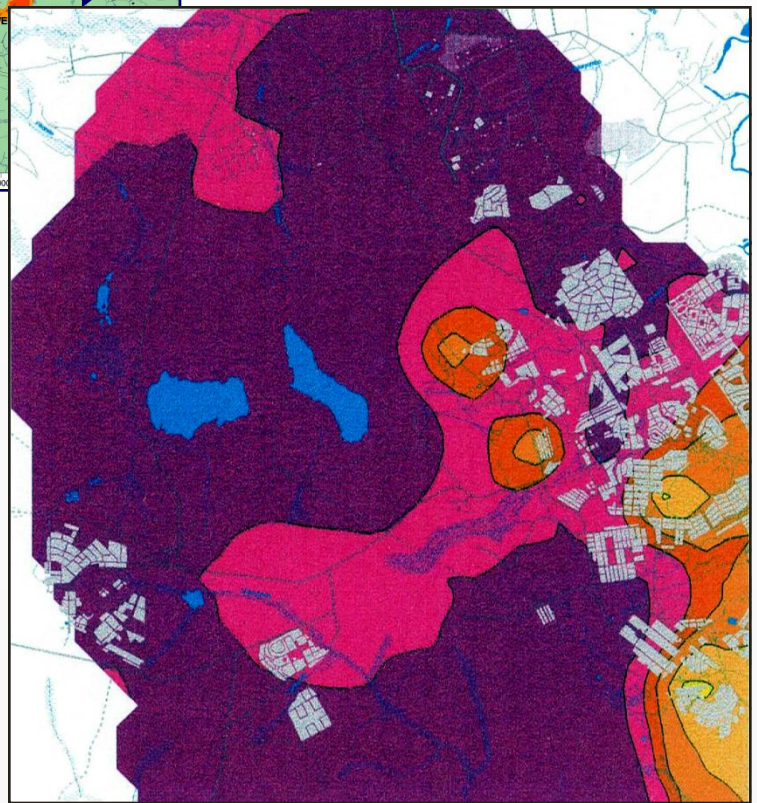
Chingola Mining Area

Gastric-available arsenic: 5% of TOTAL arsenic

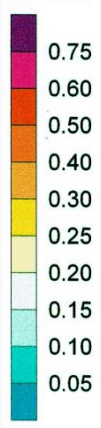


Nkana Smelter Area

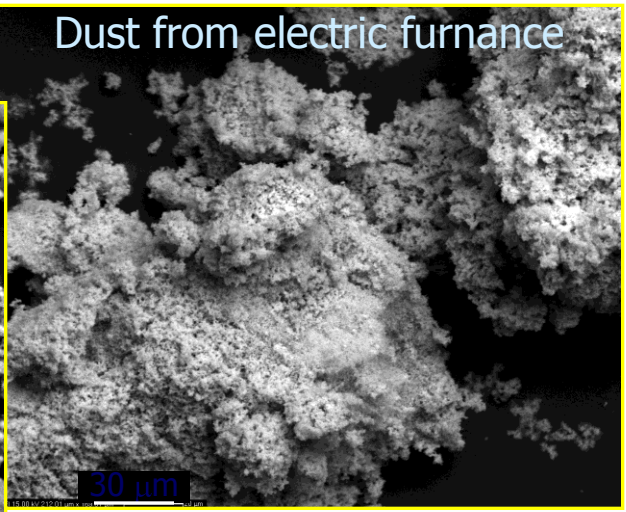
Gastric-available arsenic: 30% of TOTAL arsenic



Total As/ Available As



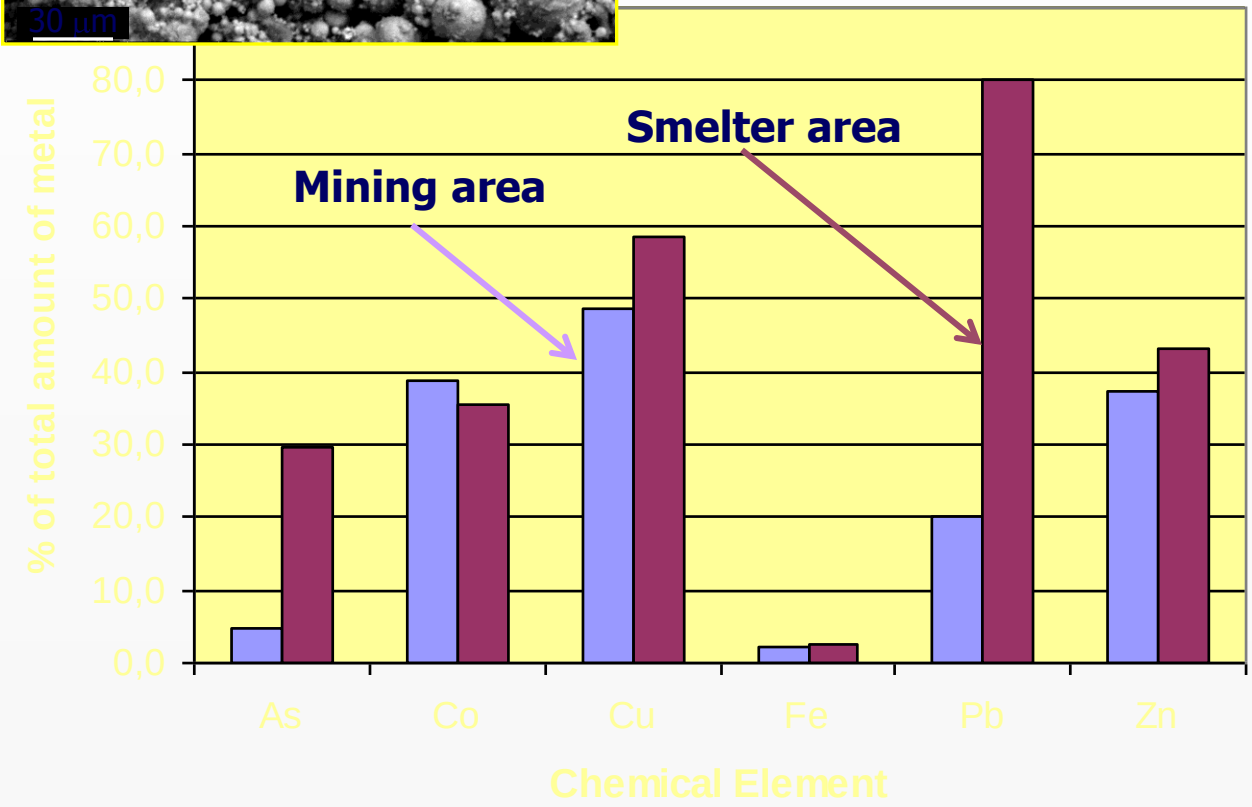
Gastric-available metals





Dust from ore crushers





BOX 2 Stream sediment sampling

• Stream sediment composite sample has to be prepared from sub-samples taken from 5 points along a 250-500 m length of the stream.

• From each sampling site, 1 kg of material (taken from the 0-25 cm depth) should be collected. Blended (composite) samples may be sieved on spot (wet sieving) or after drying of samples (dry sieving) in the field laboratory. For sieving, plastic sieve set equipped with nylon mesh (0.15 mm) has to be used to avoid contamination. The <0.15 fraction (50-100 g) is recommended to homogenize in agate ball mill to analytical fineness.

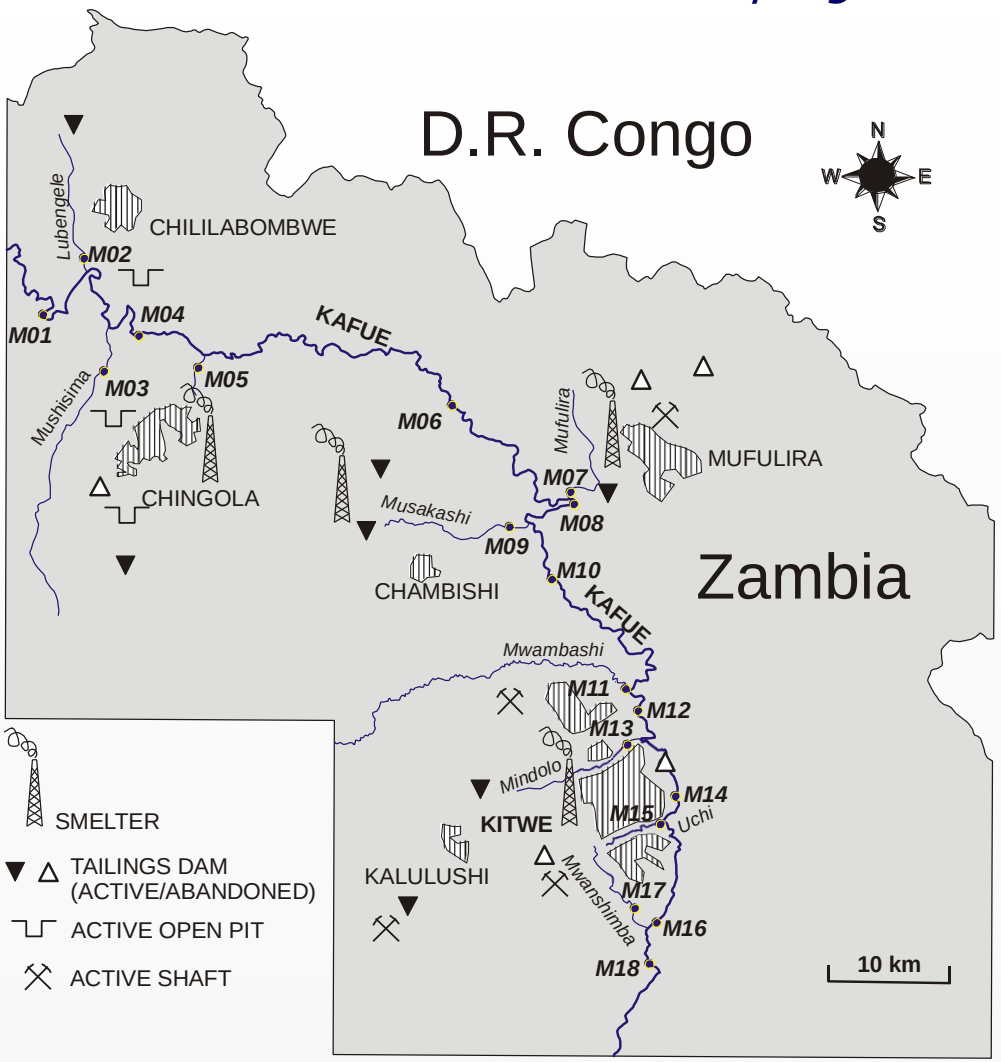
Note: **Together with stream sediment samples, panned heavy mineral concentrates may be collected on selected sampling sites. The panned heavy mineral concentrates are an excellent resource for identifying drainage catchment mineralization as well as anthropogenic contamination.**

Note: **It is recommended to collect water samples (for sampling details see above) before collecting stream sediment samples on individual sampling sites.**

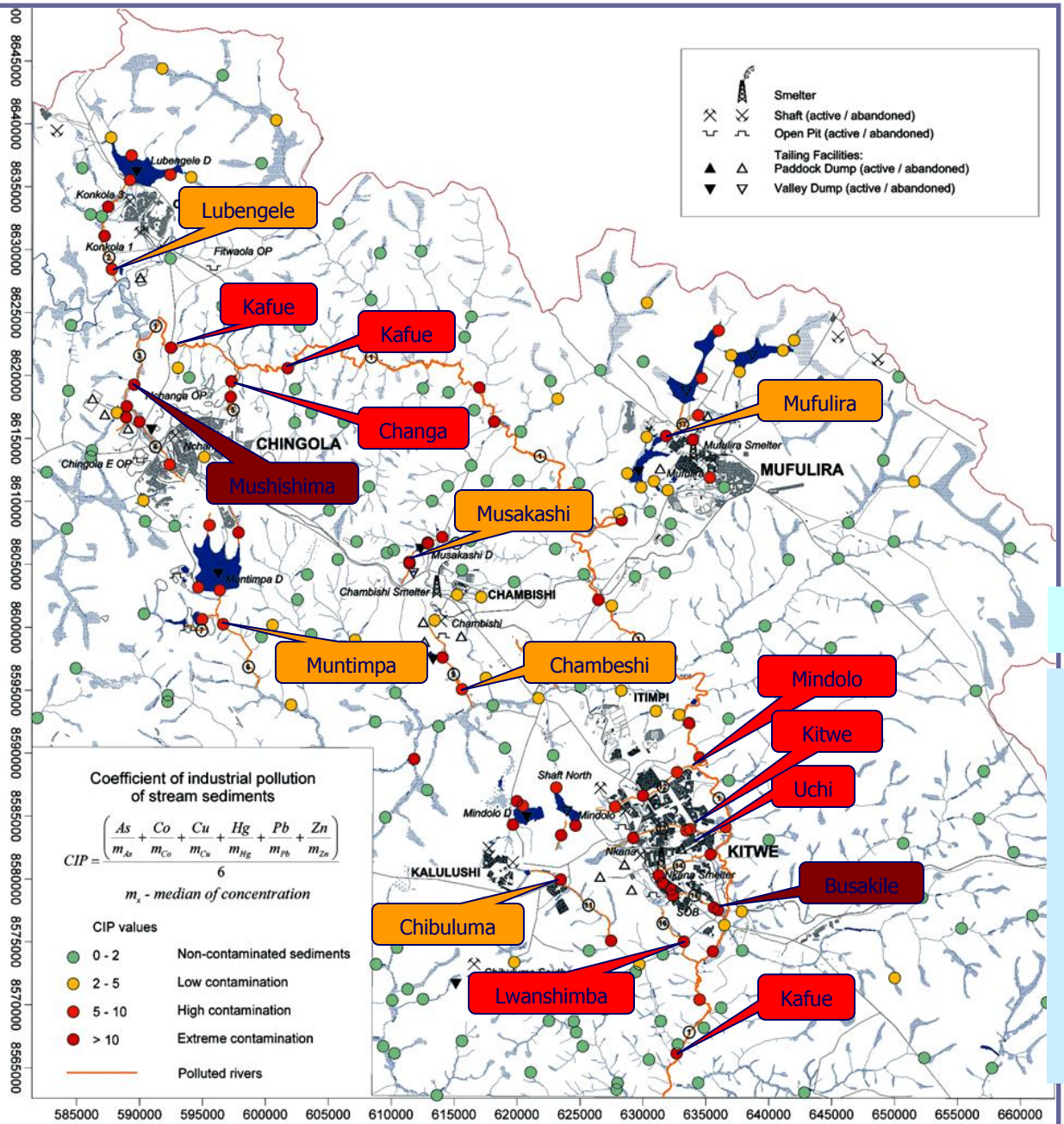

Drying of stream sediment samples


Sieving of stream sediment samples

Stream sediment sampling



COEFICIENT OF INDUSTRIAL POLLUTION - STREAM SEDIMENTS



Stream sediments,
Busakile River, Kitwe:
- As: 1296 ppm
- Co 3660 ppm
- Cu 65 465 ppm
- Hg 6.4 ppm
- Mo 48 ppm
- Ni 360 ppm
- Pb 1370 ppm
- Zn 3590 ppm
- S tot 2.1 %

Explanation:

Coeficient of Industrial Contamination

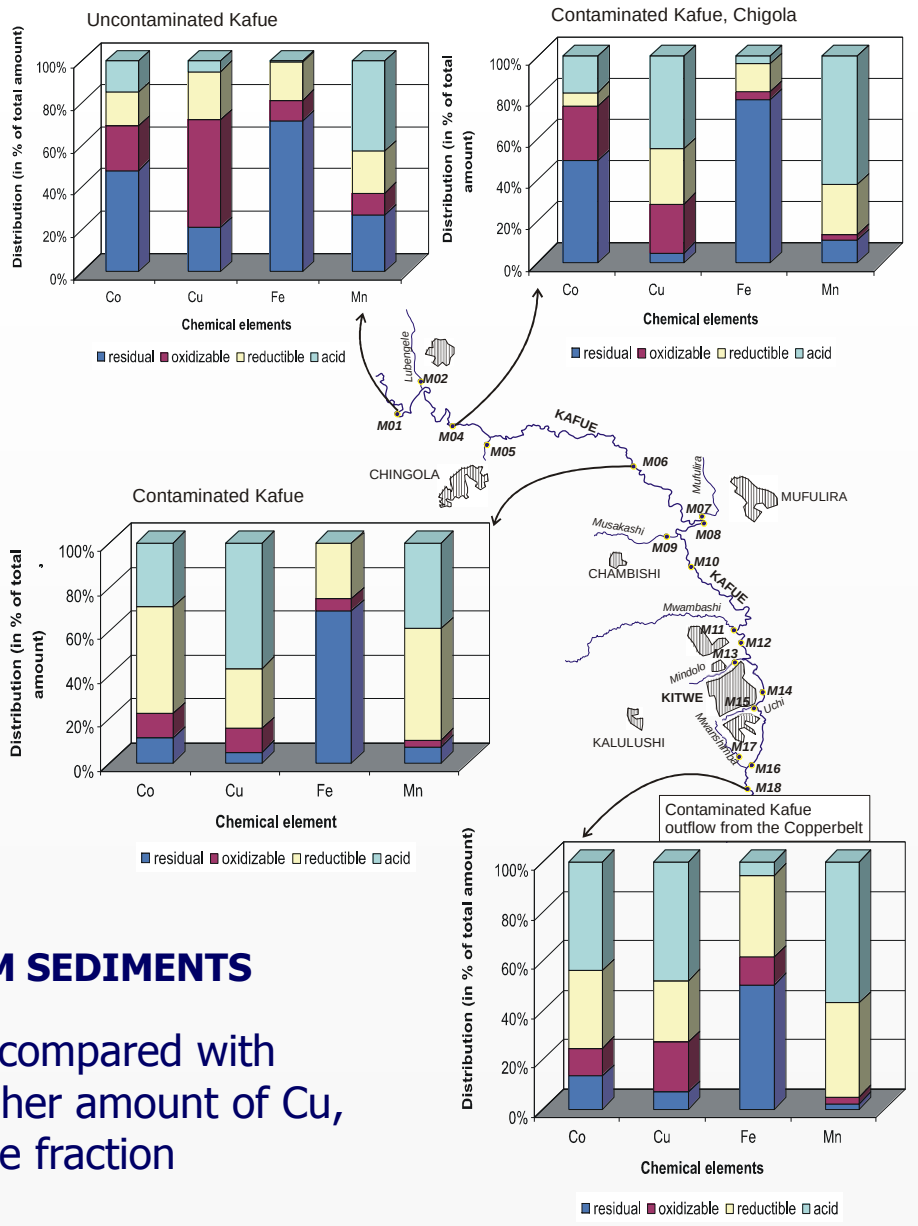
$$CIP = \frac{\left(\frac{As}{m_{As}} + \frac{Co}{m_{Co}} + \frac{Cu}{m_{Cu}} + \frac{Hg}{m_{Hg}} + \frac{Pb}{m_{Pb}} + \frac{Zn}{m_{Zn}}\right)}{6}$$

m_X – *value of the metal concentration*

STREAM SEDIMENTS

Contents of selected chemical elements in uncontaminated and contaminated sediments of the Kafue River, Zambia

Element mg.kg^{-1}	Uncontaminated Kafue	Kontaminated Kafue
Co	17-21	131-1174
Cu	115-161	1520-8837
Pb	4-13	21-54
As	0.14-0.57	1.9-7.4
Hg	0.02-0.03	0.03-0.14
Mn	103-133	395-2849



SEQUENTIONAL EXTRACTIONS OF STREAM SEDIMENTS

Results of sequential extractions show that compared with uncontaminated sediments, substanially higher amount of Cu, Co and Mn are bound to the acid-extractable fraction (exchangeable metals and carbonates)

STREAM SEDIMENTS

Comparison with the Canadian Guidelines for Sediments

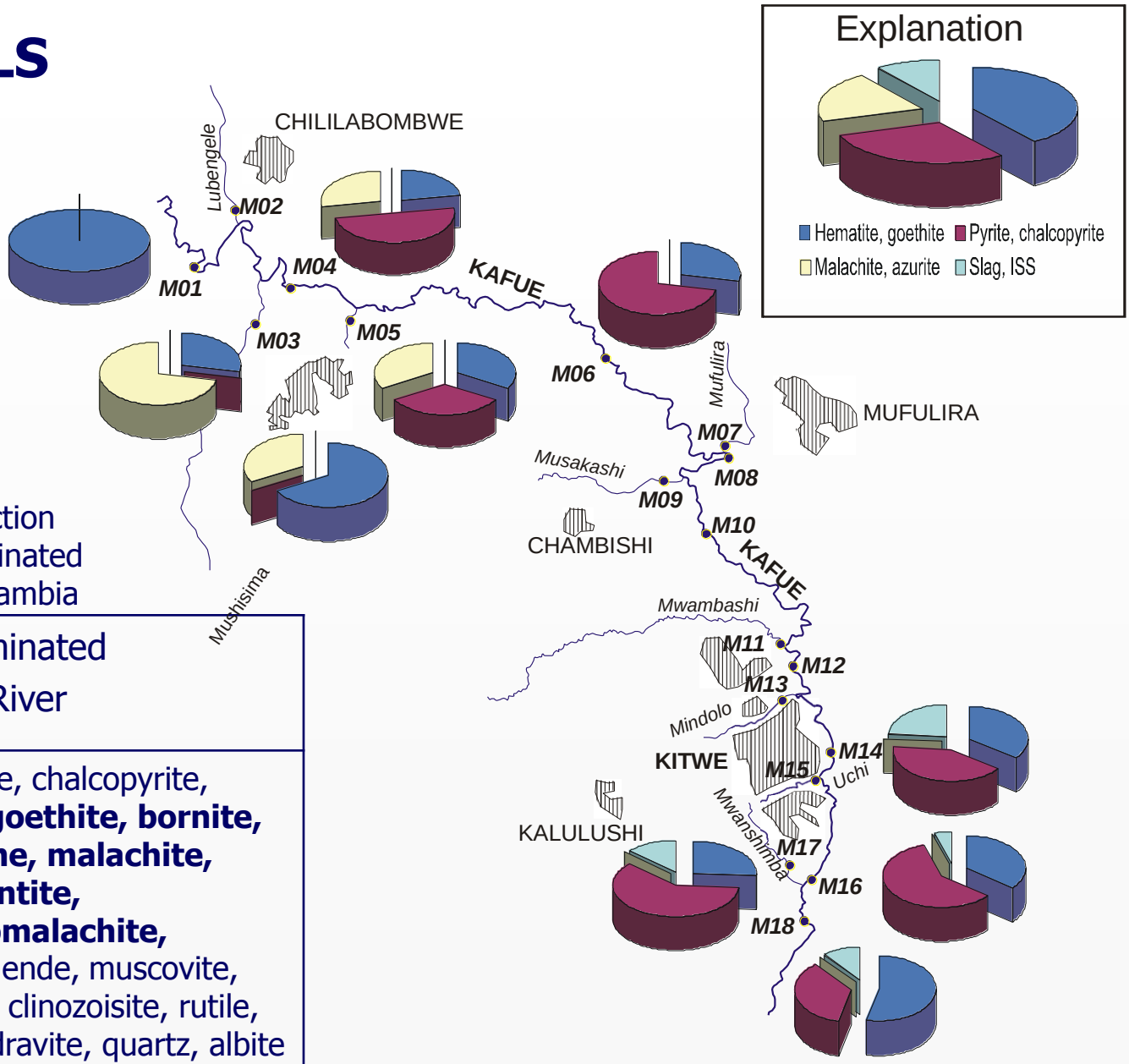
Concentrations between ISQG and PEL represent the range in which adverse biological effects are occasionally observed

Element (ppm)	ISQG	PEL
As	5.9 (8.2%)	17.0 (2%)
Cd	0.6 (0%)	3.5 (0%)
Cr	37.3 (22.9%)	90 (2%)
Cu	35.7 (98.4%)	197 (55.7%)
Hg	0.17 (8.2%)	0.49 (0%)
Pb	35 (6.6%)	91.3 (2%)
Zn	123 (0%)	315 (0%)

Concentrations above the PEL are expected to be frequently associated with adverse biological effects

Percentage of samples exceeding the ISQG and PEL values in the Zambian Copperbelt

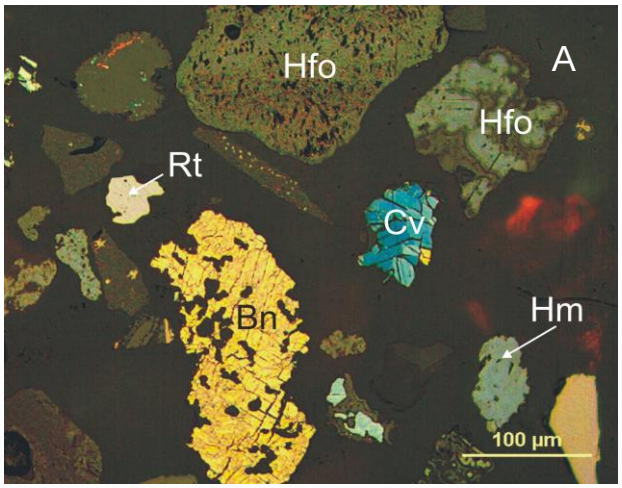
HEAVY MINERALS SURVEY, KAFUE RIVER, COPPERBELT, ZAMBIA

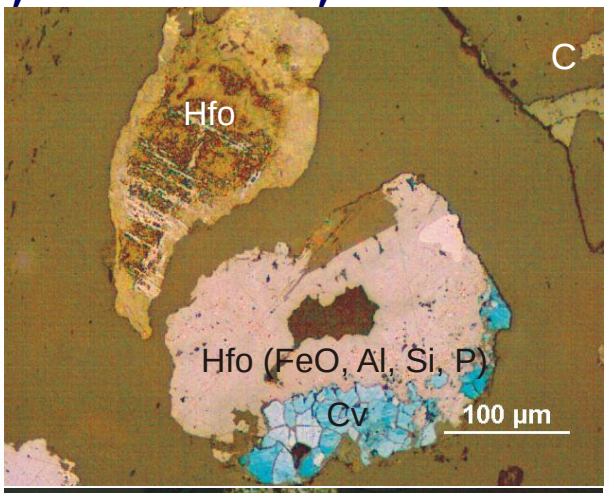


Minerals identified in heavy fraction of uncontaminated and contaminated sediments of the Kafue River, Zambia

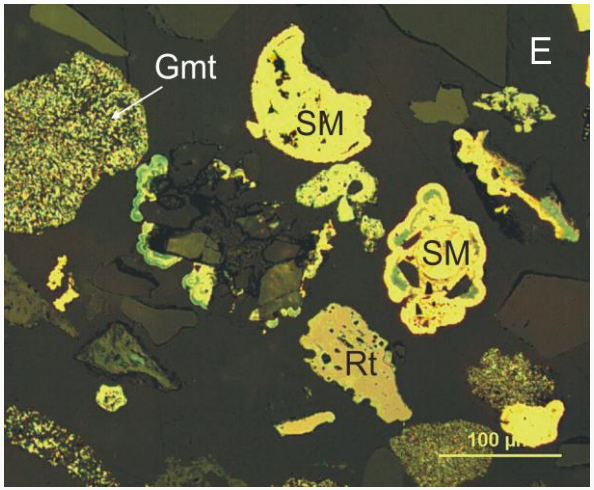
Uncontaminated Kafue River	Contaminated Kafue River
Ilmenite, hematite, hornblende, clinochlorite, rutile, zircon, dravite, apatite, quartz, albite, microcline	Hematite, chalcopyrite, pyrite, **goethite, bornite, covelline, malachite, brochantite, pseudomalachite,** hornmblende, muscovite, chlorite, clinozoisite, rutile, zircon, dravite, quartz, albite

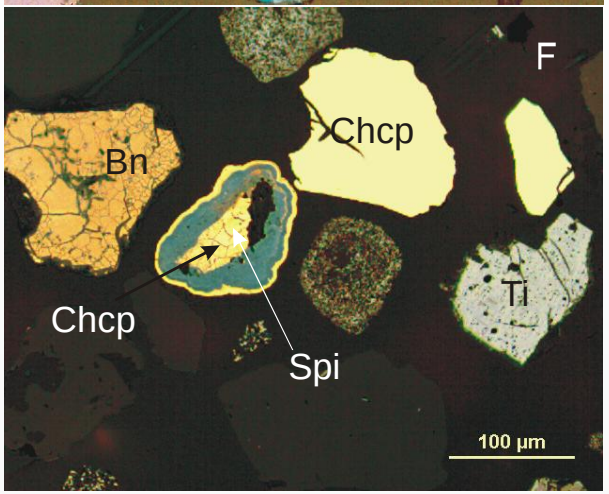
HEAVY MINERALS IN CONTAMINATED KAFUE RIVER, COPPERBELT, ZAMBIA











Microphotographs of heavy minerals in contaminated Kafue River sediments. A: Rutile (Rt), bornite (Bn), covellite (Cv), limonite/goethite (Hfo). Mushishima River, Chingola Area. B: Limonite/goethite (Hfo) with copper metal (Cu). Kafue River, downstream of the Chingola Town. C: Limonite/goethite, (Hfo), limonite/goethite with admixture of Al, Si and P and grain of covellite (Cv), Mushishima River, Chingola Area. D: Limonite/goethite. Mushishima River, Chingola Area. E: Magnetite-rich slag particle (Gmt), rutile (Rt) and intermediate solid solution (ISS) particle with oxidation rims (SM). The Uchi River, Kitwe Area. F: Bornite (Bn), chalcopyrite (Chcp), titanite (Ti) and chacopyrite with a rim of secondary spionkopite (Spi). The Uchi River, Kitwe Area.

BOX 3 Stream water sampling

•Two sub-samples of stream water have to be collected from each site:

- unfiltered water for major anion analysis,

- filtered water for cation analysis.

• This two sub-samples can be supplemented with:

- unfiltered water sample for mercury analysis,

- filtered water sample for dissolved organic carbon (DOC) analysis.

• Trace elements-free polyethylene bottles have to be used for water sampling. Bottles have to be filled with distilled water acidified with 1.0 ml of concentrated HNO_3 for at least one week before the sampling campaign.

• For filtering, 0,45-μm disposable filters mounted on disposable syringes are recommended. Filtered water samples have to be acidified on the same day as sampling by the addition of 1.0 ml of super-pure concentrated HNO_3 using a droplet bottle.

• A blank water sample has to be collected, filtered, and preserved in the same manner as the actual samples after every 20^{th} sample.

• Electrical conductivity (EC) and pH and water temperature have to be measured in the field and alkalinity has to be determined by titration in the field laboratory.

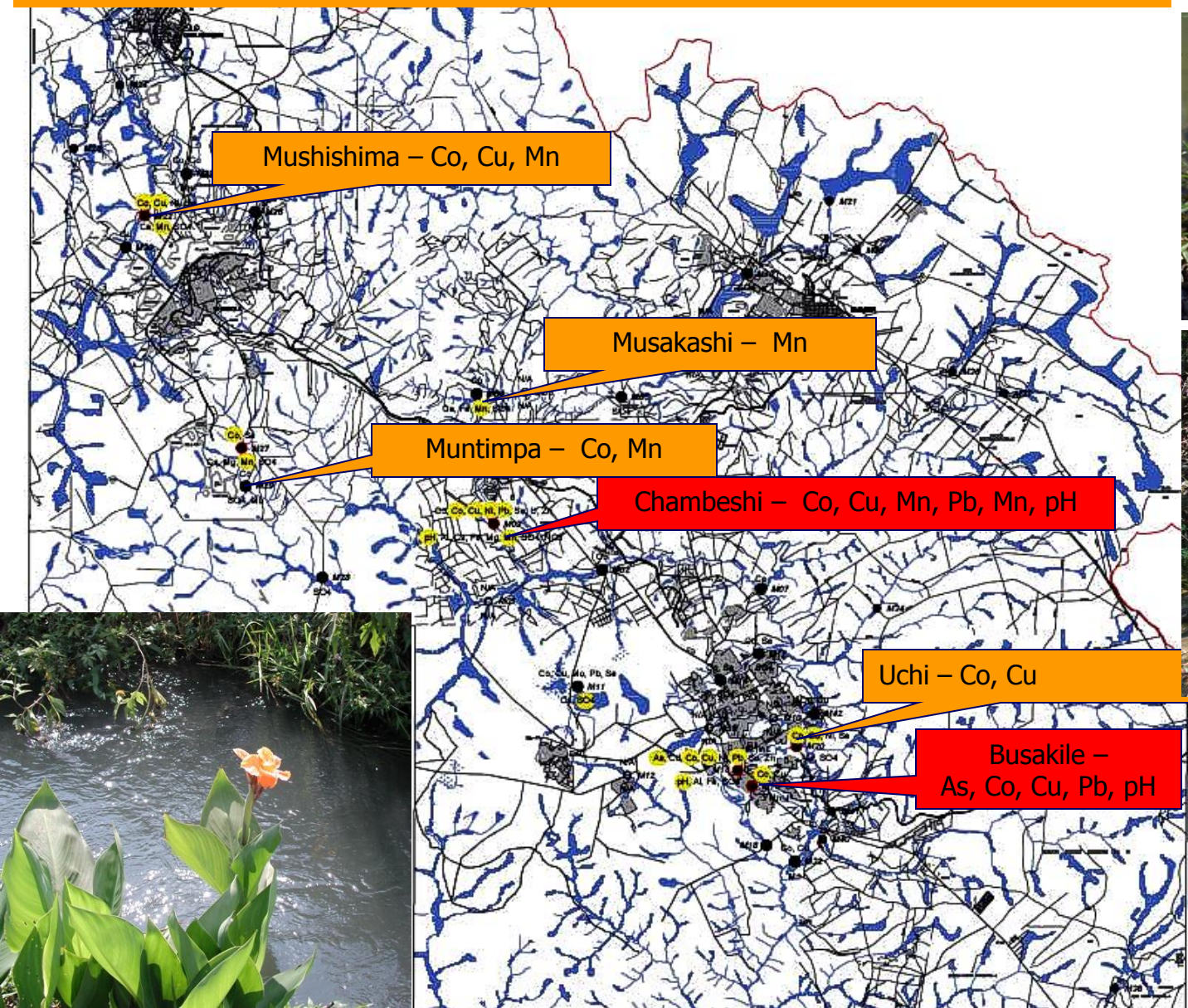
RESULTS: pH VALUES AND CONCENTRATIONS OF CHEMICAL ELEMENTS, the Kafue River

The pH values and concentration of chemical elements in uncontaminated and contaminated Kawue River water. The pH values and concentration of metals in surface water during acid spikes in the Lwanshimba and Chambeshi rivers (contaminated tributaries of Kafue) are given for comparison

	Uncontamin. Kafue (2006-2011)	Contaminated Kafue (2006-2011)	Acid spike Lwanshimba July7.2006	Acid spike Chambeshi July 7, 2006	Zambia limit efluent water	EU limit efluent water
pH	6.8-7.1	6.9-7.2	3.62	2.04	6-9	6-8
Al (ppb)	4-8	11-21	3.62	2115	2500	1500
As (ppb)	< 0.5	< 0.5-2.9	6929	872		
Cd (ppb)	< 0.05	< 0.05-3.43	6.5	2.0	50	1
Co (ppb)	< 0.05	10-30	2.0	29528	1000	10
Cu (ppb)	2.5-4.2	38-107	29528	16442	1500	30
Mn (ppb)	19-25	200-374	16442	466	1000	500
Pb (ppb)	< 0.2	0.2-0.7	317	161	500	15

RESULTS OF THE ENVIRONMENTAL-GEOCHEMICAL MAPPING SURFACE WATER CHEMISTRY

River water exceeding Czech and European Union effluent limits shown in red colour









BOX 4 Groundwater sampling

• In order to collect groundwater samples it is important to remove stagnant water of the well before collecting the sample. Many sampling practitioners collect samples after electrical conductivity (EC) of groundwater is stabilized. For water sampling, grab samplers (bailers) are recommended. They are portable, simple to use and relatively easy to clean.

• It is highly recommended to rinse bailer several times in the well water before taking sample. Groundwater samples have to be processed in the same way as surface water samples (unfiltered water sample and filtered and acidified water samples).

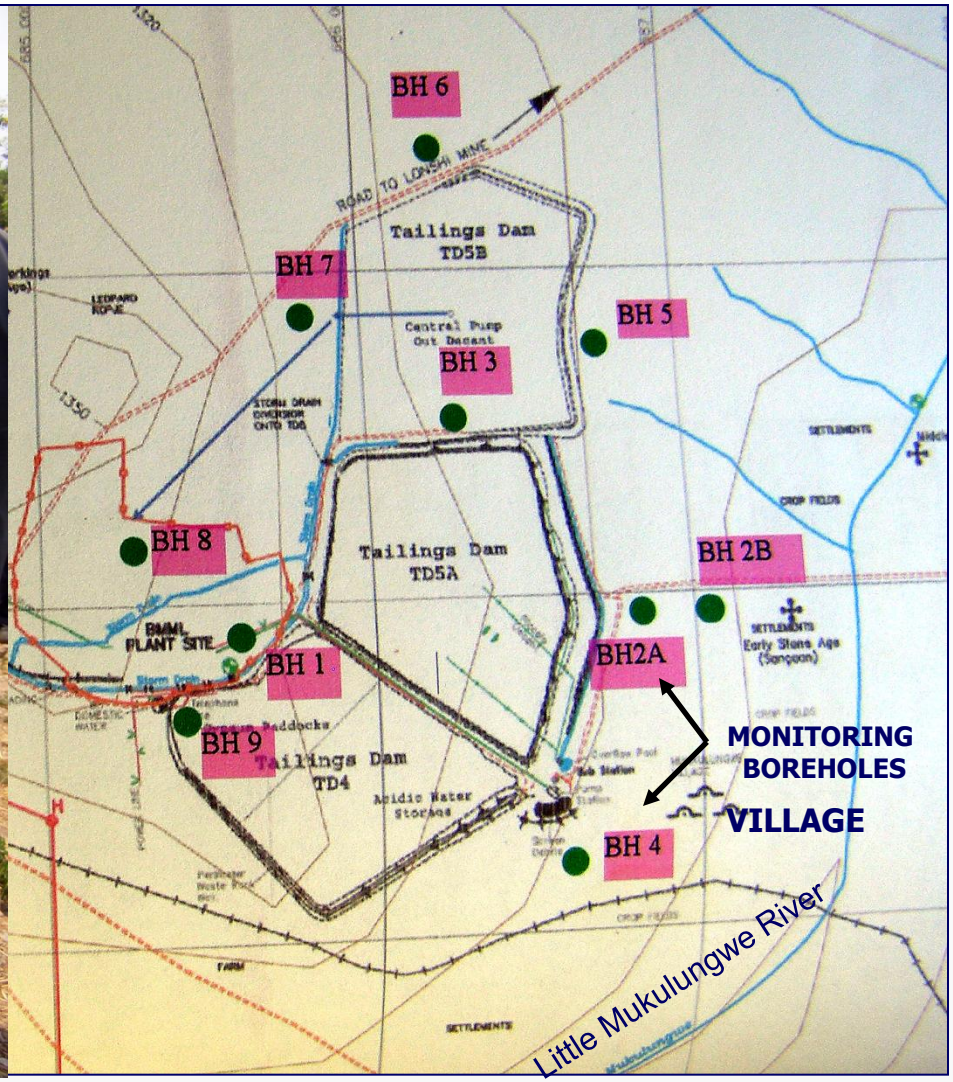
• Together with sampling, parameters such as geographic coordinates of the sampled well, sampling depth (water level), pH, temperature, electrical conductivity, oxidation-reduction (or redox) potential and dissolved oxygen have to be recorded. The alkalinity has to be determined in the field laboratory.

• Before transporting samples to analytical laboratory, samples should be kept at a temperature lower than that at which it was collected (cool box or fridge).

THE BWANA MKUBWA COPPER PROCESSING PLANT, COPPERBELT, ZAMBIA



Monitoring of groundwater quality, The Bwana Mkubwa processing plant, Zambia



THE BWANA MKUBWA COPPER PROCESSING PLANT, COPPERBELT, ZAMBIA

Bwana Mkubwa, Groundwater Monitoring Site BH 2A, East Side of the Tailing dam TD5A

	Jan	Feb	Mar	May	Jun	Jul
pH units	6.0	6.2	6.3	5.7	5.4	6.0
Electric conductivity	241	940	312	159	242	241.6
Total suspended solids TSS)	13	15	10	85	15	28.3
Total dissolved solids (TDS)	169	658	220	112	69	146
Dissolved copper	< 0.01	0.31	< 0.01	< 0.01	0.05	< 0.01
Dissolved cobalt	0.3	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Dissolved Iron	< 0.01	< 0.01	< 0.01	0.29	0.09	0.3
Dissolved manganese	0.06	0.08	< 0.01	< 0.01	0.09	< 0.01
Borehole depth (m)	28.6	28.6	28.6	28.6	28.6	28.6
Water level fom surface (m)	9.59	7.96	8.75	9.8	10.1	28.6
Well Volume (m3)	0.36	0.39	0.35	0.34	0.33	0.35

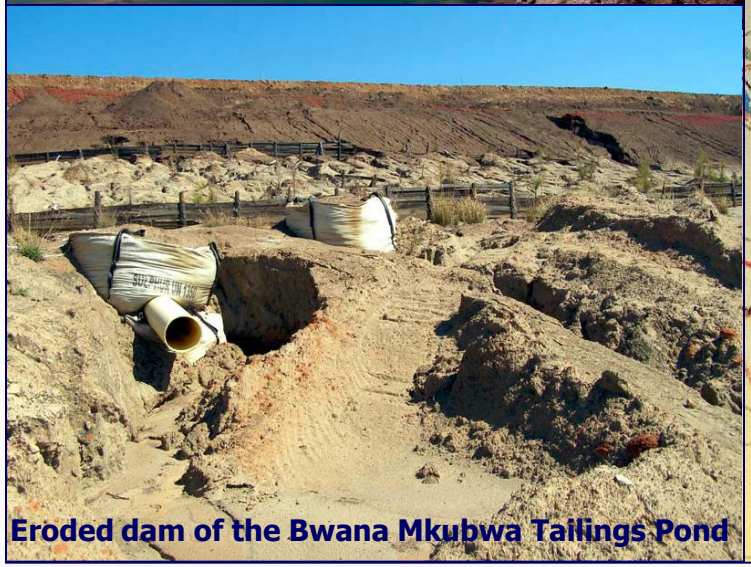
THE BWANA MKUBWA COPPER PROCESSING PLANT, COPPERBELT, ZAMBIA

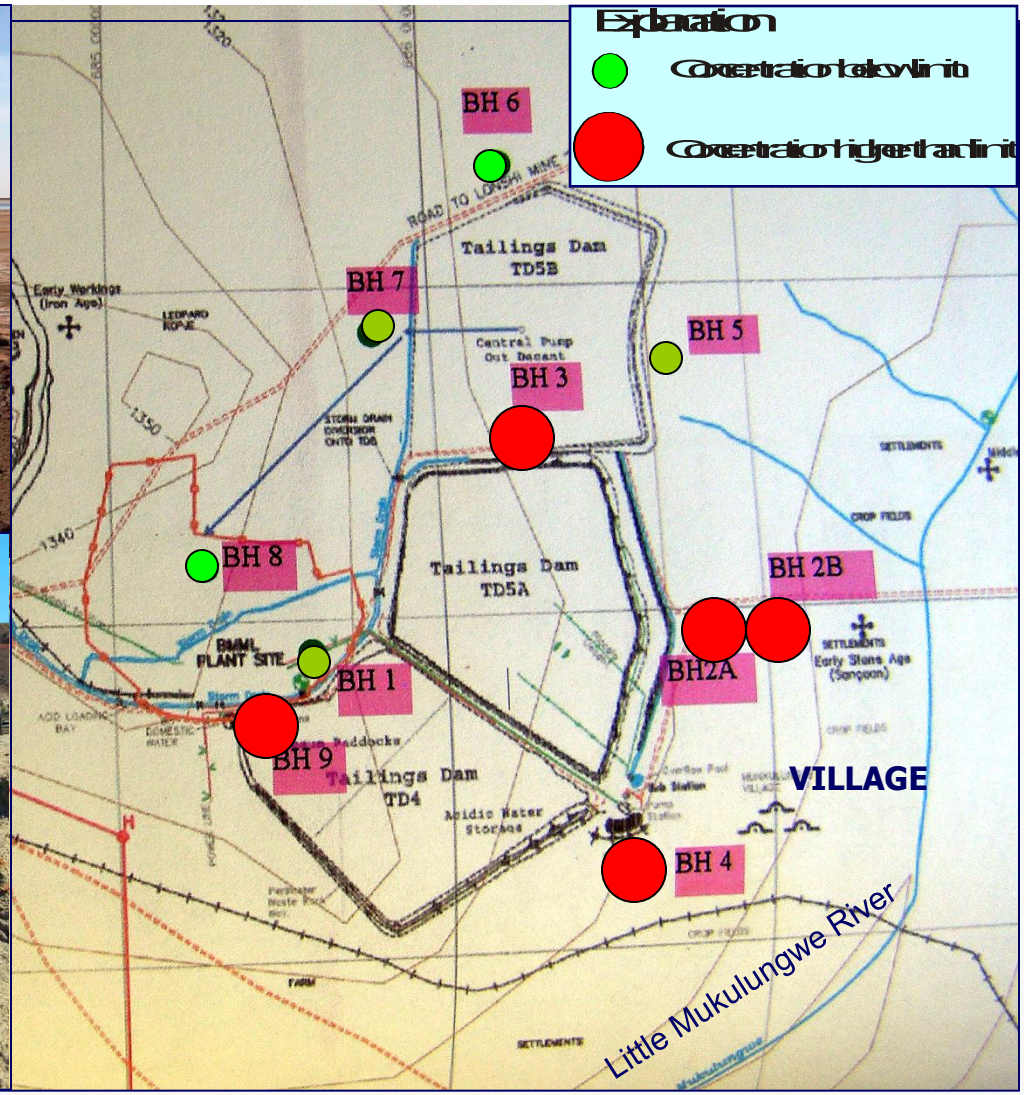
Bwana Mkubwa, Groundwater Monitoring Site BH 4 South-east Side of the Tailings Dam TD4

	Jan	Feb	Mar	May	Jun	Jul
pH units	6.2	6.2	5.3	4.1	4.4	4.4
Electric conductivity	4080	3308	3632	8205	7895	5383
Total suspended solids TSS)	51	47	40	40	70	20
Total dissolved solids (TDS)	2865	2320	2550	5778	5537	5383
Dissolved copper	< 0.01	< 0.01	39.66	384.2	317	1.39
Dissolved cobalt	0.36	< 0.01	0.91	9.01	1.67	0.48
Dissolved iron	22.5	8.5	9.9	243.1	140.2	410.5
Dissolved manganese	30.5	26.2	23.3	544.0	171.3	281.9
Borehole depth (m)	9.25	9.25	9.25	9.25	9.25	9.25
Water level fom surface (m)	4.86	3.98	3.9	4.89	5.43	5.55
Well volume (m3)	0.04	0.04	0.05	0.05	0.04	0.03

THE BWANA MKUBWA COPPER PROCESSING PLANT, COPPER CONCENTRATIONS


Surface of the Bwana Mkubwa Tailings Pond


Eroded dam of the Bwana Mkubwa Tailings Pond



BOX 5 Sampling of plants

• In order to assess the content of chemical elements in plants it is recommend to sample especially agricultural products, for example: lettuce (leaves), giant rape (leaves), cassava (leaves and tubers), sweet potato (leaves and tubers), maize (grains), rice (grains) and fodder (grass). Samples should be taken from several plants of the same species and from the same place.

• When sampling leaves of bushes and trees samples should be taken around the whole of circumference of the crown.

• The amount of collected plant material depends on the type of subsequent chemical analysis. For "wet" digestion, i.e. the decomposition of plant samples in a mixture of acids is required 1-5 g of dry sample, for more precise analyses of vegetation ash 15-30 g of dry plant tissues is needed.

• Plant samples should be straight in the field spread on a nylon sieve and washed thoroughly several times with tap water. The used tap water should be sent for chemical analysis. Samples of tubers or bulbs must be peeled prior to washing.

• It is recommended to homogenize plant samples in agate ball mill to analytical fineness (< 0.063 mm) before sending them to analytical laboratories.

Sampling of plants

It is recommend to sample especially agricultural products:

- Maize - grains
- Cassava – leaves
- Cassava – roots
- Sweet potatoes – leaves
- Sweet potatoes – roots
- Lettuce
- Millet – grains



Cassava field, Kitwe Region, Zambiua



Cassava leaves sampling in cooperation with owner



Soil rhizosphere sampling

Together with agricultural product, soil rhizosphere was sampled from the same point

CONCLUSIONS

Environmental-geochemical mapping and monitoring **allow geological surveys, the state administration, regional authorities and nonprofit organizations engaged in environmental protection to control effectively the obligations adopted by mining companies** in the field of environmental protection

Regional departments for land-use planning may use the results of monitoring in their planning activities in contaminated areas, **in urban planning, in meaningful industralization of rural areas**

On the other hand, the mining companies may use the environmental-geochemical monitoring and its results **to assess the efficiency of commitments made by them to protect the environment and to select priorities in remediation and reclamation works**

GLOSSARY

For the purpose of this Handbook, the following terms and phrases shall have the meanings set out below:

Abandoned Mine Site - A mine site that has been relinquished by its owners for the purpose of disposing of its ownership. It usually has not been closed down in a planned and orderly fashion.

Abandoned or Shut Down Mine Site - Class I: An abandoned or shut down mining operation that is assessed and found to have at least one 'significant risk' to human and/or environmental health or safety, or poses a risk to economic activity, and is therefore classified as an Environmental Mining Liability or MEL.

Abandoned or Shut Down Mine Site – Class II: An abandoned or shut down mining operation that is assessed and found to have 'no significant risks' and therefore is not considered a MEL.

Abandoned or Shut Down Mine Site - Class III: An abandoned or shut down mining operation that undergoes a pre-risk assessment and is found to have risks that are of no consequence to human and/or environmental health. These sites are not considered to be MELs.

Adverse effect - Any detrimental effect on humans, plants or animals due to exposure to a toxic substance.

Annual Exceedence Probability – The probability that an event of a certain magnitude may be equalled or exceeded in a specific year.

Area of Study: The zone potentially affected by human and/or environmental health and safety risks and/or risks to economic activities generated by an abandoned or shut down mining operation.

Atterberg Limit – A test to determine liquid and plastic limits on soil and its Plasticity Index.

Background concentration - Substance concentration in water, soil, sediment or air, at levels as found in natural environments.

Bioaccumulation - Process by which chemical substances accumulate in plants or animals via direct exposure to a contaminated source (soil, water, sediment) or indirectly by ingesting contamination from the food chain.

Cancer slope factor - An upper bound, approximating a 95 per cent confidence limit, on the increased cancer risk from a lifetime exposure to an agent. This estimate, usually expressed in units of proportion (of a population) affected per mg/kg-day, is generally reserved for use in the low-dose region of the dose-response relationship, that is, for exposures corresponding to risks less than 1 in 100.

Carcinogenic - An agent that may cause cancer.

Chemicals of potential concern - Chemicals that have hazardous properties, but will be of concern only when shown to come into contact with receptors at concentrations that would cause harm.

Chimney - Sloped or vertical mine work that is worked from the bottom upwards.

Chronic exposure - Continuous or repeated exposure to a given chemical substance for a long period of time.

Closure Plan – a legally required plan for all operating mines which must be regularly updated and submitted to MME.

Conceptual model - A written description and a visual representation of expected links between receptors and contaminants in an exposure scenario.

Cone Penetration Test – Test where a cone is introduced into the soil at a constant speed, the strength required must be measured continuously.

Contaminant - Any chemical, physical, biological or radiological substance found in the air, soil, water or biological matter that could be detrimental to human health or the environment.

Contamination - The environmental presence of substances, elements, energy or a combination of these in concentrations (or in concentrations and persistence) beyond the legal limit stipulated under current national legislation or according to international guidelines.

Cumulative effects - Synergies that result from the proximity of mining operations, where there is a combined impact on the same receptor(s).

***de manifestis* lifetime risk** - Cancer risk sufficiently large that some sort of remediation is desirable.

***de minimis* lifetime risk** - Cancer risk that is so small as to be negligible.

Direct pathway of exposure - Exposure to contaminants through direct contact with the contaminated medium, e.g., air, soil, water, through inhalation, ingestion or dermal contact.

Dose - Absorbed amount of a substance in the human or animal body from where it can exert its toxic effects, expressed per body weight (mg/kg-day).

Dump - A place used for depositing waste rock or solid waste.

Earthquake Design Ground Motion (EDGM) – Seismic ground movement expected for an analyzed area.

Ecological Risk Assessment – Process to evaluate risks to the health of ecological receptors.

Ecotoxicity - Toxic effects of chemicals on ecological receptors

Environment - The global system consisting of natural and artificial physical, chemical, biological, social and cultural elements and their interactions that is constantly being modified by human or natural action and that governs and conditions the existence and development of life in its multiple manifestations.

Environmental damage - All significant loss, diminishment, harm or impairment to the environment or one or more of its components.

Environmentally sensitive area - A portion of territory, legally protected or not, containing natural resources that are deemed unique or of special value to the authorities, scientists, environmental sectors and/or the community at large.

Excess cancer risk - Cancer risk over and above the existing cancer risk.

Exposure - Contact with toxic substances in environmental media.

Exposure assessment - Evaluation of exposure pathways of contaminants and quantification of dose in receptors.

Exposure pathway - Environmental media through which contaminants reach receptors from sources.

Exposure route - Mechanism of intake of contaminants, i.e., inhalation, ingestion or dermal exposure.

Extensometer – A device that measures movement on stress-strained ground.

Failure Mode – The manner in which an element undergoes failure, causing a loss in integrity.

Failure Modes Effects Criticality Analysis – A risk assessment procedure in which a system's potential failure modes are analyzed in terms of the combined influence of different Probabilities of Occurrence and Severity of Consequences.

Foundation – Rocks, concrete and/or soil that make up the base of a structure.

Freeboard – Vertical distance between water surface and the lowest elevation at the reservoir or pond crest.

Gallery - Horizontal or almost horizontal mine works.

Grain-size analysis – A test that determines soil particle size. Progressively, smaller screens are used to evaluate sandy soil distribution while using a hydrometer for finer grain soils (clay, silt).

Hazard - An imminent potential event or a situation that could cause harm.

Hazard index - The sum of hazard quotients.

Hazard quotient - The ratio of estimated exposure or dose and a reference exposure or dose level (e.g., reference concentration or dose).

Hazard Scenario - Description of the origin, causes and effects of risk-producing events.

Hazardous Waste - Waste or a mixture of waste that could harm public health or the environment, directly or as a result of present or future management, as a result of its acute, chronic or extrinsic toxicity, flammability, reactivity or corrosiveness.

Human Health Risk Assessment – Process to evaluate health risks for human receptors.

Indirect pathway of exposure - Exposure to toxic substances mainly through the food pathway, not through direct contact with contaminated environmental media.

Large Scale Mining Waste - Waste from mining activity consisting of waste rock, low grade ore, mineral waste from leaching, tailings and slag.

Liquefaction – Sudden loss of soil consistency, occurring when water pore pressure is equal to the cohesive force.

Liquid Limit – Soil water content generated by behaviour change from plastic to liquid state.

Low grade ore stockpile – mined ore with low grades which is stockpiled for later processing when economical or for blending with higher grade ore.

Mining Environmental Liability (MEL) - An abandoned or shut down mine, including its waste, that constitutes a significant risk to human and/or environmental health and safety and/or to economic activities.

Mining Operations - Includes all work carried out during and after the construction stage, in all facilities and workplaces of the Extractive Mining Industry, such as mines, treatment plants, smelters, refineries, metal shops, workshops, power plants, loading docks for mining products, camps, storehouses and in general all work, installations, support services and infrastructure necessary to ensure the functioning of the Extractive Mining Industry.

No-observed-adverse-effect level - Dose level of contaminants to humans or test animals at which no adverse health effects were observed.

Open Pit - Mining operation on the surface.

Phreatic Level - Soil water pressure equal to zero.

Piezometer – A device used to measure water pressure of pores on site, based on electronically pressured transducers or open stand pipes.

Plastic Limit – Soil water content where behaviour changes occur from solid to plastic.

Protected area - Any portion of territory that is geographically defined and legally established as officially protected for the purpose of safeguarding biological diversity, preserving nature and conserving the environmental heritage.

Receptor - Species, communities, habitats or ecosystems directly or indirectly exposed to one or more chemical substances associated to environmental contamination.

Reference concentration - Guideline concentration of a substance in an environmental medium against which the concentration of exposure is compared to estimate risk.

Reference dose - An estimate of a daily exposure for a given duration to the human population (including susceptible subgroups) that is likely to be without an appreciable risk of adverse health effects over a lifetime

Remediation Plan (also known as an Environmental Management Plan or a Rehabilitation Plan) - A document that describes in detail the actions and measures required to control, mitigate or eliminate the significant risk generated by a mining environmental liability.

Remediation - A series of actions and measures required to control, mitigate or eliminate a risk to human and/or environmental health or safety that is posed by a mining environmental liability, bringing the risk to an acceptable level (insignificant) and terminating the MEL designation.

Risk - The combination of an event's Likelihood of Occurrence and its Consequence.

Risk Assessment Matrix - An instrument that defines the magnitude of risk for a given Hazard Scenario based on the Likelihood of Occurrence and Potential Consequences for receptors.

Risk characterization - Integrates exposure and toxicity to estimate adverse effects on health associated with exposure to toxic substances.

Safety Factor – Ratio between the resisting forces and the disturbing forces.

Saturated Hydraulic Conductivity – Indicates the speed by which water flows through soil under a hydraulic gradient equal to one.

Seepage –Movement of water through soil.

Shaft - Vertical or sloped mining works running downwards.

Shut Down Mine Site: A mine site that has been shut down for any reason, whether temporarily or permanently, excluding shut downs for operational reasons, maintenance or other regular mine operative practice. A shut down mine site implies that the closure was carried out on a planned basis according to a predetermined Closure Plan.

Slope Indicator – A device, such as an inclinometer, which measures slope movement through time.

Small Scale/industrial Waste - Waste from mining activities not included in the above categories, such as sediment, rejected byproducts, left over reagents, ash, asbestos, tyres, etc.

Soil Liquidity Index – The index quantifying the soil water index related to liquid and plastic limits.

Soil Profile - A term used to illustrate soil strata.

Soil Water Characteristic Curve – Relation between water content in unsaturated soil and the negative pressure of water in soil pores (suction).

Stope - The rock excavation that remains after exploitation is completed in one section of the mine.

Stressor-response - A measure of adverse effects on ecosystems as a result of exposure to chemicals or physical factors.

Tailings dam - All works with safety measures that are designed to contain tailings from a wet concentration plant, including associated tailings pipes, penstocks, drainage systems. These deposits function as the final disposal place of the solid material contained in tailings transported from the plant and enable a large portion of the water in which they were transported to be recovered.

Tailings impoundment - A deposit of dry stacked tailings either end tipped and creating a slope at the natural angle of repose, or co-disposed with retaining walls built of waste rock

Tailings: Solids suspended in liquid to form a slurry that is generated and discharged from wet concentration plants from ore that has undergone one or more stages of fine crushing. The term is also applied to the solid portion of the slurry described above, or to material that is dewatered prior to discharge to the tailings impoundment for dry stacking.

Toe Berm – Material or structure installed in the lower area of the tailings slope to improve stability counterbalancing the trend towards rotational failure.

Toxicity - Inherent capacity of a substance to cause adverse effects in organisms.

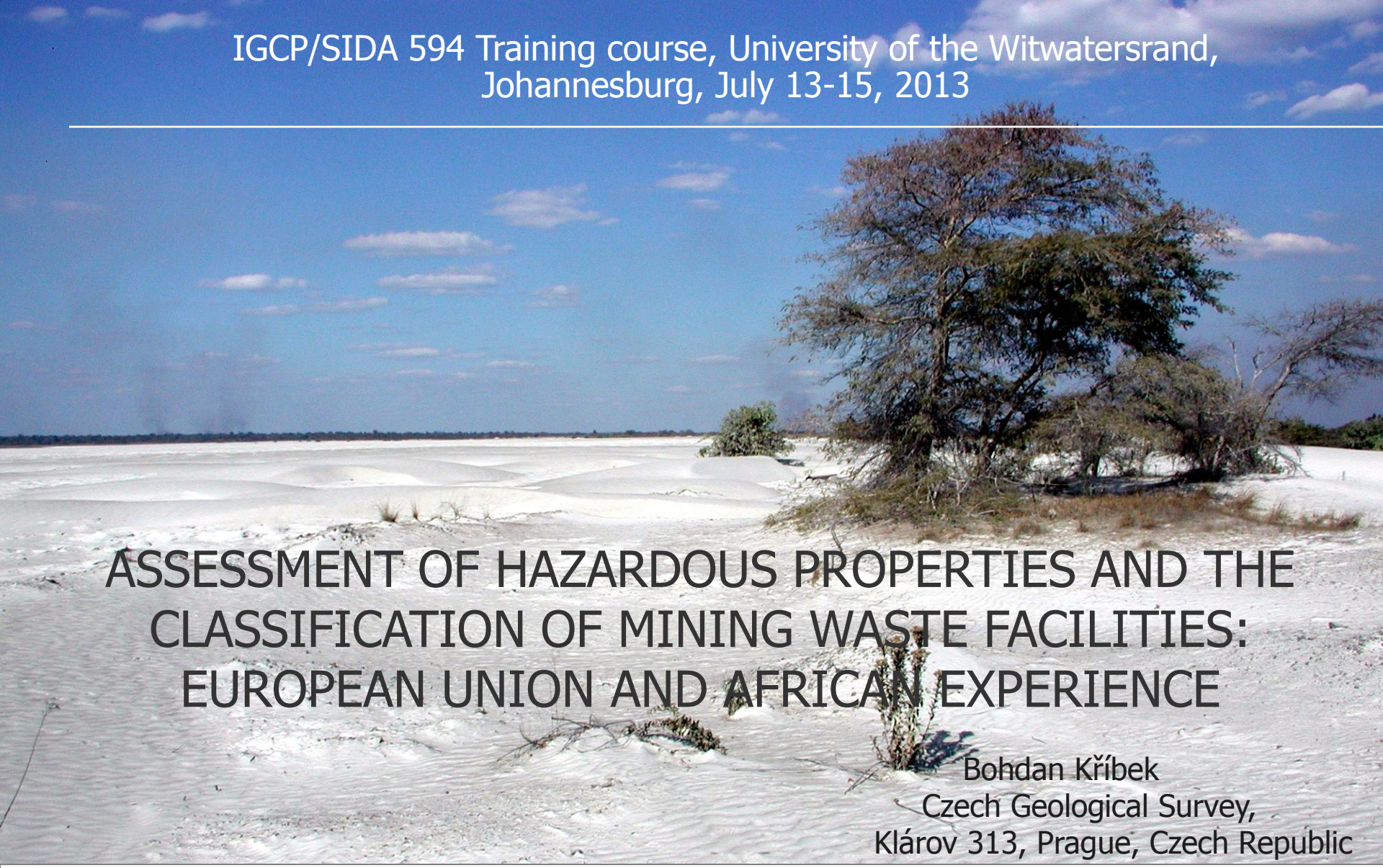
Uncertainty - A measure of the level of confidence in scientific interpretations.

Waste rock - Material with no economic value that is extracted with the ore or in mine development.

Waste rock dump - The accumulation of waste rock on the surface.

Water Content – The percentage of water in soil related to its dry weight.

IGCP/SIDA 594 Training course, University of the Witwatersrand, Johannesburg, July 13-15, 2013



ASSESSMENT OF HAZARDOUS PROPERTIES AND THE CLASSIFICATION OF MINING WASTE FACILITIES: EUROPEAN UNION AND AFRICAN EXPERIENCE

Bohdan Kříbek
Czech Geological Survey,
Klárov 313, Prague, Czech Republic

IUGS UNESCO

UNIVERSITY OF THE WITWATERSRAND JOHANNESBURG

1919 CZECH GEOLOGICAL SURVEY

UNESCO United Nations Educational, Scientific and Cultural Organization

IUGS International Union of Geological Sciences

Directive 2006/21/EC of the European Parliament and of the Council of March 15, 2006 on the management of waste from the extractive industries and amending Directive 2004/35/EC

(the Mining Waste Directive)

Category A (hazardous waste facilities) and Category non-A (non-hazardous waste facilities)

A waste facility shall be classified under **category A**, if:

a) a **failure** or **incorrect operation**, e.g. the collapse of a heap or the bursting of a dam, could give rise to a **major accident**, on the basis of a risk assessment taking into account factors such as the **size, the location and the environmental impact of the facility**; or

b) it contains waste **classified as hazardous** under Directive 91/689/EEC above a **certain threshold;** or

c) it contains substances or preparations **classified as dangerous** under Directives 67/548/EEC or 1999/45/EC **above a certain threshold**.”

STAGES OF THE ASSESSMENT

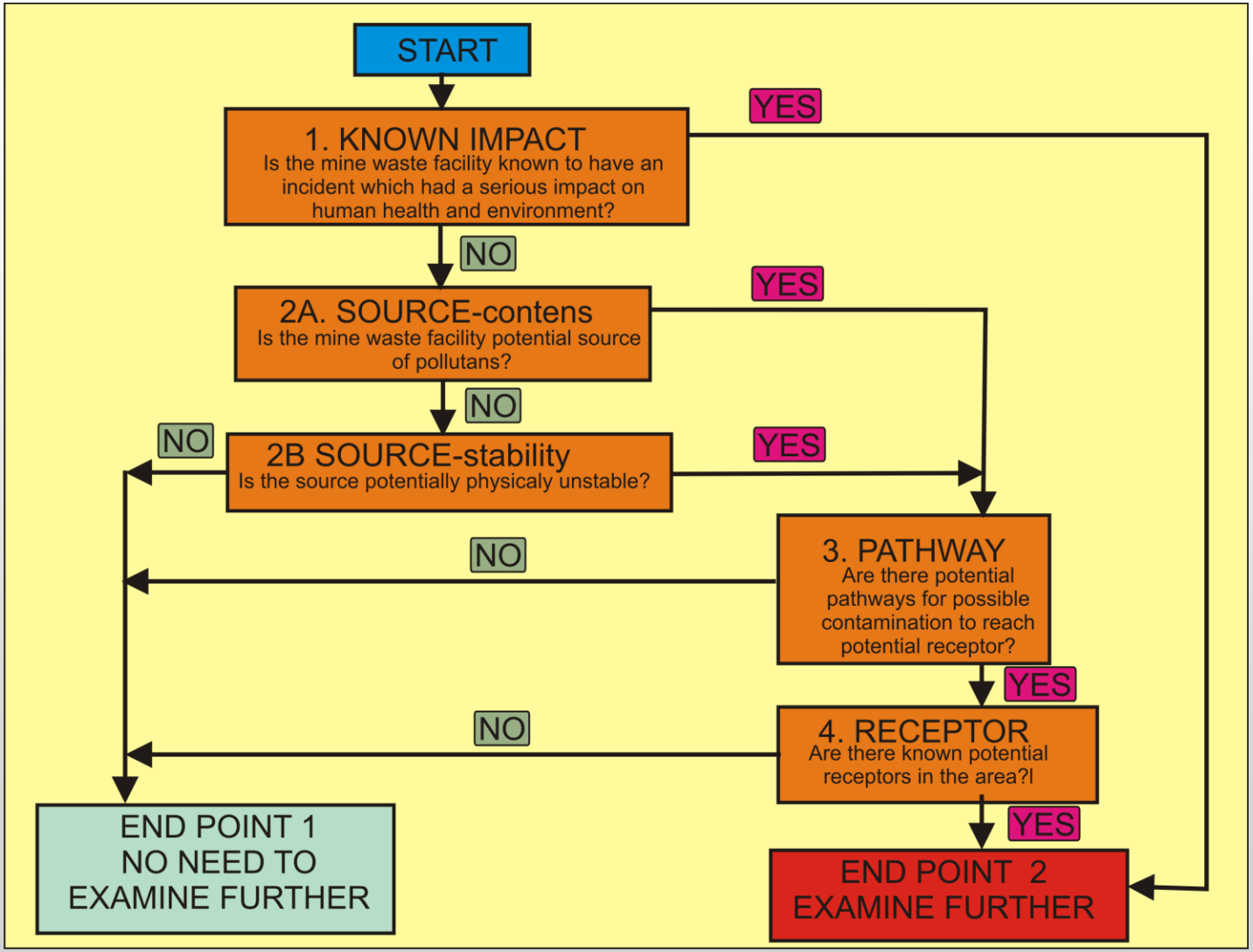
Stage I: Pre-selection characteristics of closed waste facilities

Stage II: Assessment of hazardous properties of wastes and their impact on the environment (pre-feasibility study)

Stage III: Assessment of hazardous propries of wastes and their impact on the environment – Feasibility study (EIA) and Risk assessment (ERA)

Stage I: Pre-selection characteristics of closed waste facilities

Pre-Selection Protocol Flowchart



STAGE I: PRE-SELECTION PROTOCOL (PART I)

1. General data	
1.1. Name of researcher, company, site code number	1.2 Facility owner, owner code number
1.3 District/Province/State/Country	1.4 General type of landscape use *(agriculture, forest, industrial, residential)*
1.5 Topographic data *(including terrain data from contour lines or digital elevation model)*	1.6 Census data
1. 7 Status classification *(existing monitoring data and river basin management plans of surface and groundwater bodies, land-use plans)*	
2. Waste facility type	
2.1 Waste rock heaps: *(heap, pond, backfilling of old excavation voids, backfilling of operation strip mines or operated underground mines)*	2.3. Tailings: *(backfilling of tailings into operating mines, tailing ponds, rxisting open pits and depressions, valley impoundment, off-valey impoundment)*
2.2. Waste monitoring system *(drainage, collection ditches, monitoring wells)*	
3. Basic waste facility data *(site data)*	
3.1 Area (m^2)	3.2 Volume (m^3)
3.3. Height, thickness	3.4. GPS X, Y, Z coordinates
3.5. Coordinates system, map datum	3.6 Accuracy of measurement

STAGE I: PRE-SELECTION PROTOCOL (PART II)

4. Geology	
4.1 Rock type	4.2 Grain size
4.3 Mineralogy *(primary and secondary minerals)*	4.4 Possibility of waste use *(re-use, construction purposes, aggregates, soil amendment, others)*
5. Current stage of remediations	
5.1 Current state *(in use, re-processed, closed, abandoned, remediated, unremediated, not known)*	5.2 Date of the facility closure
5.3 Remediation measures description:	
6. Wastes related incidents in the past *(dam failure, massive river water or groundwater contamination, cattle or fish mortality, others)*	
7. Contents of potential harmful chemical elements and materials in waste	
7.1. **Sulfides, AMD producing, non-AMD producing agents**	**7.2. Potentially harmful metals, metalloids and materials *(As, Ba, Be, Cd, Co, Cr, Cu, Hg, Ni, Pb, Sb, Se, Sn, Te, Tl, U, V, Zn, asbestos)***
7.3. Dangerous substances *(cyanide, mercury, flotation agents)*	

STAGE I: PRE-SELECTION PROTOCOL (PART III)

8 Stability of waste facility	
8.1 Tailings, area of lagoon (m2)	8.6. Slope of the waste heap
8.2 Tailings lagoon description	**8.9. Slope of the waste heap foundation**
8.3. Height of the tailing lagoon surface relative to surface outside facility	
8.4. Slope of the tailings dam	
8.5 Slope of the foundation	
9 Pathways of dispersion	
9.1. Wastes erosion, watercourses siltation, overflow, seepage	*9.2. Permeability of layer beneath the mine waste of tailings facilities*
9.3. Exposition of waste material to the wind (vegetation cover)	9.4. Waste cover type (*water, slag, laterite, bitumen, soil*) and cover thickness
10 Recepients	
10.1. Location of settlement *(single houses, communities, villages)*	10.2. Agricultural land, livestock, fishery
10.3. Water resources (wells, water reservoirs)	10.4. Data on location of areas protected by legislation *(National parks, games, points of interests etc.)*
10.5. Any other known serious impacts	

STAGE I: PRE-SELECTION PROTOCOL (PART IV)

11 Other data	
11.1. Conflict of interests *(water reserves, electricity lines, gas lines, land-use plans, military facilities)*	11.2. Access to the site
11.3. Possibility to collect samples *(without technical works, with light technical works, excavator, drilling only)*	
12 Recommendation (examine further – no need to examine further)	
Date, signature	Annexes: Maps, photographs, list of samples



Mufulira Tailing Pond, Zambia

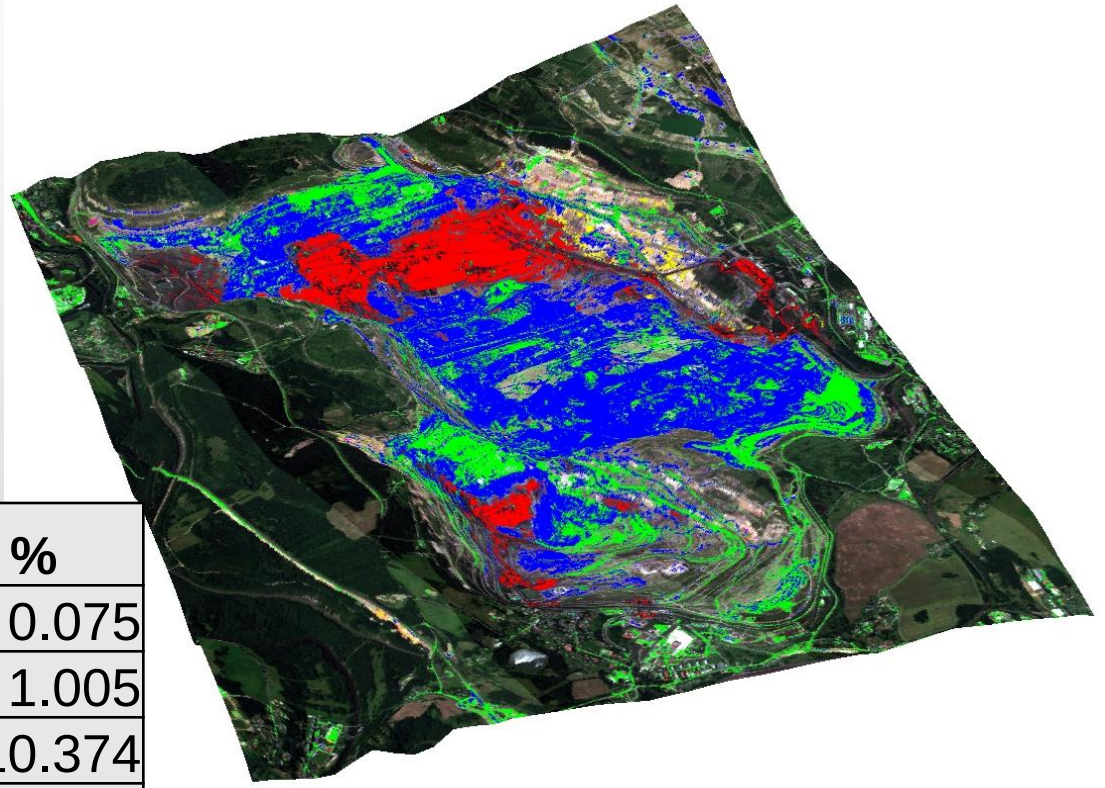


Chambishi waste heap, Zambia

STAGE I, SOURCES OF INFORMATION: Mine operators, geological surveys, municipalities, LANDSAT, Google Earth, aerial photographs, field survey..

Example:
Hyperspectral imagery
(Satelite and airborne data and ground verification)

	Class	km²	%
	Jarosite	0.008	0.075
	Goethite	0.109	1.005
	Lignite	1.126	10.374
	Granite + Clay	3.385	31.184
	Clay	6.226	57.362
	Total	10.853	100



Sokolov Coal Basin, Czech Republic


Example of airborne survey:
Mine waste heap, Chingola, Zambia
Gypsum precipitates
Active drainage
Stream contamination

STAGE II: ASSESSMENT OF HAZARDEOUS PROPERTIES OF WASTES AND THEIR IMPACTS ON THE ENVIRONMENT – **SAMPLING**

Sampling sites:

1) Background (springs, watercourses, hydrogeological wells, test pits, bored wells)

2) Waste material (hand-picked average samples, test pits, drilling)

3) Transpoprt pathways (seepage, run-off sediments bored pits, boreholes hydrogeological wells, control wells

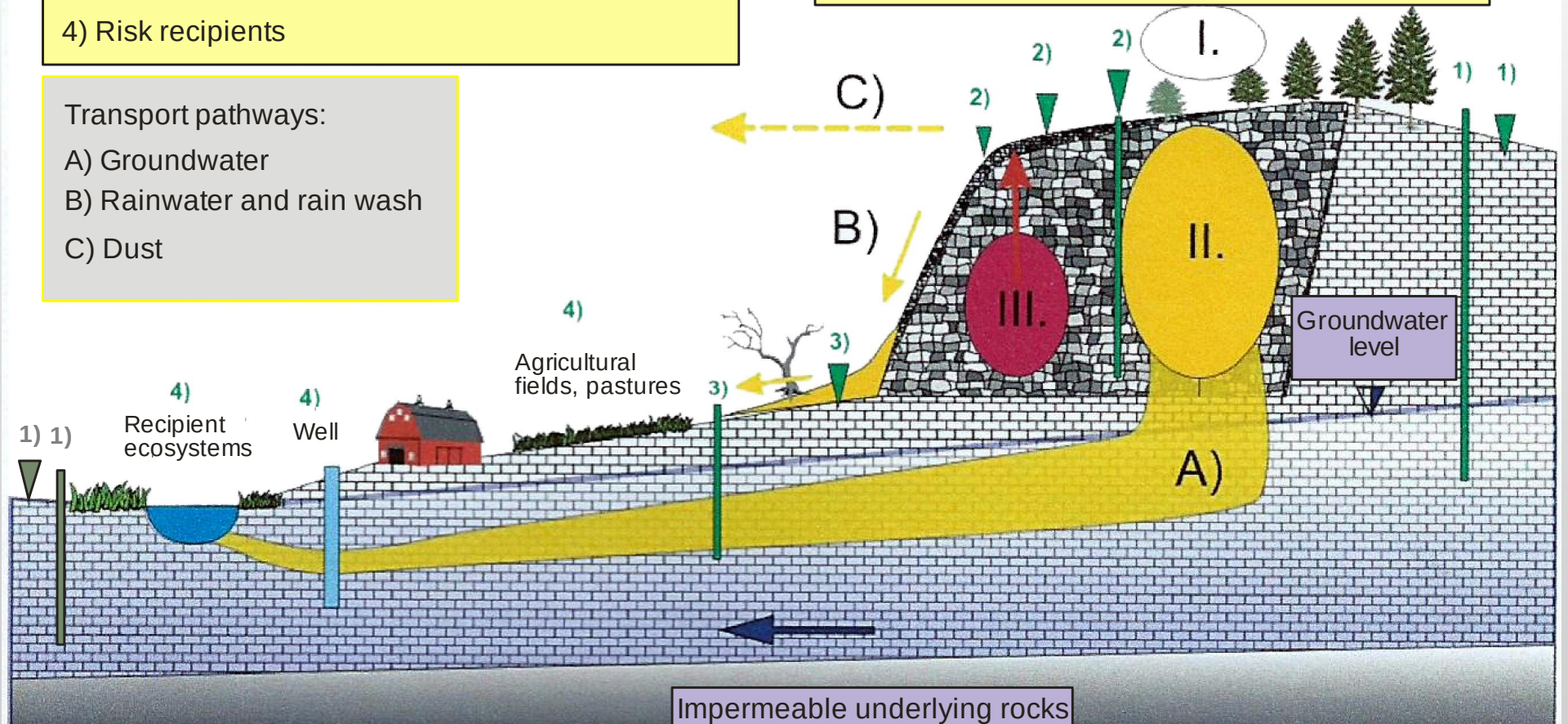
4) Risk recipients

Physical and chemical processes:

I. Physical and chemical weathering (mechanical disintegration, secondary minerals)
II. Sulfides oxidation, carbonate dissolution, acidification
III. Waste burning (coal), redistribution of metals and metalloids

Transport pathways:

A) Groundwater
B) Rainwater and rain wash
C) Dust



STAGE II: ASSESSMENT OF HAZARDEOUS PROPERTIES OF WASTES AND THEIR IMPACTS ON THE ENVIRONMENT – **TYPE OF SAMPLES AND SAMPLING DENSITY**

a) BACKGROUND SAMPLING (springs, wells, soils, agricultural prouducts, grass) (5-30 samples)

b) WASTE MATERIAL SAMPLING (hand-picked average samples, test pits (1-2 m depth) shallow drilling (3-7 m depth), waste water (3-5 samples)

c) TRANSPORT PATHWAYS SAMPLING (water run-off sediments, seepages, water from bored pits,boreholes, hydrogeological wells, control wells) (sampling wherever possible)

d) RISK RECIPIENTS SAMPLING
- soils (30- 50 samples)
- agricultural products and grass (10-20 samples)
- surface water (10 –20 samples)
- stream sediments (10-20 samples)
- water wells (sampling wherever possible)

STAGE II: ASSESSMENT OF HAZARDOUS PROPERTIES OF WASTES AND THEIR IMPACTS ON THE ENVIRONMENT – CHEMICAL ANALYSES

WASTES SAMPLING ACCORDING TO EU REGULATIONS

(1) ***Neutralization potential ratio*** **(NPR) = NP/AP**

Where: NP (neutralisation potential) = kg $CaCO_3$/t * 10 waste (calculated from C_{tot}-C_{org} = C_{carb})
Where: AP (acid potential) = Total S (wt.%)* 31.25

For NP/AP > 3, the waste is considered non- acid generating (non-A waste)
between 3-1 uncertainity interval, less than 1: acid generation waste (A-waste)
Analytical procedure: CEN/TC 292/WG

May be substituted by the determination of the net *neutralization potential* (NNP):
NNP = NP-AP
NNP values > 20 kg CaCO3/t of waste (non A waste)
NEP values **<** 20 kg CaCO3/t of waste (A-waste)
Analytical procedure after Sobek

STAGE II: ASSESSMENT OF HAZARDOUS PROPERTIES OF WASTES AND THEIR IMPACTS ON THE ENVIRONMENT – CHEMICAL ANALYSES

WASTES SAMPLING ACCORDING TO EU REGULATIONS

(2) ***The content of hazardous substances*** (Ag, As, Ba, Be, Cd, Co, Cr, Cu, Hg, Ni, Pb, Sb, Se, Sn, Te, Tl, U, V, Zn or asbestos)

Checking the content of various substances against the **threshold values** defined by the hazard properties (H1-H14) in Annex III to Directive 91/689/EEC and the risk phases defined in Directive 2001/59/EC).

(3) ***The content of substances or preparations classified as dangerous*** (cyanide, phenols, flotation agents)

Checking the content of substances classified as dangerous under Directives 67/548/EEC or 1999/45/EC

STAGE II: ASSESSMENT OF HAZARDEOUS PROPERTIES OF WASTES AND THEIR IMPACTS ON THE ENVIRONMENT – **THRESHOLD VALUES**

THRESHOLD VALUES

(a) one or more substances classified as **very toxic** at a total concentration ≥ 0.1 %,

(b) one or more substances classified as **toxic** at a total concentration ≥ 3 %,

(c) one or more substances classified as **harmful** at a total concentration ≥ 25 %,

(d) one or more **corrosive** substances classified as R35 at a total concentration ≥ 1 %,

(e) one or more **irritant** substances classified as R41 at a total concentration ≥ 10 %,

(f) one substance known to be **carcinogenic** of category 1 or 2 at a concentration ≥ 0.1 %,

(g) one substance **toxic for reproduction** of category 1 or 2 classified as R60, R61 at a concentration ≥ 0,5 %,

(h) one **mutagenic** substance of category 1 or 2 classified as R46 at a concentration ≥ 0.1%,

SERIOUS PROBLEM

STAGE II: ASSESSMENT OF HAZARDEOUS PROPERTIES OF WASTES AND THEIR IMPACTS ON THE ENVIRONMENT – CHEMICAL ANALYSES

EUROPEAN UNION THRESHOLD VALUES ARE BASED ON PROPERTIES AND CHARACTERISTICS OF DANGEROUS **CHEMICAL SUBSTANCES** CLASSIFIED AS HAZARDOUS

DANGEROUS PROPERTIES OF **MINERAL PHASES** ARE NOT AVAILABLE

THEREFORE, MEMBER STATES OF THE EUROPEAN UNION USE THRESHOLD VALUES FOR REGIONAL SCREENING OF SOIL CONTAMINATION INSTEAD

STAGE II: ASSESSMENT OF HAZARDEOUS PROPERTIES OF WASTES AND THEIR IMPACTS ON THE ENVIRONMENT

THRESHOLD VALUES FOR SOIL CONTAMINATION: Holland, Canada

	Holland		Canada, soils (mg/kg)			
	Soil/Sediment, Action (mg/kg)	**Groundwater, Action (μg/l)**	**Agricultural use**	**Residential use**	**Commercial use**	**Industrial use**
As	55	60	12	12	12	12
Ba	625	625	500	500	750	2000
Cd	12	6	1.4	10	10	22
Cr (tot)	380	30	64	64	64	87
Cu	190	75	63	63	63	91
Pb	530	75	70	140	140	600
Ni	210	75	50	50	50	50
Hg	10	0.3	6.6	6.6	6.6	50
Zn	720	800	200	200	200	360
Cyanide (free)	20	1500	0.9	0.9	0.9	8

THRESHOLD VALUES FOR SOIL CONTAMINATION

USEFUL DOCUMENTS

Holland (Dutchlist)	http://www.axys.cz/doc/en/Dutchlist.pdf
	http://www.rivm.nl/en
United Kingdom	http://www.doh.gov.uk
	http://www.defra.gov.uk/environment/land/contamined/index.htm
United States	http://www.epa.gov/ecotox/ecossl/
	http://www.epa.gov/oswer/riskassessment/index.htm
	http://www.epa.gov/ecptpx
Canada	http://www.ccme.ca/publication/list_publications.html
Australia	http://www.dec.wa.gov.au/contaminatedsites
New Zealand	http://contamsites.landcareresearch.co.nz/about.htm
	http:www.mfe.govt.nz/publications/hazardous/
World Health Organisation	http://www.who.int/en/

(ES dat) - comparison http://www.esdat.com.au (and go to Environmental standards)

STAGE II: ASSESSMENT OF HAZARDEOUS PROPERTIES OF WASTES AND THEIR IMPACTS ON THE ENVIRONMENT

ADDITIONAL CHEMICAL AND BIOLOGICAL METHODS OF WASTE SAMPLING

(1) pH of collected mine waste water (tailings ponds)

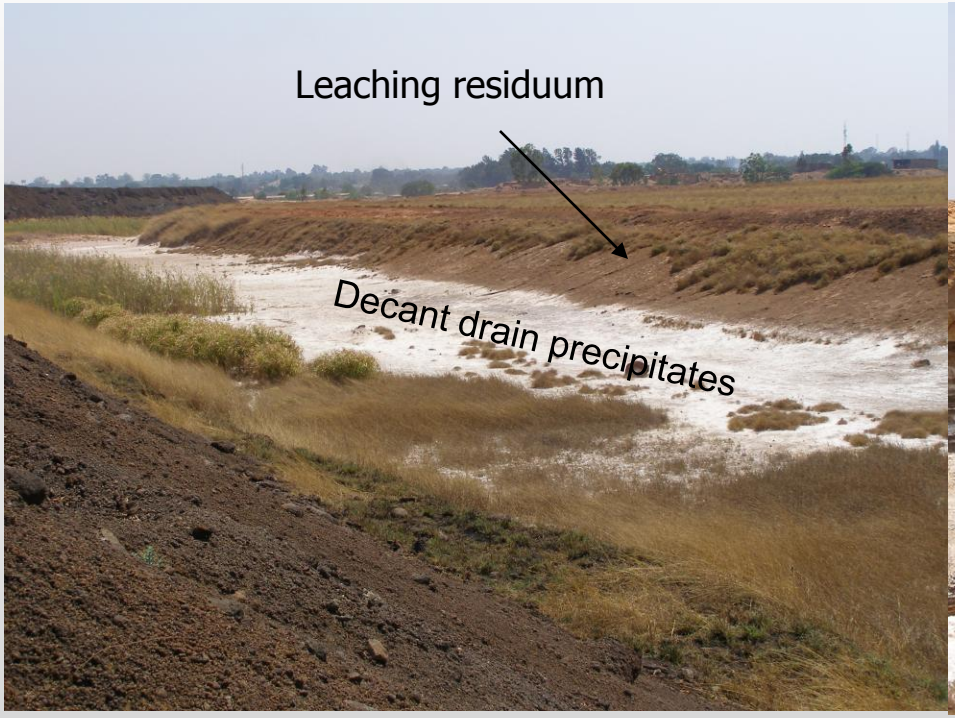
(2) pH of water leachate of wastes

(3) Chemical composition and physical properties of waste water leachate (static and kinetic tests)

(4) Ecotoxicity of waste water leachate

(5) Metals partitioning (sequentional analyses)

STAGE II: ASSESSMENT OF HAZARDEOUS PROPERTIES OF WASTES AND THEIR IMPACTS ON THE ENVIRONMENT – **EXAMPLE** – KABWE WASTES, ZAMBIA



Residuum from chemical leaching of lead and zinc ores and decant drain precipitates, Kabwe, Zambia



Flotation tailings after treatment of lead and zinc ores, Kabwe, Zambia

STAGE II: ASSESSMENT OF HAZARDEOUS PROPERTIES OF WASTES AND THEIR IMPACTS ON THE ENVIRONMENT – EXAMPLE – KABWE WASTES – **STATIC LEACHING TEST** (According to the Directive 1999/31/EC („Landfill Directive"),



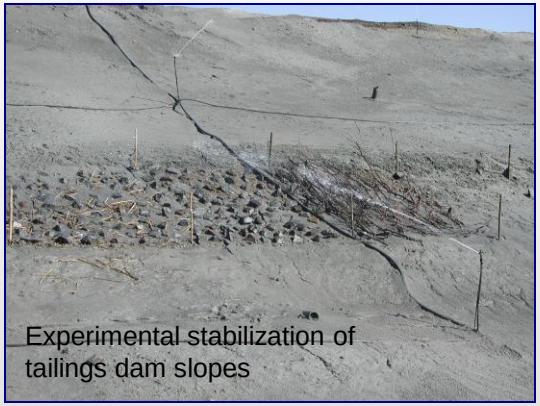
Settling pond at plant for chemical treatment of copper and cobalt ores ofthe Sable Zinc Plc. at Kabwe, Zambia, with efflorescence of cobalt and copper salts.



STAGE II: ASSESSMENT OF HAZARDEOUS PROPERTIES OF WASTES AND THEIR IMPACTS ON THE ENVIRONMENT – EXAMPLE – KABWE WASTES – **STATIC LEACHING TEST** (According to the Directive 1999/31/EC („Landfill Directive")

	EU limits (mg/kg of dry substance) L/S 2l/kg, static test			**Kabwe wastes,** Zambia (mg/kg) L/S 2l/kg, static test			
Element	Inert waste	Hazardous waste at land fills for nonhazardous waste	Hazardous waste for landsfillls for hazardous waste	Decant drain from chemicaly leached waste	Chemical leaching residuum	Flotation tailings	Active tailings after chemical leaching
As	0.1	0.4	6	0.06	< 0.05	< 0.005	0.06
Cd	0.03	0.6	3	5.15	0.204	0.204	0.352
Cr -tot	0.2	10	25	0.01	< 0.005	0.005	0.04
Hg	0.003	0.05	0.5	< 0.001	< 0.001	< 0.001	< 0.001
Ni	0.2	5	20	1.4	< 0.02	< 0.02	**9.09**
Pb	0.2	5	25	2.64	0.26	0.26	0.159
Se	0.06	0.3	4	**0.62**	< 0.05	< 0.05	**0.451**

STAGE II: ASSESSMENT OF HAZARDEOUS PROPERTIES OF WASTES AND THEIR IMPACTS ON THE ENVIRONMENT – **EXAMPLE** - **ACUTE ECOTOXICITY TEST** – ROSH PINAH, NAMIBIA



Experimental stabilization of tailings dam slopes



Dust storm over the Rosh Pinah Town



The windblown dust from the tailings dam is a potential environmental problem at the Rosh Pinah Town

STAGE II: ASSESSMENT OF HAZARDEOUS PROPERTIES OF WASTES AND THEIR IMPACTS ON THE ENVIRONMENT – EXAMPLE - **ACUTE ECOTOXICITY TEST** – ROSH PINAH, NAMIBIA

Test type	Limit value	Samples Rosh Pinah, Namibia RP-1	RP-2	RP-3	RP-4
Immediate toxicity Tested on aquarial fish (Poecilia reticulata)	Average mortality: max. 5 %	0 0	0 %	0 %	0 %
Immediate toxicity tested on water fleas *(Daphnia magna)*	Average immobilization **max. 30 %**	**85 %**	**92%**	**100 %**	**93 %**
Test on freshwater algae	Average inhibition or stimulation: **max 30 %**	10.3 %	12.4 %	**32.7 %**	**33.1 %**
Test on seeds of higher plants *(Sinapis alba)*	Average inhibition or stimulation: max. 30 %	22.6 %	4.9 %	4.3 %	15.1 %
Bacterial bioluminiscence test *(bacteria Vibrio fisheri)*	Average stimulation or inhibition: max: 30 %	12.4 %	12.6 %	9.3 %	10.1 %

STAGE II: ASSESSMENT OF HAZARDEOUS PROPERTIES OF WASTES AND THEIR IMPACTS ON THE ENVIRONMENT – **PRELIMINARY RISK ASSESSMENT**

PRELIMINARY RISK ASSESSMENT - INCIDENTS			
	LOW RISK	INTERMEDIATE RISK	HIGH RISK
INCIDENTS IN THE PAST	Without incidents	Small incidents affecting environment within a specified distance from the facility (< 1 km)	Loss of human life or incidents affecting environment in extent larger than a specific distance from the facility (> 1 km)

Stage II: ASSESSMENT OF HAZARDEOUS PROPERTIES OF WASTES AND THEIR IMPACTS ON THE ENVIRONMENT – PRELIMINARY RISK ASSESSMENT

PRELIMINARY RISK ASSESSMENT – CHEMICAL PROPERTIES OF WASTES			
	LOW RISK	INTERMEDIATE RISK	HIGH RISK
Neutralization potential ratio	> 3	3-1	< 3
Content of specified substance	Not exceeding threshold limit values for Ag, As, Ba, Be, Cd, Co, Cr, Cu, Hg, Ni, Pb, Sb, Se, Sn, Te, Tl, U, V, Zn, asbestos	Exceeding threshold limit values in the same concentration range	Exceeding threshold limit values in higher concentration ranges
Content of dangerous chemicals	Not exceeding threshold Limit values	Exceeding threshold(s) in the same concentration range	Exceeding threshold(s) in higher concentration ranges
Leachability	Not exceeding threshold(s) for innert waste	Not exceeding thresholds for hazardous wastes	Exceeding thresholds for hazardous wastes
Ecotoxicity	Not exceeding thresholds	Exceeding some thresholds	Exceeding all thresholds

Stage II: ASSESSMENT OF HAZARDEOUS PROPERTIES OF WASTES AND THEIR IMPACTS ON THE ENVIRONMENT – PRELIMINARY RISK ASSESSMENT

PRELIMINARY RISK ASSESSMENT – GEOTECHNICAL PROPERTIES OF WASTES			
	LOW RISK	INTERMEDIATE RISK	HIGH RISK
Tailings lagoon size	< 5000 m^3	5 000-10 000 m^2	> 10 000 m^2
Height of tailings lagoon relative to the landscape altitude 50 m from the dam	< 2 m	2-4 m	> 4 m
Inclination of the foundation	< 3o	3-5^o	> 5^o
Overal waste heap slope	< 20^o	20-30^o	> 30^o
Height of waste heap	< 10 m	10-30 m	> 30 m

Stage II: ASSESSMENT OF HAZARDEOUS PROPERTIES OF WASTES AND THEIR IMPACTS ON THE ENVIRONMENT – PRELIMINARY RISK ASSESSMENT

PRELIMINARY RISK ASSESSMENT – IMPACTS ON THE ENVIRONMENT			
	LOW RISK	INTERMEDIATE RISK	HIGH RISK
Surface water	Not exceeding thresholds for surface water	Exceeding threshold(s) for surface water within 1 km of the waste facility	Exceeding threshold(s) for surface water more than 1 km of the waste facility
Potable water	Not exceeding thresholds for potable water	Exceeding threshold(s) for potable water within 500 from the waste facility	Exceeding threshold(s) for potable water more than 500 m from the waste facility
Stream sediments	Not exceeding thresholds for stream sediments	Exceeding threshold(s) for surface water within 2 km from the waste facility	Exceeding threshold(s) for surface water more than 2 km from the waste facility
Agricultural products and pasture grass	Not exceeding threshold(s)	Exceeding threshold(s) within 500 m from the waste facility	Exceeding threshold(s) more than 500 m from the waste facility

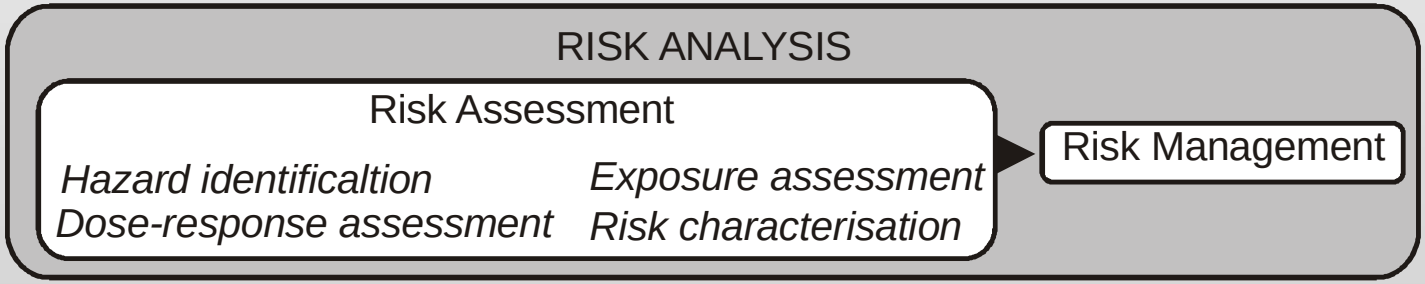
Stage II: ASSESSMENT OF HAZARDEOUS PROPERTIES OF WASTES AND THEIR IMPACTS ON THE ENVIRONMENT – PRELIMINARY RISK ASSESSMENT

PRELIMINARY RISK ASSESSMENT – IMPACTS ON THE ENVIRONMENT			
	LOW RISK	INTERMEDIATE RISK	HIGH RISK
Soils A) Agricultural land-use B) Residential land-use C) Commercial land use A) Industrial land use	Not exceeding threshold(s) for single land use category	Exceeding threshold(s) for individual land use categories within 1 km from the waste facility	Exceeding threshold(s) for For individual land use more than 1 km from the waste facility
Dust	Not exceeding threshold(s)	Exceeding short-term threshold values (24 h) for total suspended particles or particlles PM_{10} or $PM_{2.5}$	Exceeding long-term threshold values for total suspended particles, MP_{10} or $MP_{2.5}$ particles

STAGE III: ASSESSMENT OF HAZARDEOUS PROPERTIES OF WASTES AND THEIR IMPACTS ON THE ENVIRONMENT - FEASIBILITY STUDY (EIA) AND RISK ASSESSMENT (ERA)

In a technical risk-based discipline, risk is often defined as the combined effect of the likelihood of a harmful event to occur (caused by a hazard), and the magnitude of the caused harm.

Two fundamental phases are involved: risk assessment and risk management.



Examples of risk assessment models

The European Union TAC-model
The criteria and limit values for acceptance of waste at landfills for inert, non-hazardous and hazardous waste landfills was set based on a risk assessment procedure developed by the TAC Subcommittee on the Landfill Directive.

VROM (The Dutch Directorate General for the Environment)
Dutch soil remediation policy (VROM, 1994) uses soil remediation intervention values, indicative levels for serious contamination and target values.

SEPA (The Swedish Environmental Protection Agency)
Humans and eco-systems are exposed to contaminants in several ways. The potential exposure pathways are considered when developing national generic guideline values for concentration of substances in soil. These are based on the principles for deriving SSLs (Soil Screening Levels) as described by the US EPA (US EPA, 1996b). In Sweden, seven exposure pathways have been included in the human exposure model

Examples of risk assessment models

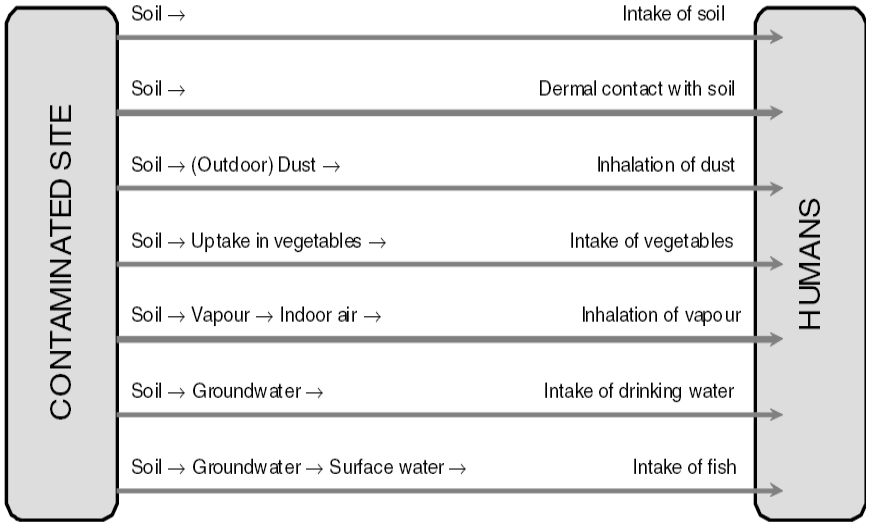
US EPA Superfund risk assessment

Human Health risk assessment

The US EPA issued an initial set of five risk assessment guidelines for human health in 1986, relating to cancer, mutagenic effects, developmental effects, exposure assessment, and chemical mixtures,

Ecological risk assessment (ERA)

ERA process evaluates the likelihood (although not always quantitatively) that adverse ecological effects are occurring or may occur as a result of exposure to one or more stressors.



US EPA Human Health Risk Assessment

EXAMPLE: DOSE CALCULATION – DUST INGESTION

Quantification of dose must be complex and must be undertaken by an expert in human health risk assessment.

The generic equation for calculating of **average daily intake (ADI),** dust ingestion:

$$ADI = \frac{C \times IR \times ED \times EF}{Body\ Weight \times AT}$$

Where:

C = Concentration of the contaminant (mg kg^{-1})

IR = Intake Rate (mg day^{-1})

ED = Exposure Duration (years)

EF = Exposure Frequency (days $year^{-1}$)

AT = Averaging Time (days)

Notes:

ADI is calculated for non-chronic, non-cancer effects.

Exposure duration is the lenght of time of contact with contaminant.

US EPA Human Health Risk Assessment

EXAMPLE: DERMALLY-ABSORBED AVERAGE DAILY INTAKE

The dermal absorbed dose (DAD) is calculated as:

$$DAD = \frac{(C_{dust} \times CF \times AF_{wtd} \times EV \times ED \times EF \times SA)}{Body\ Weight \times AT}$$

Where:
EV = Event frequency (events day^{-1})
ED = Exposure Duration (years)
EF = Exposure Frequency (days year^{-1})
SA = Skin surface area available for contact (cm^2)
AT = Averaging Time (days)
C_{dust} = Concentration of the contaminant (mg kg^{-1})
CF = Conversion factor (10-E6 kg mg^{-1})
AF_{wtd} = Adherence factor of soil/dust to skin (mg cm^{-2} event^{-1})

Note: For non-carcinogenic effects, *AT* = *AD* x 365 days year^{-1} (U.S. EPA, 2004)

US EPA Human Health Risk Assessment

EXAMPLE: CALCULATION OF HAZARD QUOTIENT FOR THE DERMAL ROUTE:

$$HQ_{dermal} = \frac{DAD}{RfD_{ABS}}$$

Where:

HQ_{dermal} = The hazard quotient for the dermal route

DAD = Dermal absorbed dose (mg kg day^{-1})

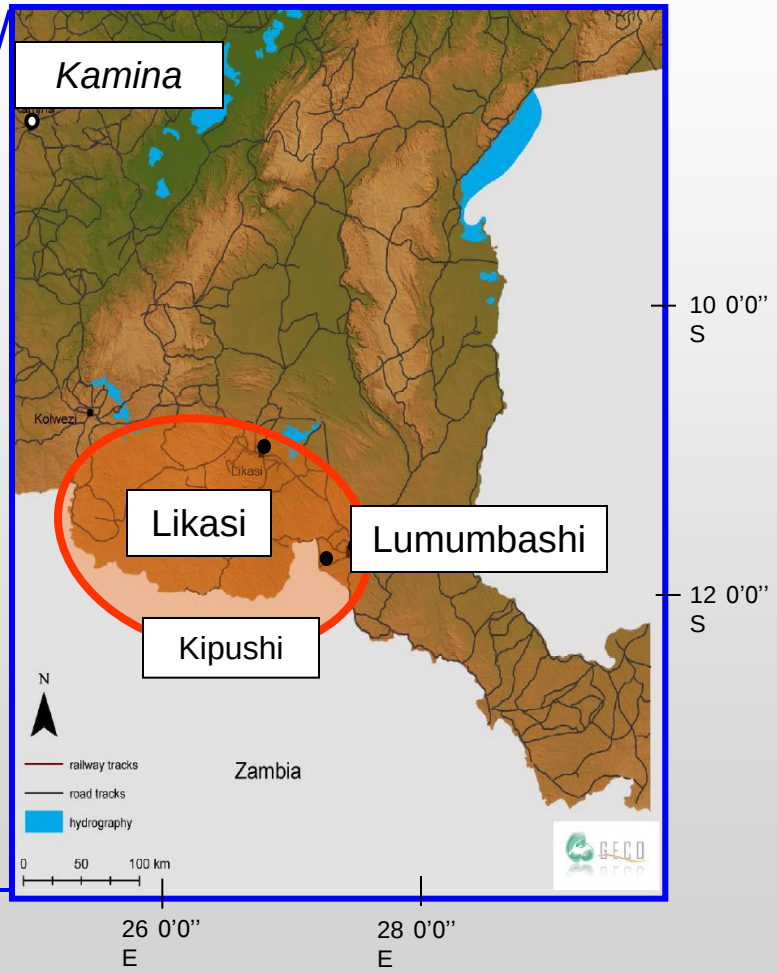
RfD_{ABS} = Absorbed reference dose (mg kg day^{-1})

Note: The estimate of total risk for exposure to soil/dust contaminants (HQ_{dust}) is based on the summation of individual risks for the oral and deraml routes.

EXAMPLE:
ESTIMATED DAILY INTAKE OF COBALT IN THE KATANGA MINING DISTRICT, D. R. CONGO

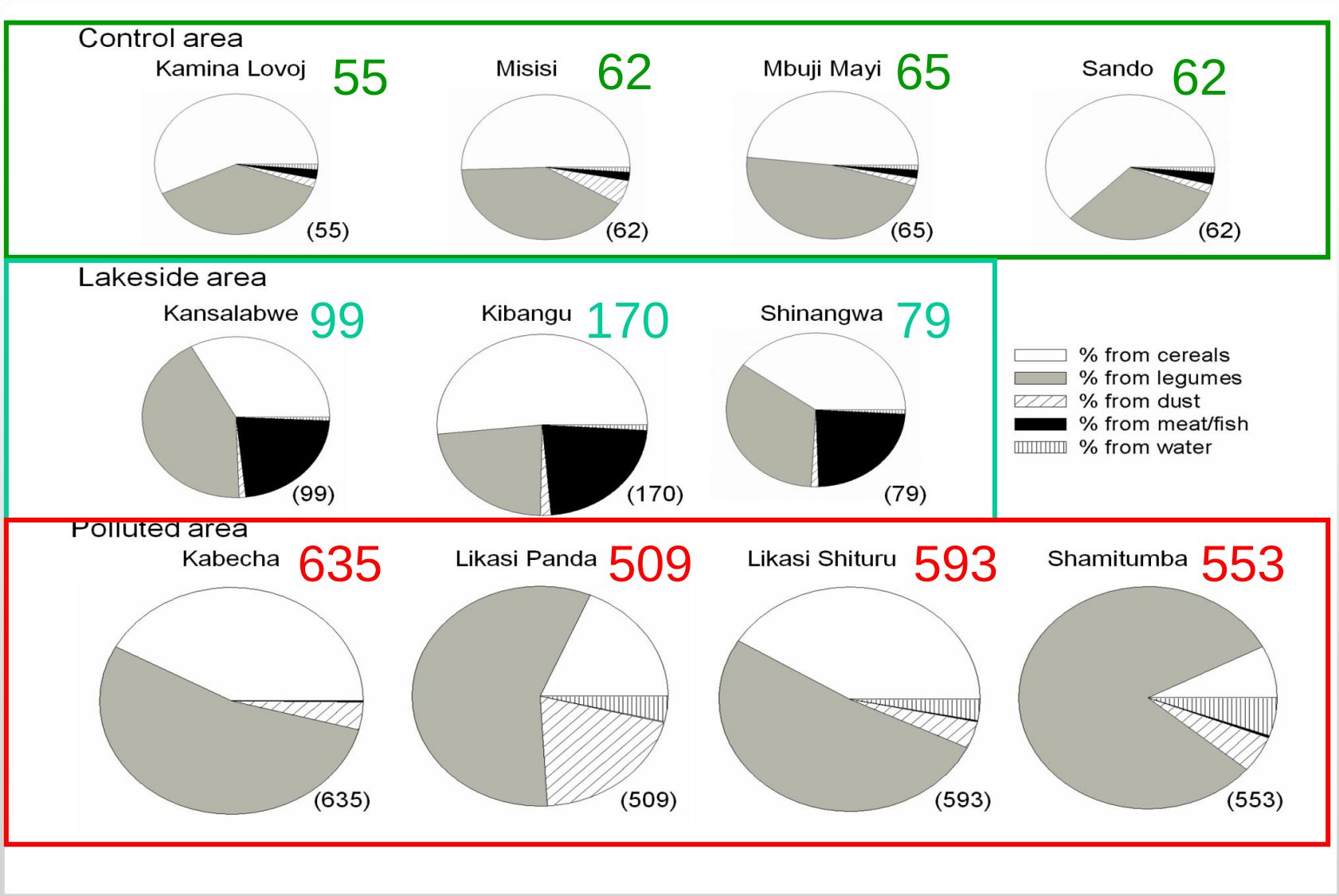
"African copperbelt"





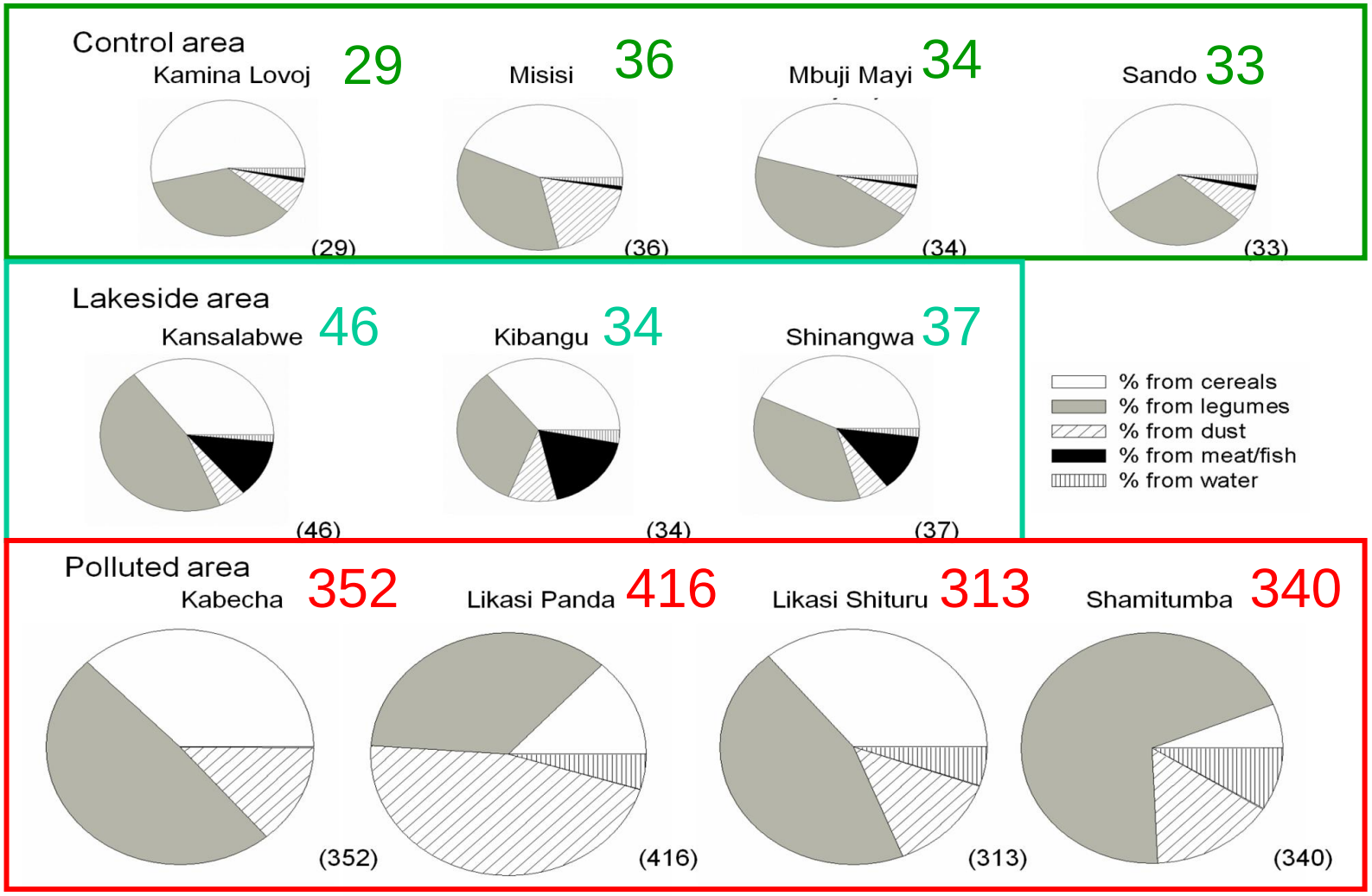
C. Banza Lubaba Nkulu[1], K. Cheyns, J. Ngoy Asosa, L. Kabamba Ngombe et al., 2012,

Copperbelt: Estimated Co intake (µg/day) – Adults



C. Banza Lubaba Nkulu[1], K. Cheyns, J. Ngoy Asosa, L. Kabamba Ngombe et al., 2012

Copperbelt: Estimated Co intake (µg/day) – Children



C. Banza Lubaba Nkulu[1], K. Cheyns, J. Ngoy Asosa, L. Kabamba Ngombe et al., 2012

You can learn more about the assessment of hazardous properties of mining waste facilities at:

THE RISK ASSESSMENT MANUAL OF ABANDONED MINE SITES

prepared by the Geological Survey of Namibia



CONCLUSIONS

Evaluation of hazardous properties of mine waste faclities takes place in three stages:

1. **In the first stage information** on waste facilities are collected. Sources of information include official report from the former operator of respective mine, Geological Survey professional papers and reports, media reports, knowledge of the assessor, etc. As a part of this stage may be (but not necessarily), basic chemical tests (determination of neutralization potential ratio, and aproximate determination of the content of dangerous substances),

2. **The second stage** (pre-feasibility study) includes assessment of **chemical** and **geotechnical properties** of wastes, assessment of transport pathways of contamination, evaluation of the impact of contamination on potential recipients and a draft design of the remediation of storage site.

3. In the third stage (feasibility study) an **environmental impact assessment** (EIA) and **risk assessment study** are carried out and a comprehensive proposal for redevelopment/remediation of storage site including technical design and budget of anticipated work to be undertaken are worked out.


Thank you for your attention

1. INTRODUCTION

1.1. Background

The exploitation of mining deposits in Namibia has been going on for more several thousand years. At first this productive activity was undertaken by Late Stone Age and Iron Age communities using very simple methods to extract ore from rich veins of gold, silver, iron and copper. These processes gradually gave way to more technical ones until reaching the sophisticated procedures that are applied today.

During this time many mines were abandoned without a suitable decommissioning process, and so many of these abandoned mines remain dotted across the country today. These operations mainly mined gold, copper, silver, tin, pyrite, lead, zinc, fluorspar, tungsten, lithium and semi-precious stones, and their ore extraction and treatment processes left sites that could pose major risks to human and environmental health and safety. Safety risks are related to the presence of unprotected shafts, open pits, waste rock dumps, tailings dams, old machinery and buildings, while health risks may be associated with polluted water, windblown dust and contaminated soil.

Of the 157 Shut Down or Abandoned Mine Sites (SD/AMS) on the GSN data base, only some are believed to present a significant risk to human and/or environmental health and safety. The mine sites that possess these kinds of risks are called Mining Environmental Liabilities (MEL).

This Manual has been prepared to (1) determine which SD/AMS pose a significant risk to human and/or environmental health and safety; (2) enable current MELs to be organised according to their risk level, which in turn will support decision-making on remediation by the authorities legally responsible for this task; and (3) enable other sites not classified as MELs to be organised into lower risk categories, thereby allowing for their regular re-assessment in future based on relative priority.

This Manual was originally developed as part of the 'MEL Remediation Framework' project being implemented by Chile's National Geological and Mining Service and Germany's Federal Institute for Geosciences and Natural Resources (BGR), under the Chile-Germany Cooperation Agreement. The original Handbook was written in Spanish for use in the Chilean mining context. BGR has had the document translated into English and customised for the Namibian mining environment, so that the risk assessment methodology can be used in Namibia.

The Manual seeks to create a technical framework to address the impacts caused by historical mining by remediating abandoned mines that pose a significant risk to humans, the environment or economic activities.

The inventory of shut down and abandoned mine sites was prepared by staff of the Geological Survey of Namibia (GSN) in the Ministry of Mines and Energy (MME) and is included in this Handbook as Annex G.

In July-August 2011, staff from the Ministry of Mines and Energy, tertiary institutions and other government ministries were given a two-day programme of theoretical training on risk assessment,

followed by four days of practical training in the field at abandoned mine sites, where the programme was pilot tested for applicability in Namibia. The Manual was revised on the basis of feedback received during the pilot testing process.

1.2. Objectives of this Handbook

The main objective of this Handbook is to make available systematic procedures for identifying which Shut Down or Abandoned Mine Sites (SD/AMS) are Mining Environmental Liabilities (MELs) and to classify these sites by risk level for prioritizing future action.

The specific objectives of this Handbook are:

- Provide a methodology so users can identify the information required for a Simplified Risk Assessment (SRA) and Detailed Risk Assessment (DRA) of a SD/AMS.
- Provide a methodology for preliminary safety analyses of tailings dams, waste rock dumps, heap leach pads, open shafts and pits and similar structures that could pose a risk to human safety.
- Provide a methodology for preliminary analyses of chemical contamination risks present in a given SD/AMS that could affect human and/or environmental health and/or impact economic activities. This methodology includes simple parameters that can be used in the field.
- Set the criteria for classifying a risk as 'significant', in terms of both site safety and contamination.
- Establish a methodology for prioritizing MELs.
- Provide guidelines for scoping, preparing, reviewing and approving DRAs conducted by third parties (consultants).

1.3. Scope of this Handbook

1.3.1. Type of Mining and Associated Processes

This Handbook has been prepared for SD/AMS associated with precious and semi-precious stones, base and precious metals, rare earth minerals, industrial minerals and nuclear fuels. It takes into account the most common production processes that may have been used in each of these mining operations to date. Some SD/AMSs date back many decades and the ore processing methods are unknown at these sites. In those that are known, the method of extraction ranges from being very basic, e.g. shaking tables, gravity separation and hand sorting, to more modern methods of ore processing such as cyanidation, flotation, magnetic concentration and smelting (Annex G).

1.3.2. Mining Site Status

This Handbook applies to those Abandoned and Shut Down Mine Sites as listed on the GSN inventory (Annex G) and should not be applied to operating mines. The locations of the AD/AMSs in Namibia are shown in Figure 1-1 and detailed maps of areas of high concentrations of sites (the Otavi Mountainland and Erongo Region) are provided in Figures 1-2 and 1-3. Note that the numbers on these maps correspond to the inventory (Annex G).

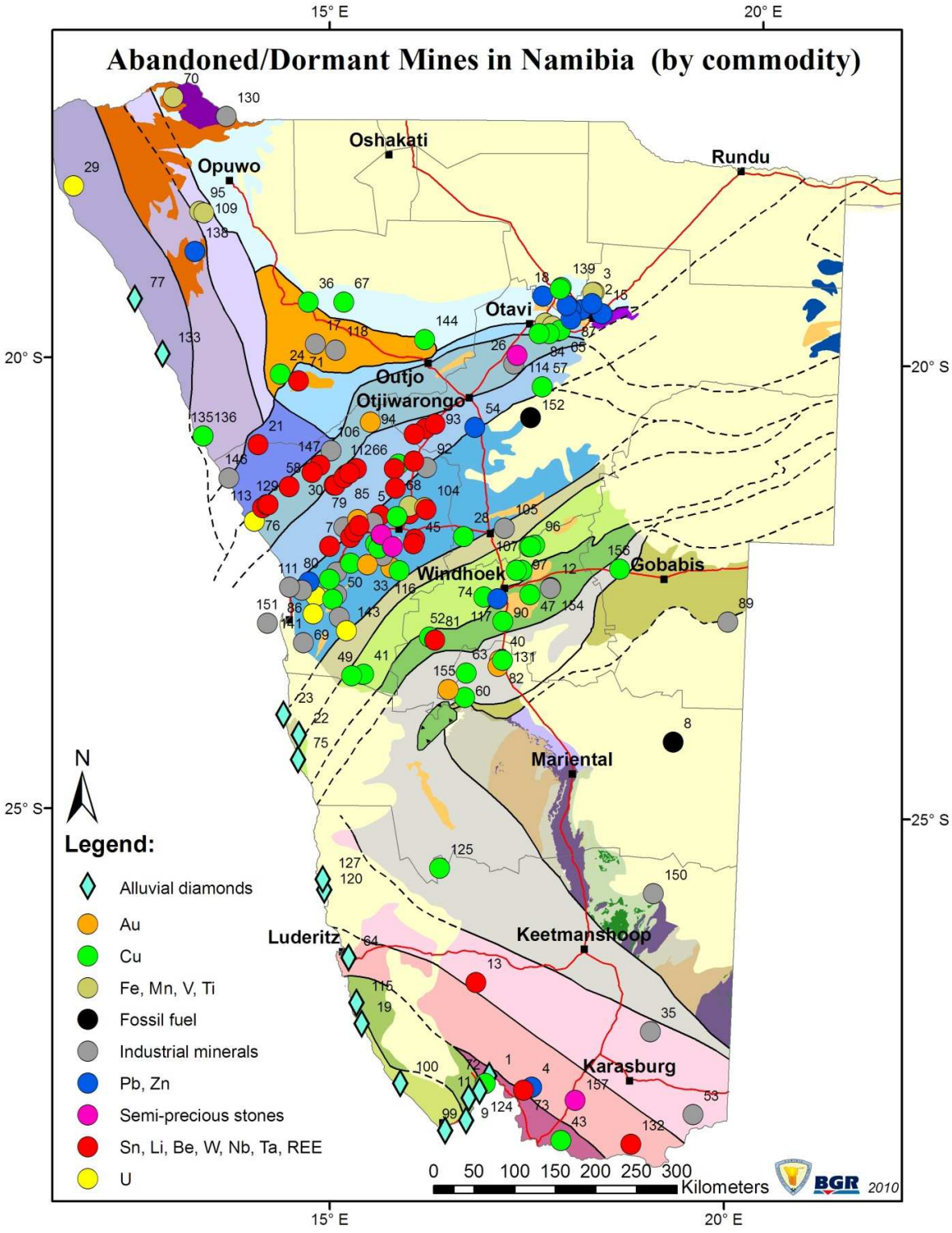


Figure 1-1: Abandoned/Dormant Mines in Namibia

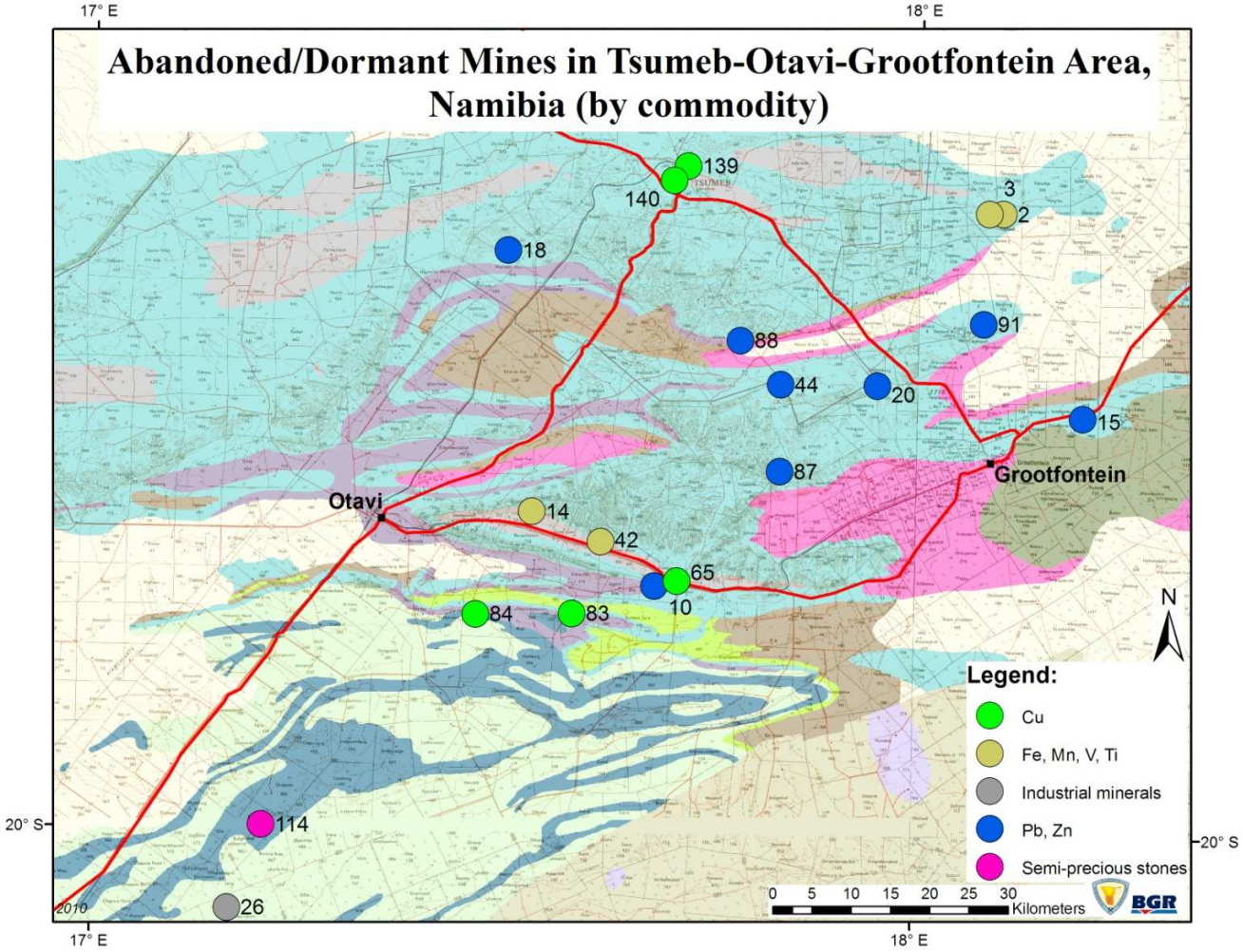


Figure 1-2: Abandoned/Dormant Mines in the Tsumeb-Otavi-Grootfontein Area

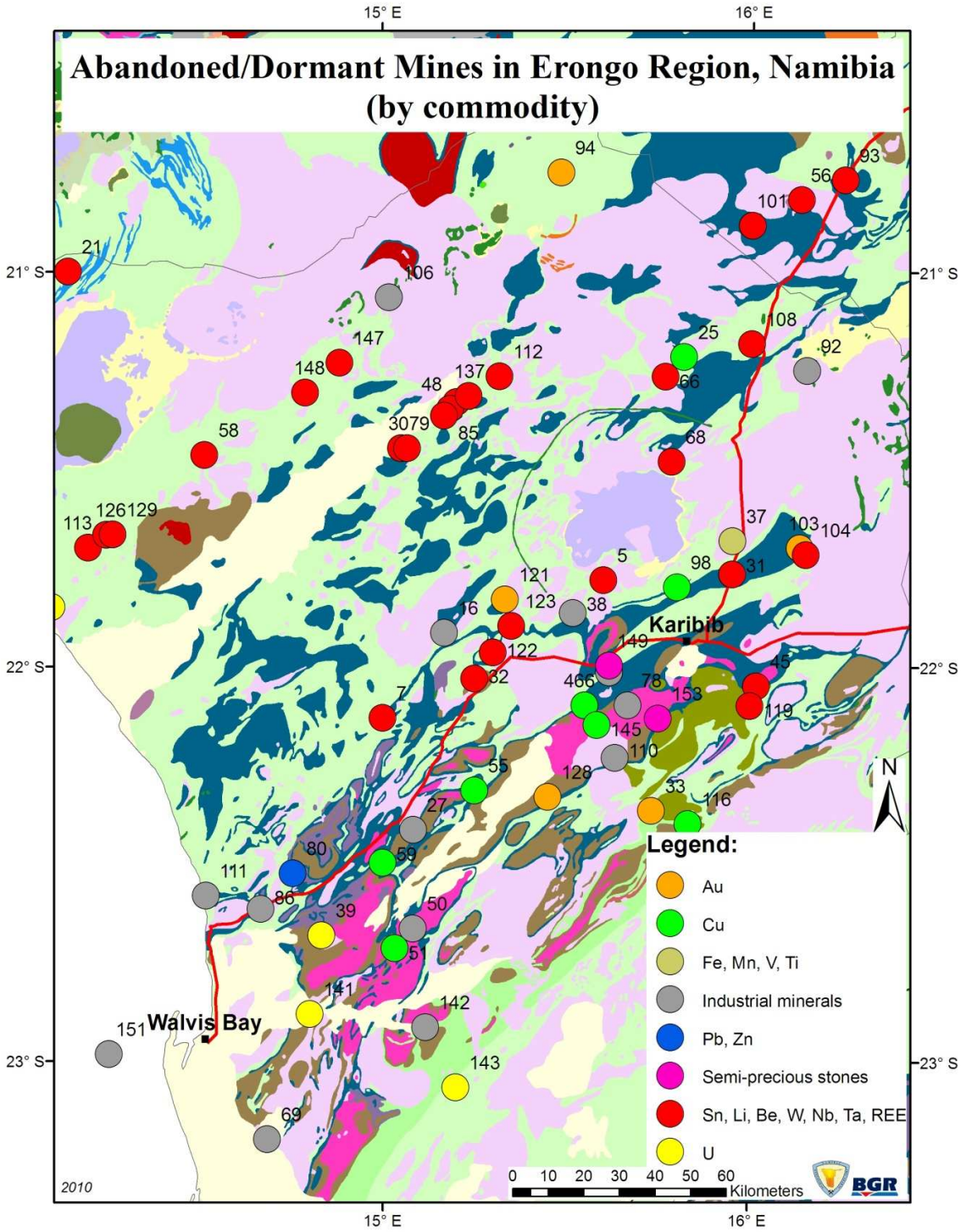


Figure 1-3: Abandoned/Dormant Mines in the Erongo Region

1.3.3 Components of a Shut Down or Abandoned Mine Site

SD/AMS include all installations and workplaces used for the mining industry such as mines, treatment plants, smelters, refineries, metal shops, workshops, explosives magazines, camps, warehouses, waste deposits, and in general all works, installations, support services and infrastructure necessary for the operation (Table 1-2).

For the purpose of this Handbook, SD/AMS components have been divided into the following groups: mine, processing plant, large scale mining waste, small scale and industrial mining waste, and associated infrastructure. Mines can be underground or open pit mines. Plants include all facilities used in ore extraction and processing that are left abandoned or shut down when operations come to a close. With regards to waste, there are two classes: large scale mining waste such as waste rock and tailings, and industrial and small scale mining waste (e.g. scrap metal, drums, pipes etc).

Finally, associated infrastructure includes support services such as explosives magazines, offices, workshops, storehouses, camps, water and electrical systems, and mine access roads and tracks. These facilities are considered apart from the plant when they are physically separated from it, i.e. when they do not constitute part of the plant itself or of any other component. However, they are not considered separate components when they are located on the same property as the plant.

Table 1-1: Components of a SD/AMS

Component	Installations / Deposits / Operations
Mine	Underground Operations Surface Operations (open pit)
Plants	Crushing plant Processing (concentrator) plant Refinery/smelter/roasting plant
Large Scale Mining Waste	Tailings dam/storage facility Tailings dry stacked or deposited otherwise Heap leach waste dump Dumps for waste rock and low grade ore Slag heap
Small scale and industrial mining waste	Small scale mining waste (concentrate, smelting and roasting dust, potentially hazardous waste, discarded solutions, lab waste). Industrial waste (scrap yards, garbage dumps).

Component	Installations / Deposits / Operations
Associated infrastructure	Explosives magazine Offices, camps, workshops, storehouses Water systems and tanks Tracks, roads and bridges Power lines and substations Wells, water reservoirs, pipelines

1.4. Basic Risk Concepts

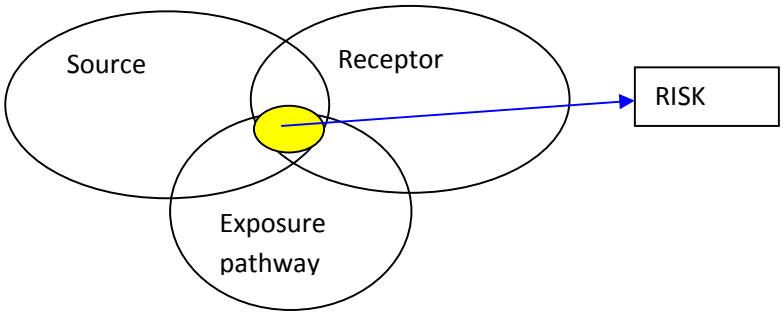
In order to use this Handbook effectively, the Assessor should have some basic knowledge of risk assessment. However, some basic risk assessment concepts are explained below to guide the Assessor in the correct application of the Handbook.

The risk assessment of a given SD/AMS will involve reviewing situations that affect physical safety and chemical (contamination) safety, as both situations can have a negative impact on people, the environment and/or economic activities. The concepts used are generally accepted and agreed upon in each case, enabling parties involved to understand the problem at hand. It is therefore worth defining the conceptual risk assessment framework for each case, for risks to physical safety and those related to contamination.

1.4.1. Risk of Contamination

For a contamination risk, three components must be present:

- There has to be a 'source' of contamination present in concentrations that will generate undesired effects on the receptor;
- There has to be at least one 'Receptor' (humans and/or animals);
- There has to be an 'exposure pathway'[1] that will bring the receptor into direct contact with the source.



[1] Exposure pathway: The way in which a chemical substance comes into contact with the organism exposed to it (ingestion, skin contact, inhalation).

Where any one of these three components is absent, there is no risk; when all three are present, however, the risk should be assessed. The description of the origin, causes and effects of the events that generate a risk is called the Hazard Scenario (HS), and the risk assessment process begins by identifying the HS. This process then continues with estimations of the Likelihood of Occurrence and Severity of the Consequences, according to the criteria and methods contained in this Handbook (section 4.2 and Chapter 6).

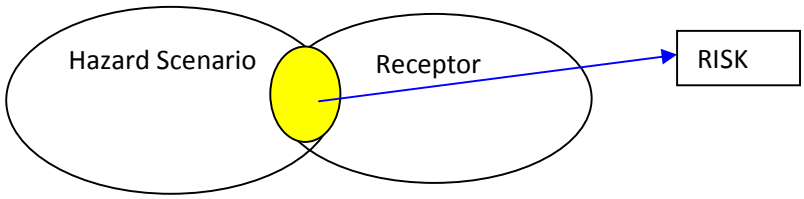
By way of example, a dry tailings dam (source of contamination) could cause the inhalation of particles (exposure pathway) by a population (receptors), making it advisable to conduct a contamination risk assessment when these three elements are present together.

Risk assessment of safety hazards uses quite similar concepts that have been arrived at through the general consensus of experts in this field.

1.4.2. Risk to Safety

To constitute a risk to human and animal safety, the environment or economic activities, the following two elements must be present:

- There must be a 'Hazard Scenario' - a situation that involves a threat to safety (open mineshaft, open pit, tailings dam, unstable structures, etc.); and
- There must be a potential 'Receptor' who could be affected by the Hazard Scenario.



Assessing the level of risk of a SD/AMS with regard to safety therefore involves estimating the Likelihood of Occurrence and Severity of Consequences for the Hazard Scenarios identified, based on the criteria established in this Handbook (section 4.1 and Chapter 5).

Environmental monitoring and Geochemical modelling

A study case of the Kolwezi mining district in D. R . Congo Copperbelt

F. T. Lubala (University of Lubumbashi)

THE IGCP-SIDA 594 TRAINING COURSE: THE ASSESSMENT OF IMPACTS OF MINING ON THE ENVIRONMENT: THE GEOCHEMIST´S APPROACH

July 13-15, 2013, University of the Witwatersrand, Johannesburg



Outline presentation

1. General presentation of the D. R. Congo Copperbelt and the Kolwezi mining District

2. Environmental geochemical monitoring

3. Remediation proposals

4. Impact of mining on human health

5. Conclusions



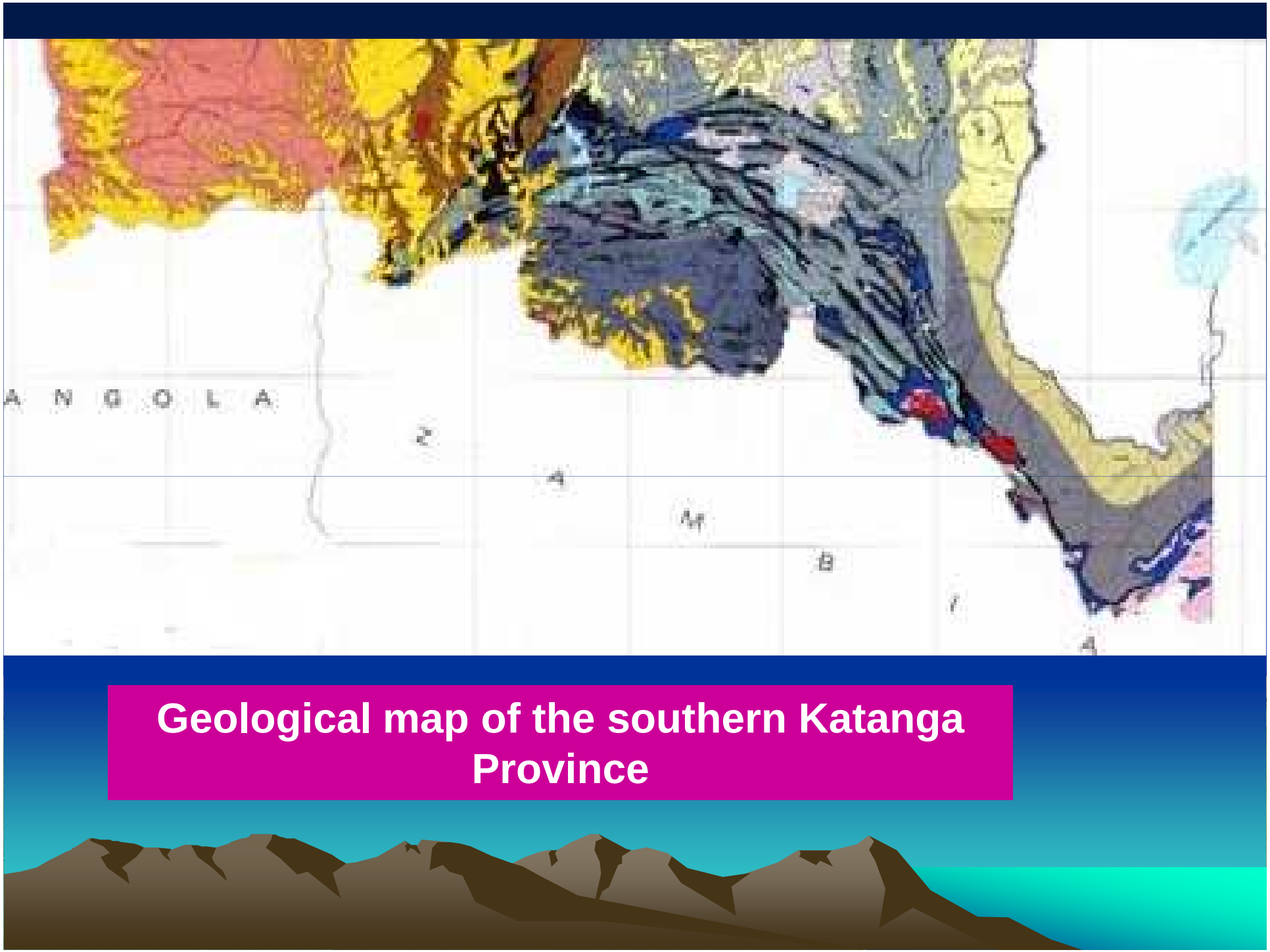
I- GENERAL PRESENTATION OF THE D. R. CONGO COPPERBELT AND THE KOLWEZI MINING DISTRICT

D. R. Congo mineral extractive industry is supported by an extensive and diversified resource base and has been for almost a century, the cornerstone of the national economy.

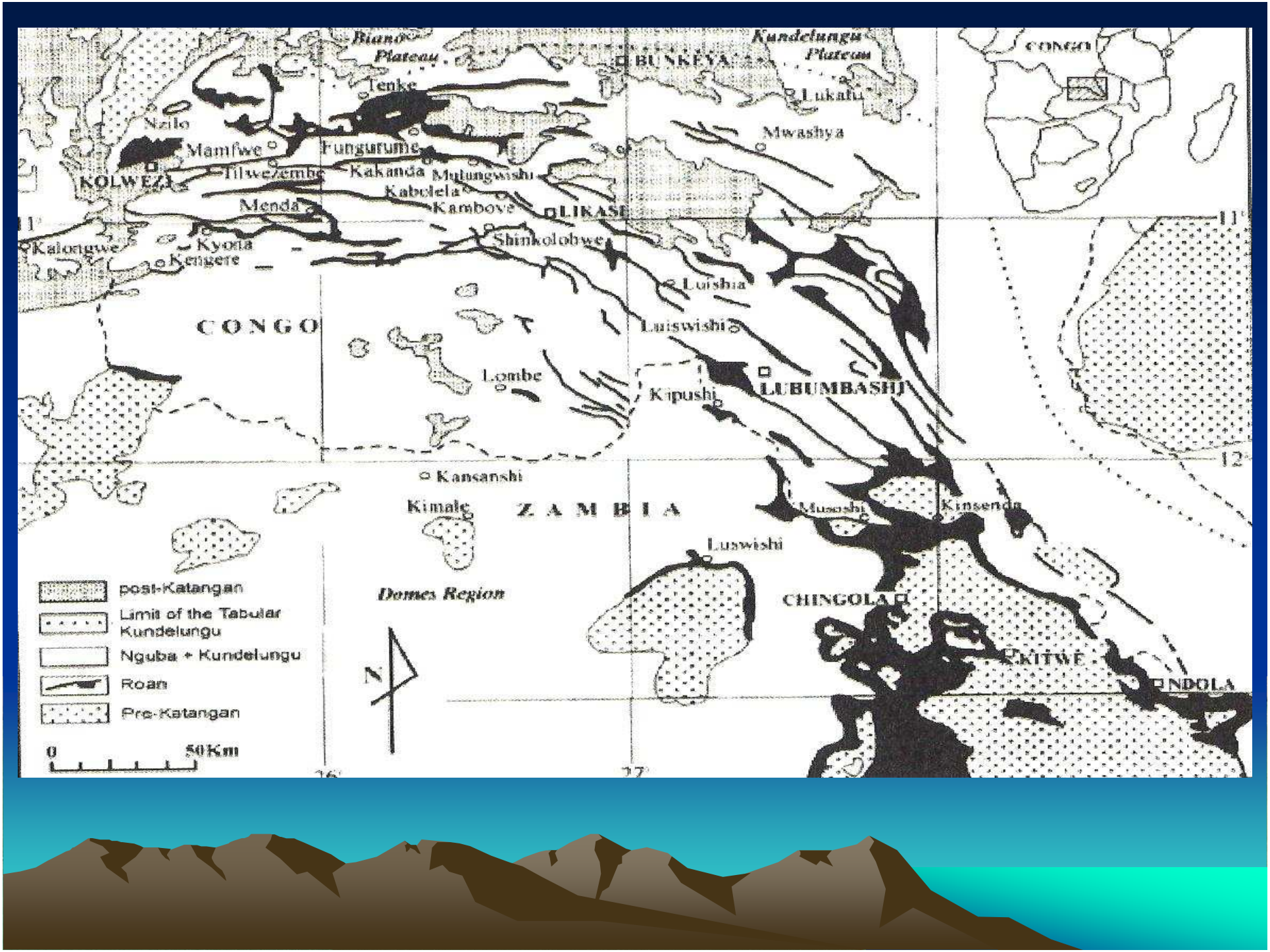
Copper and **cobalt** are the major mineral commodities of the Copperbelt and for which D. R. Congo is the leading holder of reserves.



Mineral resource	World Reserves	DRC Reserves
Copper	1.6 billion tons	160 million tons (10%)
Cobalt	4.4 million tons	2.14 million tons (48.6%)



Geological map of the southern Katanga Province


Biano Plateau
Kundelungu Plateau
BUNKEYA
CONGO
Tenke
Lukafu
Nzilo
Mwashya
Mamfwe
Fungurume
KOLWEZI
Tilwezembe
Kakanda
Mutungwishi
Kabolela
Kambove
LIKASI
Menda
Kalongwe
Kyona
Kengere
Shinkolobwe
Luishia
CONGO
Luiswishi
Lombe
Kipushi
LUBUMBASHI
Kansanshi
Kimale
ZAMBIA
Musoshi
Kinsenda
Luawishi
Domes Region
CHINGOLA
KITWE
NDOLA
post-Katangan
Limit of the Tabular Kundelungu
Nguba + Kundelungu
Roan
Pre-Katangan
0
50Km
N
11°
12°
26°
27°

In the D. R. C. up to the promulgation of the actual mining code in 2002, ore exploration, mining and processing operations were conducted and focused on profit making with no regard to the environment issues.

This led to a severe widespread contamination associated with mineral deposits, industrial activities and contamination in the three-dimensional subsurface space including: air, water, soils and vegetation.

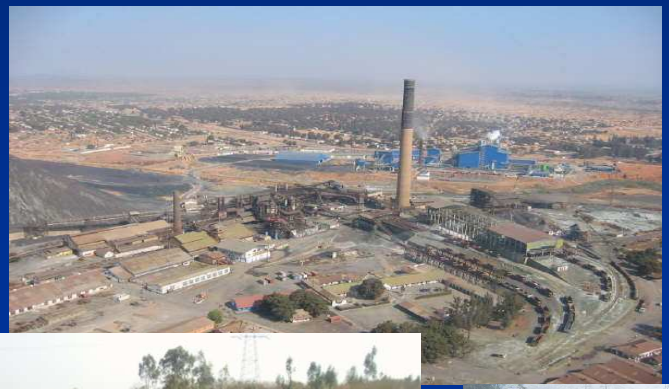


Indeed multiples problems were raised in terms of :

- long-term remediation after mine closure;
- secondary contaminated areas around mine sites;
- land use conflicts and
- abandoned mines.



In the Copperbelt, up to 1 billion cubic meters of mine tailings can be found around abandoned mines and pyro and hydrometallurgical plants











According to the Blacksmith Institute 2008, DRC - Zambia Copperbelt belongs to the top ten of the most polluted areas worldwide



Reliable geochemical data on environmental contamination by metals are poorly documented for the Katanga mining area.

This study shall act as a base for the establishment of a geochemical atlas of this area possibly to contribute to a wide assessment of the rate of environmental contamination and related human risk



The Kolwezi particular area located about 350 km west of Lubumbashi is considered to be appropriate for this talk due to the fact that mining activities are concentrated in this area since the 1920’s and produced for many decades over 60% of the total output of Cu and Co within the DRC Copperbelt.



This city has a population estimated between 500,000 and 750, 000 living directly or indirectly from mining activity




©2007 Google



During history of the Kolwezi district mining for Cu and Co ores, huge volume of tailings had accumulated.

Cu, Zn, Pb processing plants in the vicinity, released for nearly 6 decades solid waste forming the largest dumps in the whole D. R. C. Copperbelt.




Musonoï carrière
Data SIO, NOAA, U.S. Navy, NGA, GEBCO
© 2013 Google
Image © 2013 DigitalGlobe
©2007 Google™

II - GEOCHEMICAL ASSESSMENT



Samples were collected from:

(i) Surface and sub-surface soils
(ii) Endemic plants
(iii) Agricultural plants
(iv) Stream sediments
(v) Surface and ground water

following a specific protocol for collection and processing samples.



Surface and subsurface sampling of abandoned open pit tailings













Tailings and Stream sediments sampling, Musonoi River

Sampling surface water









Iron hydroxide precipitates (ochres)

and groundwater












Rendlia altera




Lopholarna deltombei


Bulbostylis fusiformis

Agricultural products

- Cassava – leaves
- Cassava – roots
- Sweet potatoes – leaves
- Sweet potatoes – roots
- Maize - grains




Cassava and sweet patatoes field


Sampling agricultural product, and soil rhizosphere


Cassava roots sampling


Cassava leaves sampling


Topsoil horizon and
Lower soil horizon sampling

III- ENVIRONMENTAL THREATS CAUSED BY MINING AND PROCESSING MINERALS AND WITHIN THE D. R. C. COPPERBELT



Sources of anthropogenic contamination in the studied area include:

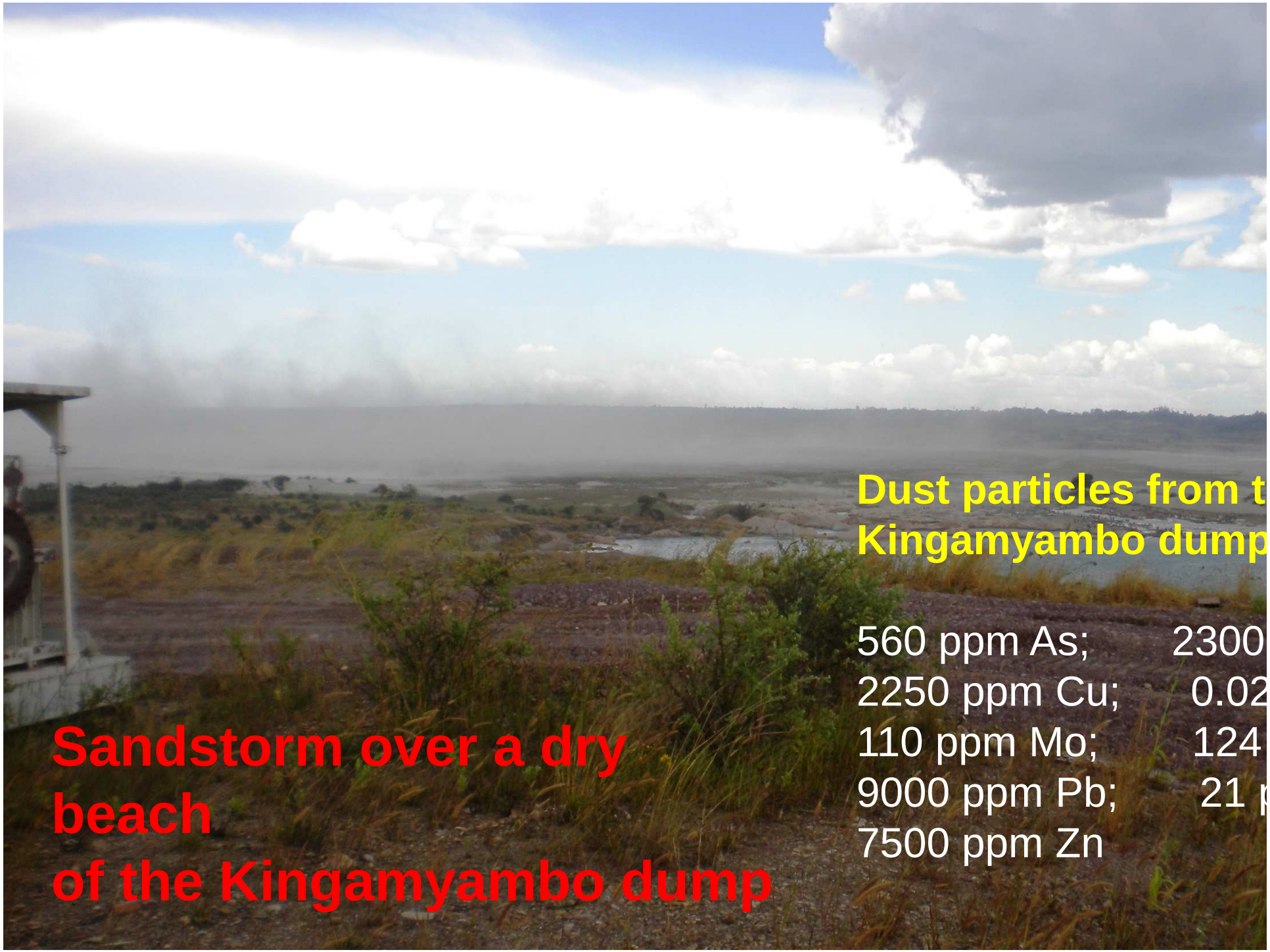
- Soils and Plants:

- Dust from dry parts of tailing impoundments
- Transport of concentrate and products



- Surface Waters and Stream Sediments
- Industrial water discharged into the watercourse
- Seepage and owerflow from tailing impoundments
- Erosion and washout of fine-grained particles from spoil banks and tailing impoundments (siltation)
- Abandoned heavy mining equipment's
- Artisanal diggers mining




Dust particles from t
Kingamyambo dump
560 ppm As; 2300
2250 ppm Cu; 0.02
110 ppm Mo; 124
9000 ppm Pb; 21
7500 ppm Zn
Sandstorm over a dry beach
of the Kingamyambo dump





Iron hydrooxide precipitates

contain :

400 pppm As;
20 ppm Be;
1900 ppm Co;
350 ppm Cr;
8500 ppm Cu;
650 ppm Mo;
500 ppm Ni;
3000 ppm Pb;
270 ppm Se
13000 ppm Zn.

Stream sediments, Musonoie River



- As: 1150 ppm
- Co : 7660 ppm
- Cu : 65465 ppm
- Hg : 10 ppm
- Mo : 48 ppm
- Ni : 370 ppm
- Pb : 12370 ppm
- Zn : 35550 ppm
- S tot 4.2 %


Water erosion of the
Kingamyambo Slimes

Abandoned equipment





Artisanal mining

This activity has become widespread in the abandoned mines within the Katanga province and particularly in the Kolwezi mining district towards the 2 decades.

It involves ***thousands diggers*** mostly young male and female and even children working in very **poor and dangerous conditions.**



Their activity consist with:

- ***hand picking*** Cu-Co ores from tailings

- ***recovering by gravity*** Cu-Co concentrates from fine grained stream sediments.



Artisan diggers
















Average chemical composition (%) of dumps
Si: 8.1 %
Ca: 1.5
Al: 1.2
Fe: 26.4
Zn: 16.8
Cu: 2.5
As: 0.6
Pb: 2.7
Mn: 0.2
Ba: 0.16
Cd: 0.17
Co: 0.04
Cr:0.01
Ni: 0.03
S: 4.5

Artisan diggers operating on dumps















Depollution programmes .....



The assessment of those previously mining areas is of great interest in setting up a more comprehensive programme for site depollution based on the one hand on the retreatment of the tailings and on the other hand on the phytoremediation technics.



Synoptique global

Sites de Production, de Stockage et de Décharge des Rejets Miniers au Katanga (R. D. Congo): Inventaire - Valorisation - Restauration - Impact sociétal

Opérateurs Miniers (RDC)
Université de Lubumbashi (RDC)
ULG (Belgique)
Université du Québec (UQAT) (Canada)
LEM INPL-CNRS (France)

Inventaire

- Compilation des inventaires passés
- Localisation géographique
- Caractérisation cristallochimique
  - stérile
  - rejet de flotation
  - rejet métallurgique
- Aspects géotechniques et hydrogéologiques
- Classification économique et impacts

Russhi Mining Sprl (RDC)
Université de Lubumbashi (RDC)
ULG (Belgique)
LEM INPL-CNRS (France)
Université du Québec (UQAT) (Canada)

Valorisation

Rejets solides valorisables

- Traitement minéralurgique
- Traitement métallurgique

Rejets produits

Restauration

Gestion intégrée

Russhi Mining Sprl (RDC)
Université de Lubumbashi (RDC)
LEM INPL-CNRS (France)
Université du Québec (UQAT) (Canada)

Rejets solides non valorisables

- Désulfuration
  - traitement partiel
  - partie non sulfurée
  - partie sulfurée
- Traitement de surface (inertage/passivation)
  - traitement global
  - production d'un rejet non réactif
- Recouvrement
- Remblais/charge minérale

❑ Intégration directe dans le processus industriel

Partenaires à définir

Impact sociétal

- Qualité de vie
- Santé

Ph. de Donato (DR CNRS)
M. Kongolo (CR INPL-Pr Associé UQAT))

2010

Essais de phytostabilisation des sols contaminés des sites pollués de la Gécamines et du quartier Penga Penga (Avec la graminée *Rendlia altera)*



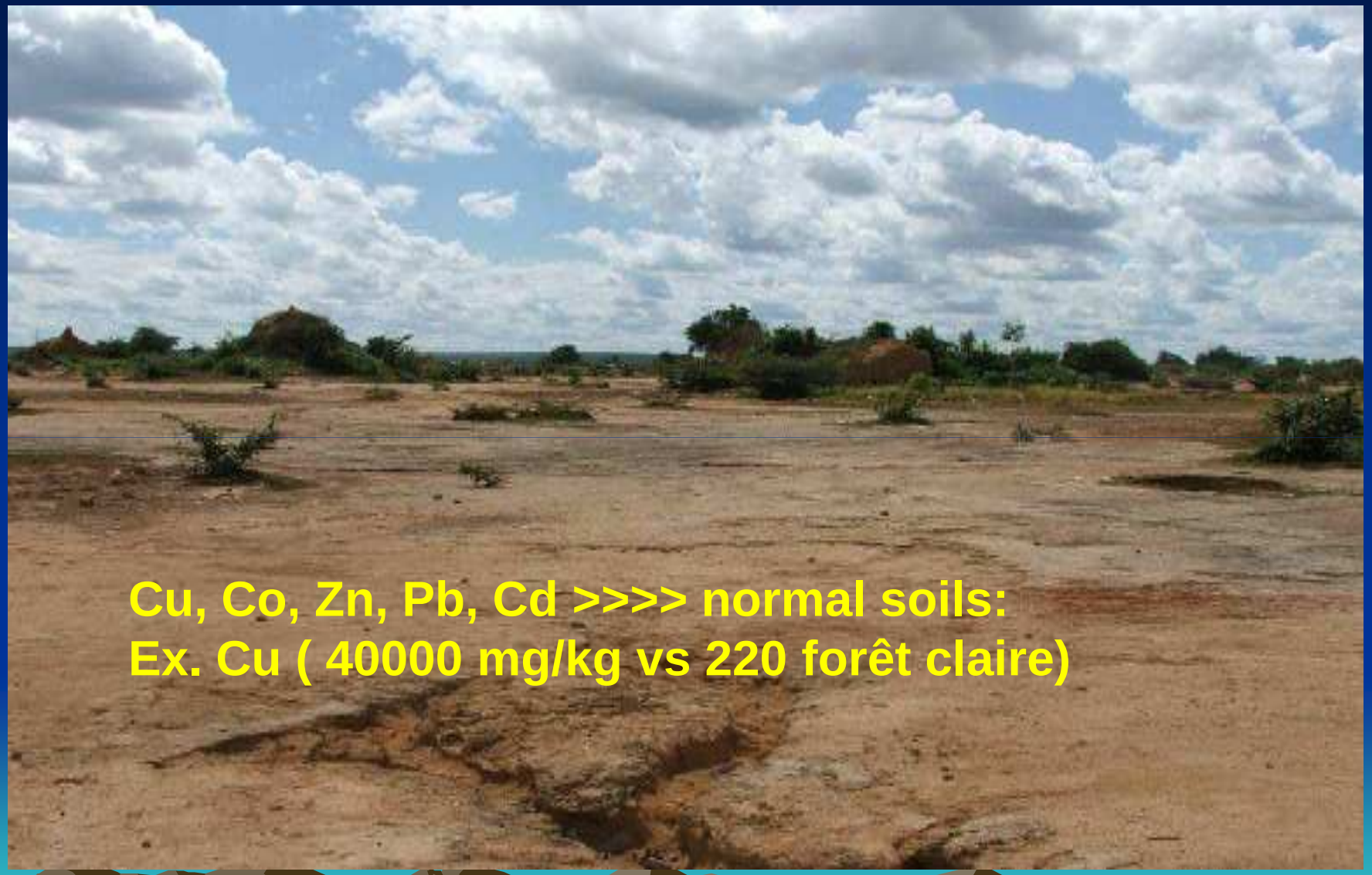
Dégradation de la végétation et larges bandes de sol dénudé par les retombées des poussières métallifères au niveau du cimetière de la GCM.



Pelouse de *Rendlia altera* sur sol riche en Cu et autres métaux à la mine de l'étoile (Kalukuluku)



Dispositif expérimental de phytostabilisation au quartier Penga Penga


Cu, Co, Zn, Pb, Cd >>>> normal soils:
Ex. Cu (40000 mg/kg vs 220 forêt claire)

Microchloa altera: suitable plant for phytostabilisation of contaminated soils around smelters





5 other selected species for phytostabilisation of the contaminated soils in the DRC Copperbelt

Acacia auriculiformis, Dichrostachys cinerea, Syzygium guineense, Leucaena leucocephala, Piliostigma thonningii



Impact of mining activities on human health



The human health impact of the historic and current mining and processing of heavy metals in the D. R. Congo Copperbelt is poorly documented.

A preliminary assessment of the exposure of the population of the Katanga province living in the mining areas using biomonitoring was first published some years ago (Banza et al. 2008).



This first study revealed a substantial contamination of population especially in children to several metals,.

The urinary concentrations found in this population are the highest ever reported worldwide.



These extremely high levels toxic metals in the urine of these subjects from the general population of Katanga confirm that they are significantly exposed to these metals through their environment.



The exact routes of exposure – through the air, the diet (staple foods, specific vegetables, meat or fish), and/or the soil and suspended dust – remain to be established.



Several diseases such as lung, kidney, cancers, congenital malformation have been reported and are currently investigated.



CONCLUSIONS AND RECOMMENDATIONS



1. The **results obtained from the geochemical assessment of tailings, stream sediments, soils and vegetation in the Kolwezi mining district allow to characterize the extent of contamination.**

2. **Multiple anthropogenic sources of heavy metals have been identified**



3. The impact of heavy metal concentration in tri-dimensional subsurface space **on human health is evidenced through reported diseases and cogenetic malformations.**

4. The development of a program of health care involving long-term monitoring of these heavy metal content in the blood of people working or living in the vicinity of mines is of utmost importance.



5. A public awareness of environmental risks for population living in contamined area should be launched.

6. Mining companies operating in the area are warned to deal with environmental protection by using appropriate technologies.



Thank you
Merci beaucoup

for your attention



2. RISK ASSESSMENT METHODOLOGY FOR SD/AMS

2.1 Stages of Risk Assessment and Prioritization of SD/AMS

The **SD/AMS Risk Assessment** process contained in this Handbook is based on a widely used methodology—the Failure Mode, Effects, Criticality Analysis (FMECA)[1]. This methodology will enable the identification of SD/AMS that are Mining Environmental Liabilities (MEL) and those that are not.

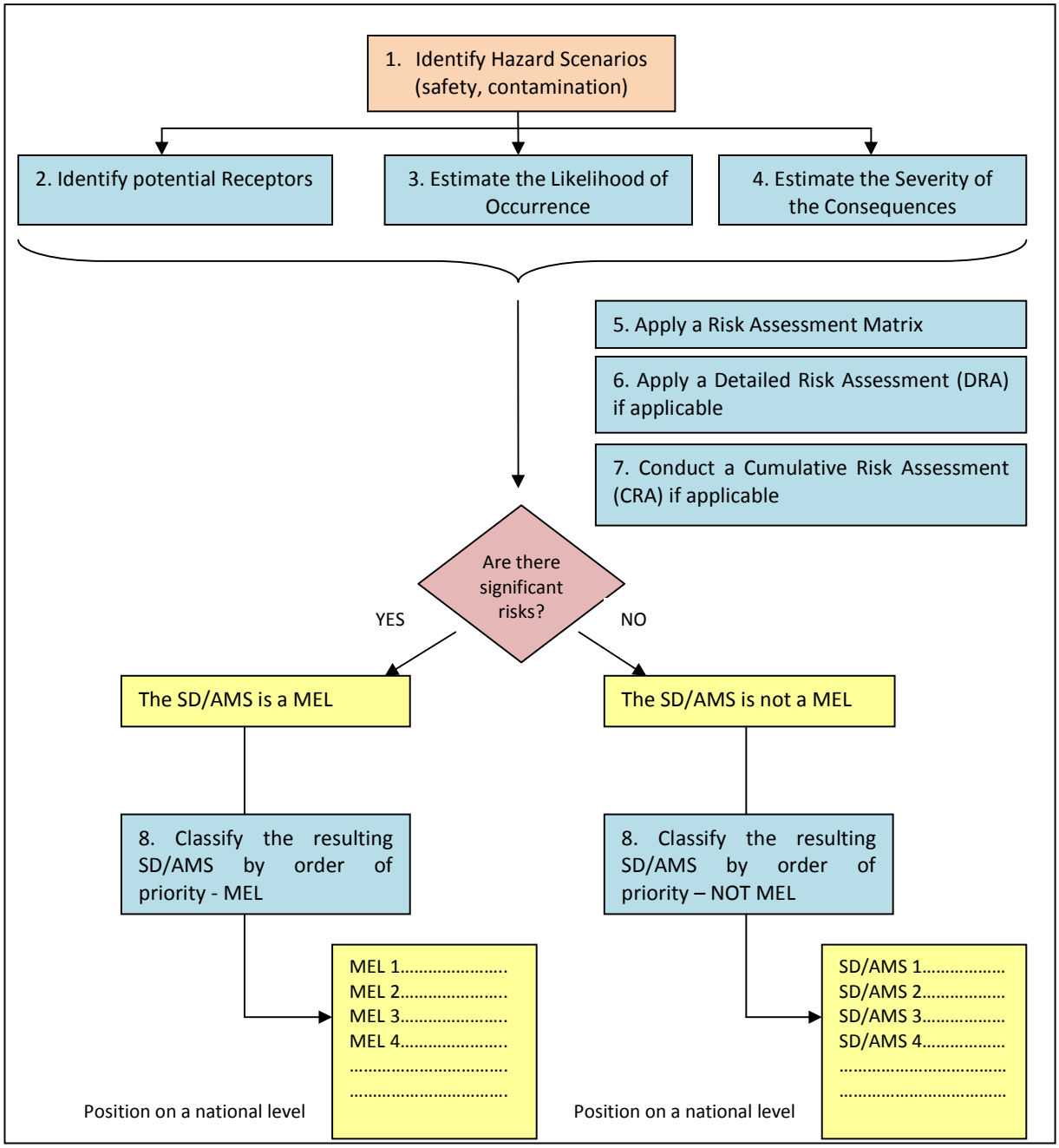
Risk assessment of SD/AMS using FMECA principles follows the stages outlined below (Figure 2-1):

1. Identify situations that involve a risk, called **Hazard Scenarios**.
2. Identify potential affected parties, called potential **Receptors**.
3. Estimate the **Likelihood of Occurrence** (Probability) of each Hazard Scenario.
4. Estimate the **Severity of Consequences** to receptors.
5. Apply a **Risk Assessment Matrix** to distinguish 'significant' and 'not significant' risks, which will enable mine sites to be classified as MELs or not.
6. Apply a **Detailed Risk Assessment (DRA)** methodology in cases where the simplified risk assessment leaves a certain degree of uncertainty.
7. Conduct a **Cumulative Risk Assessment (CRA)**, which involves a review of the assessment where another SD/AMS exists nearby or in the same location.
8. Classify the resulting SD/AMS by **order of priority** according to the magnitude of risk present.

The application of this risk assessment methodology will produce a preliminary list of SD/AMS that are MELs, and a second list of sites that are not MELs. Both lists will order sites from greatest to least risk, thereby providing useful information for future remediation programs.

[1] FMECA is an extension of Failure Mode and Effects Analysis (FMEA). The criticality analysis method is used to chart the probability of failure modes against the severity of their consequences, thus highlighting the failure modes with the highest priority and severity of consequences (http://en.wikipedia.org)

Figure 2-1: Schematic Diagram of Risk Assessment Process for SD/AMS



2.1.1 Identification of Hazard Scenarios

The first step in risk assessment is the identification of Hazard Scenarios present in a given SD/AMS. This involves an exhaustive review of all operational and works areas at the mine site and the identification of potential receptors associated with each of the scenarios identified. There are two possible types of **Hazard Scenarios** associated with a SD/AMS:

1. Those related to safety, such as accidents, falls, slides, etc., that require direct exposure to the elements of a SD/AMS and often have immediately obvious effects.

2. Those related to the contamination that an SD/AMS can generate and that require a vehicle such as soil, air or water to reach receptors and produce the undesired effects. The negative effects of contamination on receptors are usually manifested over a longer timeframe.

In practice this stage involves filling out two tables, one for safety (see for example, Table 4-4) and one for contamination (see for example, Table 4-11) where Hazard Scenarios are recorded for each environmental component of the SD/AMS.

Hazard scenarios that a SD/AMS may contain are detailed in Sections 4.1 and 4.2 of this Handbook, which address Safety Risk Assessment and Contamination Risk Assessment, respectively.

2.1.2 Identification of Receptors

As part of the Risk Assessment of a SD/AMS, the receptors present in the area under study should be identified (Chapter 3). SD/AMS may have a negative effect on one or more of the following receptors:

- People
- The Environment
  - Aquatic life
  - Terrestrial fauna and flora
  - Protected or environmentally sensitive areas
- Economic Activities
  - Agriculture (crop production)
  - Agriculture (animal husbandry and game farming)
  - Aquaculture/Fishing
  - Tourism.

2.1.3 Assessing the Likelihood of Occurrence.

The risk associated with a Hazard Scenario will depend on the Likelihood of Occurrence of that scenario and the Severity of its Consequences. The first of these variables is estimated with a 'Probability Index' (PI) that ranges from 'High', 'Moderate', and 'Low' to 'Negligible'. The PI is a qualitative assessment of the likelihood of a negative effect occurring, depending on the circumstances and conditions present in the Hazard Scenario.

This Handbook provides the tools required to estimate the Probability Index for each of the Hazard Scenarios that are identified (Annexes A1 and B1), to enable their standardised application by different risk assessors.

2.1.4 Assessing the Severity of Consequences

The physical safety of receptors can be affected in many ways by a risk that is present at a mine site. Individuals may suffer injury or even death from accidents at mine sites and workings (e.g. from falling into mine shafts, cuts or punctures with sharp objects, etc.). Environmental components such as wild fauna and livestock can also be affected directly by injury as well as by safety failures (e.g. when a tailings dam ruptures and causes the sudden release of slurry), with the potential loss of animal or plant life inhabiting the zone of impact. This situation can also affect crops and other economic activities that are inside the zone of influence of a failure when it occurs.

Contamination can also affect human health when people come into direct contact with a contaminant through an exposure pathway such as inhalation, ingestion or skin contact. The environment or economic activities may also be affected by contamination when the quality of ecosystems or productive land is diminished due to the presence of harmful substances in the air, water or soil (Table 2-1).

For assessing the Severity of Consequences, five categories have been established: 'Catastrophic', 'High', 'Moderate', 'Low' and 'Negligible'. It should be noted that 'Catastrophic' severity is reserved for Hazard Scenarios that affect humans, while the highest magnitude of severity for those affecting the environment and/or economic activities is 'High'. Sections 4.1, 4.2 and Chapter 6 of this Handbook offer criteria for assessing the Severity of Consequences for safety and contamination Hazard Scenarios identified.

Table 2-1: Criteria for defining the Severity of Consequences

Receptors	Criteria for Defining Severity of Consequences	
	Safety	Contamination
Humans	Physical injury or loss of human life	Harmful to human health.
Environment	Loss of species and/or habitat for aquatic or land-based life forms. Negative impacts on protected or vulnerable areas.	Proportion of species in a population which may be potentially affected by contamination or where contamination can enter the human food chain via contaminated products
Economic Activities	Physical injury or loss of game and livestock Loss of land area for growing crops, raising livestock or loss of aquatic medium for products grown or extracted therein.	Area potentially affected with regard to crops, livestock and game in terms of grazing and number of water points. Potential contamination of aquatic products that are grown, raised or extracted from a polluted medium.

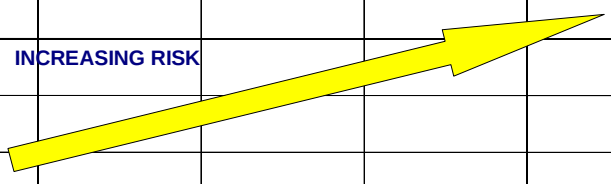
2.1.5 Applying the Risk Matrix

The magnitude of risk is determined by the combination of the two factors involved. This operation is carried out through a Risk Matrix, a dual-entry table that gives a single risk magnitude value by combining the Likelihood of Occurrence (Probability) and Severity of Consequences (Table 2-2).

It is logical therefore to assume that a Hazard Scenario will have a greater magnitude of risk when it is more likely to occur and has more severe consequences. Inversely, the Risk will be less when Likelihood of Occurrence is lower and the Severity of its Consequences less.

Table 2-2: Risk Matrix

	SEVERITY OF CONSEQUENCES				
PROBABILITY INDEX	Negligible	Low	Moderate	High	Catastrophic
High					
Medium					
Low					
Negligible					



The Risk Matrix presents a series of possible combinations of Likelihood of Occurrence and Severity of Consequences that together determine the level of risk. The most important or **significant** of these are **marked in red** in Table 2-3, while other combinations for which the risk is lower or **'not significant'** are **marked in green** in Table 2-3.

A risk is considered **'significant'** when the magnitudes of both factors used to determine it (Likelihood of Occurrence and Severity of Consequences) are high.

A risk is considered **'not significant'** when the magnitudes of both factors used to determine it (Likelihood of Occurrence and Severity of Consequences) are low.

Using the Risk Matrix allows the risks associated with the Hazard Scenarios of a SD/AMS to be assessed, making it possible to classify these into one of two categories: significant, located within the red area in the table, and not significant, appearing in green. A given Risk Matrix will have as many 'entries' as it has Hazard Scenarios identified.

Table 2-3: Significant and Non-significant Risk[2]

	SEVERITY OF CONSEQUENCES				
PROBABILITY	Negligible (A)	Low (B)	Moderate (C)	High (D)	Catastrophic (E)
High (4)	b7	a1	a4	a7	a9
Medium (3)	b4	b8	a2	a5	a8
Low (2)	b2	b5	b9	a3	a6
Negligible (1)	b1	b3	b6	b10	b11

2.1.6 Indications for Conducting a Detailed Risk Assessment, DRA

It may be necessary to conduct a DRA when any of the risks assessed in the Simple Risk Assessment (SRA) are uncertain, shedding doubt on the validity of the results obtained. In that case, the risks need to be more precisely assessed to determine whether the risk is significant or not.

[2] The coding system establishes a scale of magnitude of risk. More details may be found in Section 7.2.1

A Detailed Risk Assessment (DRA) for a SD/AMS should be undertaken when:

- The SRA of the SD/AMS indicates that the greatest risks detected in the site are not significant and therefore the site is not a MEL, but there is some uncertainty about the assessment undertaken, i.e. it is possible that a risk may have been **underestimated** and is actually significant. The detailed assessment of risks about which there is uncertainty enables a more precise assessment of the risks of the SD/AMS and the determination of whether or not it is a MEL.

- The SRA identifies one or more significant risks and therefore the SD/AMS will be classified as a MEL, but there was some degree of uncertainty in the risk assessment, i.e. one or more risks could have been **overestimated**, but may not be significant risks. In this case, the detailed risk assessment will clarify whether the site is actually a MEL or not.

- A DRA is not indicated when there is enough certainty about the presence or absence of significant risks, allowing the site to be classified as a MEL or non-MEL with confidence.

Section 4.5 of this Handbook provides more detail on how to determine when a DRA is called for.

2.1.7 Risk Assessment due to the Proximity of Other Sites

Once the Simplified Risk Assessment is carried out for a given SD/AMS, it must be determined whether there are other SD/AMS inside or overlapping the Area of Study. Where one or more additional SD/AMS do exist nearby and have a part of the Area of Study in common with the first, the Area of Study must be redefined and all receptors present in this new area need to be identified (using the methodology described in Section 4.4). Then the potential cumulative effects of multiple Hazard Scenarios grouped close together must be assessed.

Once the Area of Study is updated, the Simplified Risk Assessment for each SD/AMS must also be revised, taking into account the possible presence of new receptors that were not considered previously.

2.1.8 Classification of MEL and Non-MEL Sites

A SD/AMS is classified as a **Mining Environmental Liability** when the assessment yields one or more **'significant'** risks (Figure 2-2). Sites in this category of SD/AMS are considered MELs and are designated **Class I** (Table 2-4).

In contrast, an SD/AMS is not considered a **MEL** when none of its identified Hazard Scenarios present a significant risk. These sites shall be denominated **Class II** and will require regular follow up of the risks assessed to ensure they do not become 'significant' over time with changes in conditions or assessment criteria. The frequency of these follow up assessments of Class II sites will conform to technical criteria set out by MME.

A third group of SD/AMS, called **Class III**, includes all mining sites that presented insignificant risks during the initial screening analysis and therefore do not require further assessment at this time. For this reason Class III sites are not addressed in this Handbook.

Once all SD/AMS have been classified into MELs and non-MELs, an organised list can be drawn up of all sites assessed based on their relative priority. This list can be used for future remediation programmes. The order of sites on this list will be defined by the magnitude of risk and the number of risk scenarios in each SD/AMS (Chapter 7).

Table 2-4: Classes of SD/AMS

SD/AMS	Class	Description
MEL	I	Sites for which at least one significant risk to human and/or environmental health and/or safety or to economic activity has been identified.
Non-MEL	II	Sites for which all risks identified are considered non-significant but require regular follow up to monitor possible future degradation.
Non-MEL	III	Sites with insignificant risks according to the initial screening assessment, that do not require a follow up risk assessment using the methodology presented in this Handbook, because conditions are stable and are unlikely to degenerate any further.

2.2 SD/AMS Risk Assessment Approach

The Risk Assessment of SD/AMS should determine which sites present a significant risk to human and/or environmental health and safety, or to economic activities; in other words, the assessment enables sites to be identified as MELs or non-MELs.

The methodology herein offers an effective and efficient way of conducting the entire risk assessment process, based on the following principles:

- Use the greatest amount of information available about the SD/AMS, including that collected through the initial screening assessment.
- Define a process for **Simplified Risk Assessment (SRA)** that MME officials can use to conduct risk assessments of SD/AMS. In duly justified cases, where there is uncertainty about the validity of the MEL/non-MEL classification, a complementary methodology has been designed, called **Detailed Risk Assessment** (DRA). DRAs may require the participation of external experts (non-MME personnel). This strategy seeks to optimise the use of resources

allocated for assessment and prioritisation of SD/AMS.

- Conclude the process with **accurate, verifiable and reproducible results** which include a list of sites classified as MELs prioritised by the magnitude of their risks; and a list of sites classified as non-MELs, similarly organised in descending order of risk.

The simplified methodology can be effective for assessing a broad range of risks. However, given the wide range of circumstances present in SD/AMS, it is to be expected that in some cases it will be difficult to establish the significance or insignificance of risks using the simplified methodology. This may result in the incorrect classifications of sites as MEL or non-MEL, and in these cases (where there is uncertainty) it will be necessary to use a more detailed assessment methodology.

Considering the above, this Handbook describes two levels of risk assessment:

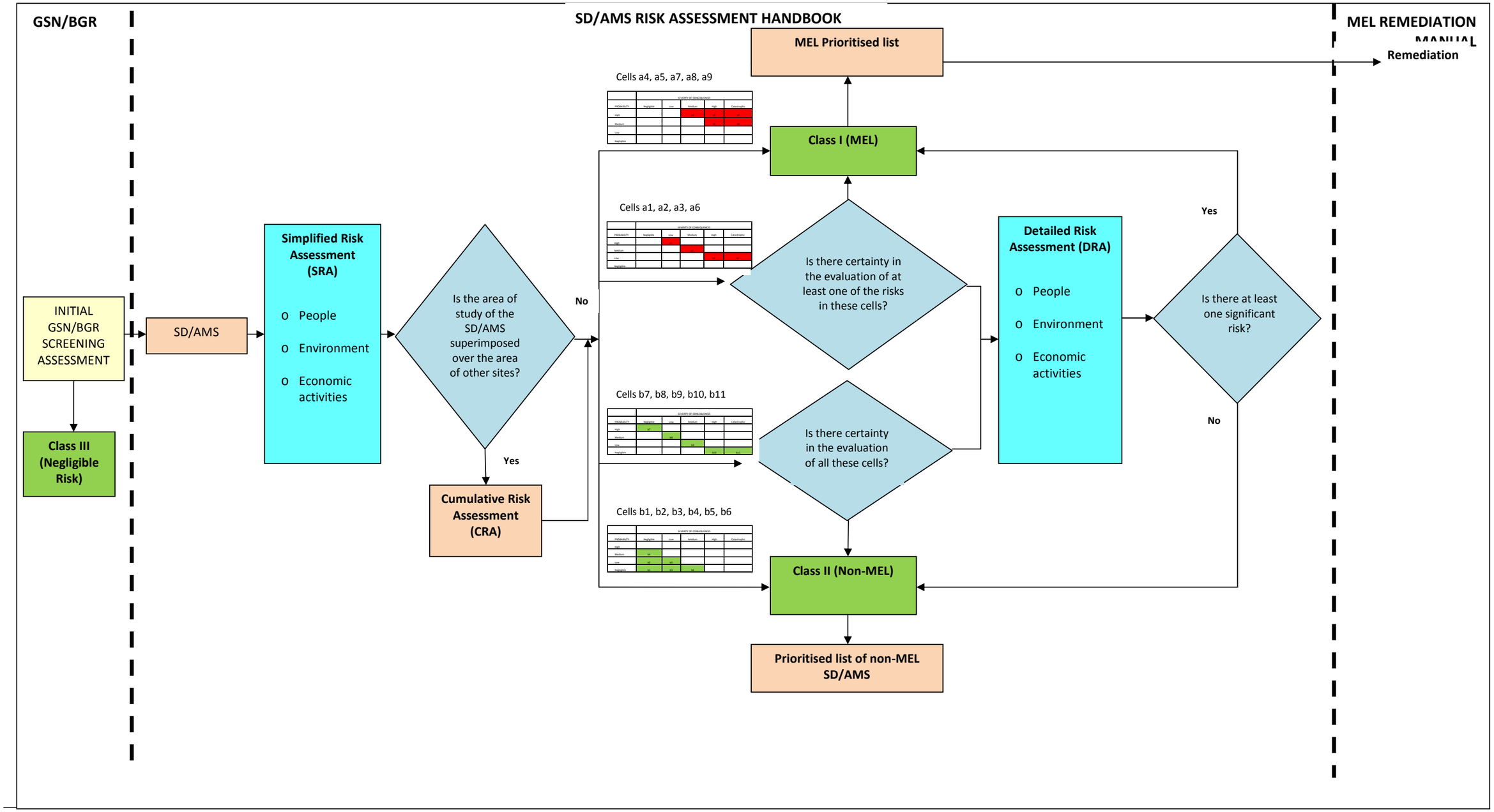
- *Simplified Risk Assessment (SRA)*: through which government officials can assess the risk of SD/AMS using the technical criteria and procedures provided in this Handbook.

- *Detailed Risk Assessment (DRA)*: to be applied to specific risks where there are grounds to suspect that the result obtained in the SRA is not entirely valid. In conducting the DRA it may be necessary to hire **external experts** to support government personnel in conducting field studies and applying specific analytical techniques. Their participation will enable a more accurate determination of risk. This Handbook reviews the methodologies currently in use for this kind of study, as well as lists that will help auditors in reviewing expert reports.

Thus, the basic risk assessment methodology for all SD/AMS will be the SRA, and only in some cases will a DRA be conducted. This approach is expected to optimize the use of resources during the process of identifying MELs, avoiding unnecessary and costly assessments for cases where the magnitude of risk of a site can be accurately assessed using the SRA.

Figure 2-2 offers a general flowchart of the risk assessment process for SD/AMS, up to the generation of the two prioritised lists of sites classified as MELs and non MELs, respectively.

Figure 2-2: SD/AMS Risk Assessment Process



2.3 Suggestions for the Assessor

When applying the procedures outlined in this Handbook, the Assessor should take the following into consideration, among other aspects:

- As the assessment is concerned with safety and contamination issues, professionals with expertise in mining safety and environmental issues should participate in the process.
- The Assessor should collect the greatest amount of information possible about the SD/AMS being assessed, not only from MME/GSN but from other public services and private studies.
- To facilitate future reviews and updates, the Assessor should leave a complete record of the entire assessment process for the site, using the recordkeeping and procedural systems established by GSN. Annex E of this handbook provides a Risk Assessment Record Form (RARF) to provide the Assessor with a format for logging this information.
- The Simplified Risk Assessment (SRA) of a given SD/AMS using the methodology offered in this Handbook should take 1 to 2 weeks, including preparation time, field inspection and preparing the assessment results in the office and/or lab. It is important to recall that the SRA seeks to determine whether the site is a MEL or not, and not to define remediation measures. More time will be required when the Assessor deems it necessary to conduct a Detailed Risk Assessment (DRA) for a particular site.

Additional note: The Assessor should be aware of safety concerns at all times in the field. The sites to be visited are abandoned mines that have not been decommissioned properly and therefore may present health and/or safety risks to the field team. The MME's Safety Expert will determine whether the conditions at a particular site are safe enough to enable the required information to be collected. Where the safety expert deems the site unsuitable for this work, the Assessor should collect the information required as he/she deems most appropriate, noting clearly the situation and grounds for his/her choices. For safety reasons it is advisable that more than one individual participate in the field visit, particularly where the site is in a remote area or presents other kinds of risk.

3. PREPARING THE ASSESSMENT AND FIELD VISIT

3.1 General Aspects

This section describes:

- In-office preparation of the assessment by the Assessor before visiting the site.
- Field inspection visit by the Assessor to collect all information required according to Handbook procedures.

To properly prepare the risk assessment of a SD/AMS, the Assessor must collect and analyze as much information as possible to ensure he/she builds a comprehensive picture of the situation at the site.

It is important that the preparatory stage of the assessment be tailored to the level of complexity of the SD/AMS under study; in other words, sites in remote areas with few installations and no hazardous material deposits will not require as much documentation as sites with more mine works, hazardous waste and/or tailings deposits, especially if they are located near populated areas, environmentally sensitive areas or productive zones. In those cases more detailed information will be required because there will be more components involved in defining safety and/or environmental risks.

Once the preparatory stage in the office is complete, the Assessor will conduct the field inspection to collect all information required to assess the site risks.

One important tool that the Assessor will use in this process is the **Risk Assessment Record Form (RARF),** which is meant to assist the Assessor in applying the procedures outlined in this Handbook step by step, create a log of the process and collect information from the site (Annex E). This instrument is available in hard copy and digital format (Excel file). Additional information on using the RARF can be found in Annex E.

3.2 Stages in Preparing the Assessment

The stages that the Assessor should follow in preparing the risk assessment are as follows:

1. Information gathering
2. Map preparation
3. Definition of the Area of Study
4. Description of Receptors in the Area of Study

5. Summary of Assessment Preparation

6. Preparation for site visit

3.2.1. Information Gathering

The first stage involves gathering all pertinent information related to the site. This task should begin with a review of the file that was prepared by GSN and contained in the Mine Inventory Data Sheet (MIDS) (Annex G). This information includes:

- Form for the site.
- Inventory of documents and copies.
- Sketch of the location, plans, images and photographs.
- Record of samples, laboratory certificates and analytical reports.

The Assessor's first job is to carefully review all of the above information in order to become familiar with the information contained therein, namely:

- Identification of the site (coordinates, location name, etc.).
- Last known owner/rights holder.
- Type of primary and secondary minerals extracted and process used.
- Regional and site geology.
- Existence of maps to scale, with the site location indicated.
- Size, location and description of the works and installations present at the site.
- Presence of hazardous waste.
- Environmental setting:
    - Climate;
    - Hydrology and water use;
    - Geohydrology;
    - Physiography;
    - Social issues; and
    - Land use.

The list above should be considered a basic checklist that the Assessor can work through point by point to ensure that the necessary information has been collected. This list will also reveal any gaps that need to be filled in with information from other sources.

=> In the RARF (Baseline Sheet 1 in Annex E) the Assessor shall record all information available about the site from GSN and lab reports on water and solid waste if available.

When information for the assessment is lacking, additional information available from MME's central and/or regional offices should be gathered and reviewed. Where necessary, information may also be sought from other public environmental services such as the DWA, MET, MAWRD, MOHSS, relevant municipalities, regional offices, the National Planning Commission, Namibian Chamber of Mines, and others. Information may also be found on the Internet. It is recommended that the enquiries sent to these entities be directed to key informants with practical knowledge of mining operations.

One or more field visits may be needed to gather information to describe the environmental and socio-economic situation of a site. During these visits it is sometimes beneficial to interview individuals residing or working in the surrounding area.

3.2.2. Map Preparation

Special attention should be paid to the availability of maps, as these will serve as the basis for a number of aspects of the assessment. When initiating the assessment it is therefore important that the Assessor obtain the following elements from the MIDS and other sources:

- Official topographic maps scaled at 1:50,000, as available.
- Aerial photographs or orthophotographs from the Directorate of Surveys and Mapping.
- Satellite images that can be obtained from 'Google Earth'[1] (Plate 3.1) or Landsat images provided by NASA[2].

The quality of these elements may vary according to the sharpness of the images, graphic content and how recently they were taken. By comparing images from different sources the Assessor can determine which offers the best quality cartographic information.

Once the best source of information has been selected, the Assessor will proceed to prepare the **Risk Assessment Base Map (RABM)**. The Assessor will use this map on site to support the risk assessment process, and the recommended scale is 1:5,000 or higher. Obtaining this base map may entail one or more of the following tasks (the entries are listed in order of descending quality of the final product):

[1] http://earth.google.com/
[2] https://zulu.ssc.nasa.gov/mrsid/

- Printout of a satellite image (e.g. Google Earth) or aerial photograph, geo-referenced to exact scale (1:5,000 or more detail). This is the most desirable option and requires high quality digital cartographic information and colour printing facilities.

- Colour photocopy of the topographic map (1:50,000), increasing the scale where possible.



Plate 3.1: Google Earth image of Klein Aub mine showing the relationship between the old tailings dam (centre) and the village (left)

Once the base map has been chosen and printed or enlarged, this will serve as the RABM. The RABM is the cartographic document to which all field notes will refer and upon which measurements will be based, although other existing maps, photographs and/or images may also be useful at different stages of the assessment and for specific tasks. The RABM must include the coordinates and document its projection system – preferably one which supports GPS coordinates.

To determine which map projection was used for a map, satellite image and/or aerial photograph, the Assessor should consult the written documentation accompanying each item. For official topographic maps the projection is clearly indicated on the map itself. Where aerial photographs are used, the text files accompanying the digital maps should be reviewed for this information. The Assessor can also refer to the metadata[3] for these images published on the Internet. Similarly for satellite images, the projection used can be verified by referring to the documentation that accompanies each image.

=> In the RARF (Baseline Sheet 2 in Annex E) the type of cartographic information available will be logged, as well as the main features of the RABM (scale, projection system, etc.).

From the review of the topographic maps and/or images obtained, the Assessor should be able to

[3] Metadata: Data about data.

obtain a precise idea of the topography of the site and local water systems. By studying the photographs and satellite images the Assessor can also obtain a general overview of the surrounding area, including an idea of the general land use patterns, the presence or absence of water courses and water bodies, the location of populated areas, and so on.

The preparation of the base map is a crucial stage in the assessment, as it will serve as the basis for information collected during the risk assessment process, such as:

- Distances from the site to drainage bodies and other receptors;
- The form and size of river catchments and sub-catchments, which can be used to determine rainfall runoff and flow volumes which may affect the site;
- The direction of surface runoff flows.

Two or more copies of the RABM should be printed and one should be reserved for preparing a final, 'clean' version.

3.2.3. Definition of the Area of Study

Once the available information has been analyzed and the RABM is ready, the Assessor should define the Area of Study. This is the zone that could potentially be affected by the abandoned or shut down mine site in terms of risks present to human health and safety, the environment and/or economic activities.

The **preliminary** boundaries of the Area of Study should be established before the first field visit, with the boundaries traced directly onto the RABM. The final boundaries of this Area will be determined later when the SD/AMS and surrounding areas are visited.

The Area of Study should be established on a case by case basis, and should include:

a) the entire **area occupied by the site** when it was in operation; plus

b) the areas **that could be affected**, directly or indirectly, by contamination or safety related events (such as the sudden release of tailings from a failed tailings dam).

The criteria to be applied in the case of (b) are as follows:

b.1) Included in the Area of Study are **surface water courses** (perennial, seasonal and ephemeral rivers[4], drainage lines and washes, wetlands, farm dams, etc.) that could be

[4] A perennial river or stream is one which flows throughout the year; a seasonal river or water course is one which flows for a few months, usually every year but only during the rainy season; an ephemeral watercourse is one which only flows for a short time (days or weeks) following rain in its catchment area. The latter may not flow for several years.

affected by drainage or runoff containing contaminants from the mine site. The length of the watercourse to be considered within the Area of Study will be determined by the point below which, in the Assessor's judgment, no adverse effects from the site will be experienced. Criteria to be used in determining this point may include:

- Location where contamination is no longer detected, using pH readings;
- Location where turbidity (by sight) or the presence of salts (recorded with a conductivity sensor) attributable to the SD/AMS are no longer recorded;
- Location where an increase in biodiversity is noted (vegetation reappears on the banks of a water course, for example).

For the purposes of the assessment, measurements taken upstream from the site should be compared with different points downstream from the site.

b.2) Also included in the Area of Study are **groundwater aquifers** (primary and secondary; perched and deep) that could be affected by seepage and infiltration from runoff containing contaminants from the mine site. The Assessor will determine the surface area to be included in the Area of Study based on field observations, map interpretation and borehole census data, if available.

b.3) In addition to the above, **soil, plants, human and animal receptors** downwind of pollution sources associated with the mine and process plant should also form part of the Area of Study. Dust may have originated from, and may continue to arise from stacks, tailings dams, waste rock dumps, low grade stockpiles, access roads, haul roads and open pit operations. The Assessor will define the distance from the site to be considered, based on field observations (i.e. visible dust lying on the ground or accumulating in the lee of bushes and hillocks), dust monitoring and/or modelling if available (Plate 3.2), and interviews with local residents.

The distance that dust will travel will depend on a combination of factors including: the particle size of the dust (finer particles will remain suspended in the atmosphere for days or even weeks, and can be dispersed over a wide area); the specific gravity of the particles; average moisture content; and prevailing wind speed and direction.

If the SD/AMS plant had gaseous emissions, there may be a residual plume area where soils and other receptors may have been affected (Plate 3.2). If the mine conducted air quality monitoring during operations and/or modelled gaseous emissions, then this information should be available on the MIDS. But for most of the older SD/AMS the critical information required to determine the area of influence (e.g. stack height, emission velocities and temperature etc) and all relevant weather data are unlikely to be available.

Thus the Assessor will need to rely on other information such as the type of process plant used, the typical gas emissions associated with that type of plant, and whether there is visible evidence of a gas plume in the downwind direction, such as trees with the 'stag horn' effect[5], dead or dying vegetation, rusting roofs of houses and anecdotal evidence from nearby residents.

b.4) **Soil** that might be contaminated from the disposal or spillage of any hazardous or polluting materials e.g. tailings, hydrocarbons, sulphuric acid etc., should be included within the Area of Study. Annex A (section A.2.2.2) includes criteria for calculating the Area of Study in such cases.

b.5) Also included in the Area of Study are **residential zones** that regularly consume agricultural, livestock, game, fishing or aquaculture products from the areas indicated in the above points (Plate 3.2). In other words, the inhabited sectors whose regular food supply includes products grown in or obtained from an area affected by the site.

=> In the RARF (Baseline Sheet 2 in Annex E), areas that could be affected by the site will be identified and a brief rationale given for their inclusion.

In summary, after a preliminary analysis of the mine site, waste deposits and processing plant, the Assessor should include on the map: (a) the areas these occupy; and (b) their respective zones of influence.

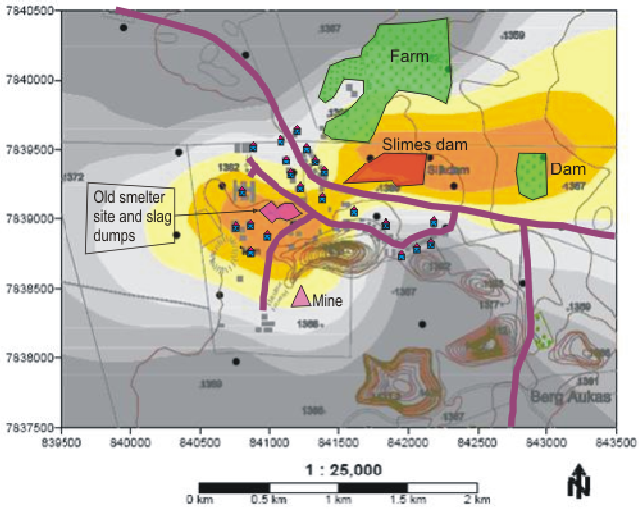


Plate 3.2: Map of Berg Aukas mine showing the extent of pollution beyond the mine structures. The map also highlights residential areas. This type of map helps to define the Area of Study

[5] Severe gas pollution can cause the upper branches of trees to die and lose their leaves, giving it the effect of a stag's horns.

3.2.4. Description of Receptors in the Area of Study

The Assessor shall determine which receptors are present in the Area of Study. This task begins in the office, where the information gathered is analyzed and observations are made about the cartographic information and satellite images.

Later, during the field visit, the receptors identified will be confirmed and the information required for the assessment will be collected. In certain cases it may be desirable to conduct interviews with local residents to collect additional information the Assessor deems necessary (water uses, distance of visible dust, human activity within the Area of Study, etc.). For the purposes of this Handbook, receptors have been grouped into three main categories: People, the Environment and Economic Activities; each of these should be described using the procedure outlined below.

3.2.4.1 People

All individuals residing in or visiting the Area of Study of the SD/AMS are considered potential receptors. These groups of individuals may be exposed to risks from both unsafe elements and contaminants.

Residents include all individuals living permanently in the Area of Study of the SD/AMS (Plate 3.3). Potential visitors include people coming to the site for tourism, recreation, sports and/or for economic reasons such as to graze animals, farm the land, or obtain construction material (Plate 3.4) or scrap metal, etc.

Similarly, if the Area of Study contains drinking water intake works for a given population that lives outside of the Area of Study, these individuals should be considered potential receptors that may be affected by the site.



Plate 3.3: The village next to Otjihase mine frequently experiences dust from the tailings dam (in foreground). The residents of this village therefore live within the Area of Study.



Plate 3.4: Contractors at Berg Aukas have been removing slag and fly ash for brick making from the dump leaving a dangerous, unsafe working face. It has also been found that this ash and slag are toxic.

The following information is required to characterize receptors **living** in the Area of Study:

- Name of locality
- Type of settlement. Possible types include:
  - City. Urban centre with more than 100,000 inhabitants.
  - Town. Urban centre with between 5,000 - 100,000 inhabitants.
  - Village. Rural population centre with less than 5,000 inhabitants.
  - Farm. A commercial farm with several houses and cottages on the property belonging to the farm owner, farm manager and the farm workers.
- Coordinates for the settlement. When it is a small village the coordinates at the centre should be recorded. For farms, the location of the main farmhouse, and the residential building nearest the mine site (if it is different to the main farmhouse) should be recorded. For larger places (towns and cities) coordinates should be recorded at both the centre and the edge of town closest to the mine site.
- The age profile of people living permanently in the Area of Study.
- Identification of surface water collection points for human consumption and stock watering points. Provide GPS coordinates or identify on a map.
- Existence of wells supplying groundwater for human and stock consumption. Geographic location. Provide GPS coordinates or identify on a map.
- Existence of fountains and springs located downstream from the mine site.

To characterize **visitors** to the site, the following information should be collected for individuals who are not permanent residents of the Area of Study but who enter the mine site with some frequency:

- Number of visitors entering the site, estimated frequency of visits and reasons for visit.
- Mode of entry.

- Purpose of entry e.g. for fishing, quad biking, grazing, recovery of materials (Plate 3.4).
- City or town of origin.
- Ages of individuals entering the site, with special attention to the entry of children and/or youth.

It is important that this information is corroborated with local inhabitants, particularly with regard to the number and frequency of visitors to the site and the existence of drinking water within the Area of Study.

=> Where appropriate, the presence of individuals residing in or visiting the Area of Study, along with the information indicated above, will be logged on the RARF (Baseline Sheet 3 in Annex E).

3.2.4.2 The Environment

The SD/AMS risk assessment also requires a description of the environment on and surrounding the mine site. This refers to the natural and cultural elements whose presence in the Area of Study should be recorded. In this Handbook environmental receptors have been divided into three categories: aquatic life, terrestrial fauna and flora, and protected or environmentally sensitive areas.

Aquatic Life

For the SRA, it will be assumed that all surface water bodies and watercourses (perennial, seasonal and ephemeral) have aquatic life as potential receptors. Bodies of water include rivers, streams, lakes, dams, wetlands and vleis, fountains and springs, lagoons, salt flats, and the coastline.

To enable the assessment of the magnitude of risk that a SD/AMS poses to aquatic life, the Assessor should estimate the surface area and/or length of water bodies present in the Area of Study. Once the dimensions of the water bodies present in the Area of Study are known, any **aquatic species** in that area with an official protected status must be identified (e.g. listed on the IUCN Red Data List under the following categories: Critically Endangered, Endangered, Vulnerable, Near Threatened, Least Concern[6], or listed as protected under Namibian law). In addition, a list of species caught for human consumption must be made. This will result in a description of especially relevant species that could be affected by the Hazard Scenarios present in the SD/AMS.

[6] www.iucnredlist.org

In order to carry out an informed SRA on the environment, it is recommended that the team should include an ecologist who is trained to look at indicators of environmental health. Basic key indicators of aquatic health which should be observed on site include:

- The health of riverine vegetation (reeds, grasses, trees);
- Presence of fish;
- Presence of dead fish, birds and animals;
- Piscivorous birds such as egrets, herons, kingfishers, hammerkop, ducks, fish eagle;
- Birds which feed on aquatic invertebrates and plants such as most waders, ducks, coots, moorhens;
- Bird and animal foot prints in the mud along the edge of the water;
- Presence of dragonflies, water beetles, molluscs and other invertebrates;
- Frogs (calling);
- Water quality indicators such as colour, turbidity, salt crusts, algal blooms, temperature, flow status.

Terrestrial Fauna and Flora

For the risk assessment it must be assumed that the Area of Study contains wild flora and fauna as potential receptors. To address this aspect, first the Assessor will estimate the surface area of all land inside the Area of Study using the means at his or her disposal (maps, images, etc.).

Along with this, a general description of the terrestrial flora and fauna present in the Area of Study and the surrounding area should be prepared. In particular it is important to determine whether there is evidence of any officially protected flora and/or fauna species (see above) and whether any species are harvested for human consumption.

Some of the required information can be obtained from MET and from published sources such as the Atlas of Namibia (Mendelssohn et al. 2002) before going to site, but this will need to be augmented by observations made on site by a trained ecologist. Some of the information that needs to be recorded includes:

- Types of ecosystems represented (woodland, savanna, succulent karoo, desert, etc.).
- Health of the vegetation, including indicators such as cover density, species diversity, growth forms, discolouration and the presence of invader species.
- Presence of main species of fauna and flora inside the Area of Study, with special reference to protected species.

- Presence of dead specimens.
- Tracks and signs of the presence of animals such as tracks, droppings, signs of feeding (browse lines, grazing pressure), scent marks, shed skins (reptiles), skulls, etc.
- Estimation of abundance (where applicable).
- Conservation status, including whether the species is endemic (where applicable).

Protected or Environmentally Sensitive Areas

The Assessor should identify the proximity or inclusion of Protected or Environmentally Sensitive Areas in the site's Area of Study. The information can be obtained from MET and from published sources such as the Atlas of Namibia (Mendelssohn *et al*. 2002) and should include:

- Presence or proximity of Protected or Environmentally Sensitive Areas in the Area of Study.
- Name of Protected or Environmentally Sensitive Area.
- Conservation status or protection category. These may include:
  - National Parks;
  - Game Parks;
  - Recreation Areas;
  - Private Nature Reserves;
  - Conservancies;
  - Marine Protected Areas;
  - Ramsar sites;
  - Important Bird Areas;
  - Trans-frontier Conservation Areas (TFCAs).
- Areas of natural or cultural value, such as: groundwater conservation areas; National Monuments; and forest reserves.
- Environmental components that could be affected by the safety and/or contamination of a SD/AMS (soil, natural vegetation, wildlife, water bodies, cultural heritage sites, etc.).
- Source of information consulted.

> ***=>*** *In the RARF (Baseline Sheet 3 in Annex E) environmental elements present in the Area of Study are recorded, along with basic information requested in each case.*

3.2.4.3 Economic Activities

SD/AMS can threaten economic activities such as crop farming, game farming and livestock activities, tourism, fishing and aquaculture. Because of their importance for subsistence and economic development, this Handbook considers such activities to be potential receptors of the risks identified.

Where productive areas are located inside the Area of Study, these should be included in the risk assessment. It is best to estimate the area used and therefore potentially affected by the site, as this will determine in part the magnitude of the risk assessed.

Tourism

The information which needs to be collected regarding tourism is:

- Types of tourism carried out in the Area of Study.
- The area(s) used for tourist activities.
- Number of residential units in or adjacent to the Area of Study (e.g. lodges, chalets, camp sites, etc.).
- Number of people employed in tourist activities in the Study Area on a permanent or temporary basis.
- Number of people who visit the Area of Study every year.



Plate 3.3: Old crumbling mine infrastructure can pose a safety risk to tourists, as at this old building at Bogenfels Mine in the Sperrgebiet

Agriculture: crop production

The following aspects will need to be documented in this regard:

- Type of productive activity –specify crops.
- Area and location in relation to the Area of Study and distance from the site.
- Location and method of extracting irrigation water.

- Identification of the level of production:
  - Subsistence;
  - Communal;
  - Commercial.
- Number of people who regularly eat crops potentially affected by the SD/AMS.
- Number of individuals working in agricultural production and their employment pattern throughout the year.

Agriculture: Game farming and livestock activities

Make a note of the following:

- Type of productive activity – specify species farmed.
- Area used for the activity, its location *vis à vis* the Area of Study and distance from the site.
- Location and method of extracting drinking water for animals or location of water source where animals drink.
- Identification of level of production:
  - Subsistence;
  - Communal;
  - Commercial.
- Number of people who regularly consume animal products (meat, milk, eggs) potentially affected by the SD/AMS.
- Number of individuals working in this activity and their employment pattern throughout the year.

Aquaculture and Fishing

The information to be gathered in this case includes:

- Type of productive activity – list species farmed.
- Location of the activity in relation to the Area of Study, distance from the site.
- Identification of the level of production:
  - Subsistence;
  - Communal;
  - Commercial.
- Number of people who regularly eat fish or aquaculture products potentially affected by the SD/AMS.

BOX 1
CASE STUDY: BERG AUKAS

Berg Aukas was a lead-zinc-vanadium mine that was operational on and off from 1920 to 1979. Subsequently the area was used mainly for agriculture and the abandoned mine buildings have been used as a Youth Training Centre since the early 1990s.

In 2005 and 2007, comprehensive geochemical surveys were conducted at the site to analyse the contamination of water, soils, forage and crops to determine if there were any health risks.

The study showed that most parts of Berg Aukas are severely contaminated with lead, zinc, cadmium, arsenic and vanadium, particularly in the soils of the old ore processing area (see Plate 3.2).

The abandoned mine tailings and slag dumps have been left unattended since 1979 and show signs of severe wind and water erosion. This means that the effects of pollution, through the aerial deposition of heavy metal particulates, have been spread to areas far away from the source.

Zinc and lead levels in grasses used for forage on and around the tailings dam were found to be in excess of accepted 'safe' levels for dry forage.

The concentrations of arsenic, lead and zinc in cassava and sweet potato leaves as well as roots were found to be well in excess of WHO limits for food.

As a result of these studies, the Government of Namibia relocated the National Youth Service training camp and famers have been informed about the levels of contamination in forage and crops around the tailings dam.

This demonstrates the importance of conducting a thorough risk assessment prior to land use decisions being made on old mine sites.

Since this section deals with identifying productive activities, it is important that the Assessor interviews local inhabitants and officials, as these individuals will have information on traditional productive activities and new development projects that may be planned for the future.

=> In the RARF (Baseline Sheet 3 in Annex E) economic activities observed in the Area of Study will be identified along with the basic information requested about them.

3.2.5. Preparing the Field Visit

For preparing the field visit, this Handbook has a **Guide for Preparing and Implementing the Field Visit,** available in print and digital format (Annex F). Assessors should review this Guide **before the field visit**, to ensure that the Assessor remains safe during the visit and that the objective of the trip is fulfilled. The Guide covers the following issues, among others:

- Confirm activities previously performed in the office.
- Define any third party interviews that have to be conducted beforehand.
- Offers a checklist for personal protection for the Assessor to use in the field.
- Provides a checklist of measuring instruments that may be necessary.
- Provides protocols for specific tasks that have to be carried out in the field.

A key aspect of planning at this stage is to put together the assessment team. Depending on the location of the SD/AMS and the nature of the hazards present, the team should include at least an Environmental Geologist and an Environmental Scientist familiar with the area of the site. For particularly dangerous sites, it may be advisable to include a mining engineer or civil engineer depending on the safety hazards present.

3.2.6. Summary of Assessment Preparation Stage

Once the administrative work is finished (described in sections 3.2.1 to 3.2.4), the Assessor should ensure preparations are complete and the following elements are available:

1. The **MIDS** containing all of the information collected about the site.
2. The **Risk Assessment Base Map (RABM)** showing the preliminary boundaries of the Area of Study for the site and also a preliminary identification of receptors.
3. The **RARF** (in Excel format) containing all information collected to date. This form will also be used for collecting information on site.
4. The **Guide for Preparing and Implementing the Field Visit**, duly filled out according to the conditions of the site being assessed.

3.3 Field visit

The field visit may last one or more days, depending on a number of factors such as the size of the site, its complexity and/or ease of access, climatic conditions, etc.

The specific objectives of this inspection are:

- Identify and describe the **mine workings, process plant and all wastes and deposits** present in the SD/AMS.
- Identify and describe the Safety and Contamination **Hazard Scenarios** present.
- Confirm the **boundaries of the Area of Study**, set out in preliminary form prior to the field visit.

- Identify and describe the **Receptors** present in the Area of Study (individuals, environmental components and economic activities).
- Gather the information necessary to estimate the **Likelihood of Occurrence** of each Hazard Scenario, considering the combination of circumstances.
- Gather the information necessary to estimate the **Severity of the Consequences** for each Hazard Scenario, taking into account the number of receptors involved and/or the severity of damage.

The sections below give a step by step description of how the Assessor should address each of the objectives outlined above during the field inspection:

3.3.1 Identification and Description of Installations, Deposits and Works

3.3.1.1 Identification of Installations, Deposits and Works

The Assessor should begin identifying the **mine workings, process plant and all wastes and deposits** at the SD/AMS with a walk-through. Each one of these elements should be identified with the corresponding code (section 4.1.2.1). Some criteria to assist the Assessor in identifying individual components on site are given below:

- All installations, deposits or works that the Assessor deems to represent a risk to human safety, to the environment, or to economic activities, should be specified. This means that each shaft and/or adit present on a site should be identified separately; similarly, individual quarries or pits that are not a continuous unit should also be identified individually, as should separate deposits of large scale and small scale mining waste and adjoining infrastructure (roads, storehouses, camps, etc.) located in distinct sectors.
- However, the Assessor should not specify minor installations, deposits or works that do not represent a safety or contamination risk; these may include small building structures, small mounds of topsoil or overburden, access tracks, etc.
- Due to their nature and size, ore treatment plants (in general) include different internal structures that represent distinct kinds of risks. The Assessor should identify the Plant as a single unit, describing the structures remaining inside (sumps, tanks, pipes, unstable walls, offices, etc.).
- Any installation, deposit or work located inside a plant will only be identified separately (including any kind of adjoining infrastructure) when the Hazard Scenario it represents is very different from those present in the plant itself. This would be the case, for example, for large waste deposits located inside such a plant.

3.3.1.2 Description of Installations, Deposits and/or Mine Works

Once the Assessor has identified the installations, deposits and/or works present, he or she must prepare a description of these, including their size and most relevant aspects for safety and/or contamination issues (see details in section 4.1.2.1).

=> All installations, deposits and works at the site will be recorded on the RARF (Cover page 2 in Annex E). To accompany the description, geographic coordinates of the place and digital photographs showing the general state of that element should be included.

3.3.2 Identification of Hazard Scenarios for each Installation, Deposit or Work

As a second step in the field, the Assessor should identify **Hazard Scenarios** that are present at each of the installations, deposits and or works (see details in sections 4.1.2.1 and 4.2.2.1). To determine these, the Assessor should consult Tables 4-3 and 4-10, which enumerate all scenarios considered within the scope of this Handbook.

Classification of waste present on site, e.g. **hazardous waste** (whether in deposits, in remnant indoor structures, or contaminated equipment or soil), should be made by the Assessor based on the Pollution Control and Waste Management Act[7], administered by the MET. In most cases a sample of the waste will need to be taken (using bottles or plastic bags) for analysis in the lab. Each sample obtained in the field should be labelled by the Assessor (with permanent marker) with a code identifying the SD/AMS, the Hazard Scenario from which it was obtained, the number of the sample, and date obtained.

=> The RARF will contain a record and description of the Hazard Scenarios present (SHS Step 1 and CHS Step 2 in Annex E). The Assessor should take digital photographs to suitably illustrate the scenarios identified. The images can be inserted in digital format into the RARF (Appendix 3 Photographs).

3.3.3 Drawing the Boundaries of the Area of Study

During the field inspection, the Assessor will define the area that could be affected by the negative impacts (safety or contamination) of each of the scenarios being assessed. These observations will enable the delimitation of the **Area of Study** associated with each Hazard Scenario identified on the

[7] This Act is still to be promulgated.

site. Any adjustment to the Area of Study made by the Assessor in the field should be recorded on the RABM that was brought to the site.

3.3.4 Characterization of Receptors for each Hazard Scenario

Once the perimeter of the Area of Study has been confirmed, the Assessor may now turn to identifying the **Receptors** present in the area. The observations made during this inspection will allow the Assessor to correct and/or complete the information gathered in the preparatory stage. This includes confirming the number of individuals that inhabit or visit the Area of Study, the presence of crops, livestock, etc. During this process the Assessor may decide to gather additional information by interviewing individuals residing in the area surrounding the SD/AMS.

It should be noted that each Hazard Scenario identified on site will have its own kind and number of associated receptors. For example, tailings from a deposit that are blown by the wind will affect receptors situated within the area of influence of the contamination plume, while the release of contaminants from this same deposit, such as runoff after rainfall, may affect a different group of receptors located downriver. As a result, the Areas of Study and receptors may be quite different for each Hazard Scenario.

=> Once the inspection of receptors is concluded, the Assessor should record the results on the RARF (Baseline Sheet 3 in Annex E).

3.3.5 Field Information Required to Determine the Likelihood of Occurrence of each Hazard Scenario

For each of the Hazard Scenarios identified as either a safety or contamination concern, the Assessor should collect the field information required to determine its **Likelihood of Occurrence**. To assist the Assessor in determining the Probability in each case, the Handbook provides a series of Guides for Calculating the Probability Index (Annexes A1 and B1). The Assessor should take copies of these Guides into the field in order to select the most suitable one on site and record all of the information required.

=> The Assessor will record the information required for estimating the Probability Index of each Hazard Scenario on the RARF (SHS Step 2; CHS Step 3 in Annex E).

3.3.6 Field Information Required to Determine the Severity of the Consequences for each Hazard Scenario

Once all potentially affected receptors have been characterized, the Assessor can now apply the criteria specified in the Handbook to determine the **Severity of the Consequences** for each Hazard Scenario (see details in section 4.1.2.3 and 4.2.2.4). To do this, the Assessor will use Tables 4-6 and

4-14 to assign a value to this indicator based on the number of receptors potentially affected and/or the seriousness of any harm that may be caused.

=> In the RARF (SHS Step 3; CHS Step 4 in Annex E) the Assessor will record the Severity Value obtained for each Hazard Scenario.

This process should be repeated for each installation, deposit or work identified for the site.

3.3.7 Final Review of Field Inspection

The field visit concludes with a review of all the information gathered. At this time the Assessor must ensure that: (1) all installations, deposits and works have been visited; (2) all Hazard Scenarios present on site have been described; and (3) enough information has been collected to enable the estimation of Likelihood of Occurrence and Severity of the Consequences.

It is crucial that the Assessor record all pertinent information from the field visit on the RARF. This information will support the assessment, provide grounds for conclusions drawn, and facilitate any subsequent reviews by other government officials. The information recorded includes not only the technical matters addressed in this Handbook but also any observations that may be useful for subsequent site visits, especially in regard to access and/or safety conditions.

IGCP/SIDA 594 Training course, University of the Witwatersrand, Johannesburg, July 13-15, 2013

Lead and Copper Isotopes in Environmental Sciences

Martin Mihaljevič

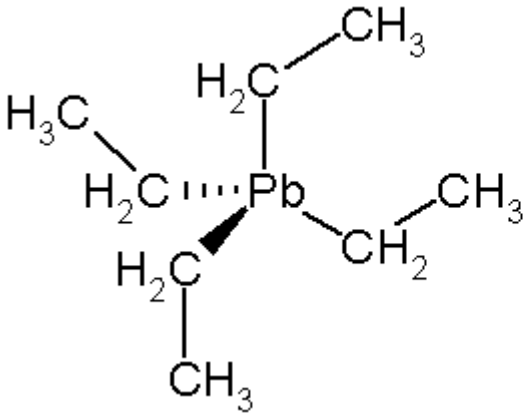
Institute of Geochemistry, Mineralogy and Mineral resources
Faculty of Science, Charles University

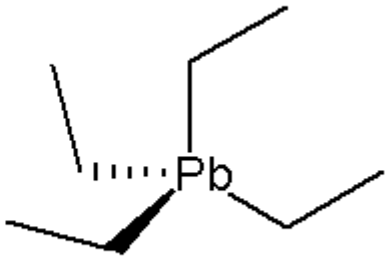
Introduction

- Metals are global contaminants
- Geochemical archives
- Pb and Cu isotopes
- Metodological approaches
- Practical applications

Lead







ILUSTRAČNÉ FOTO

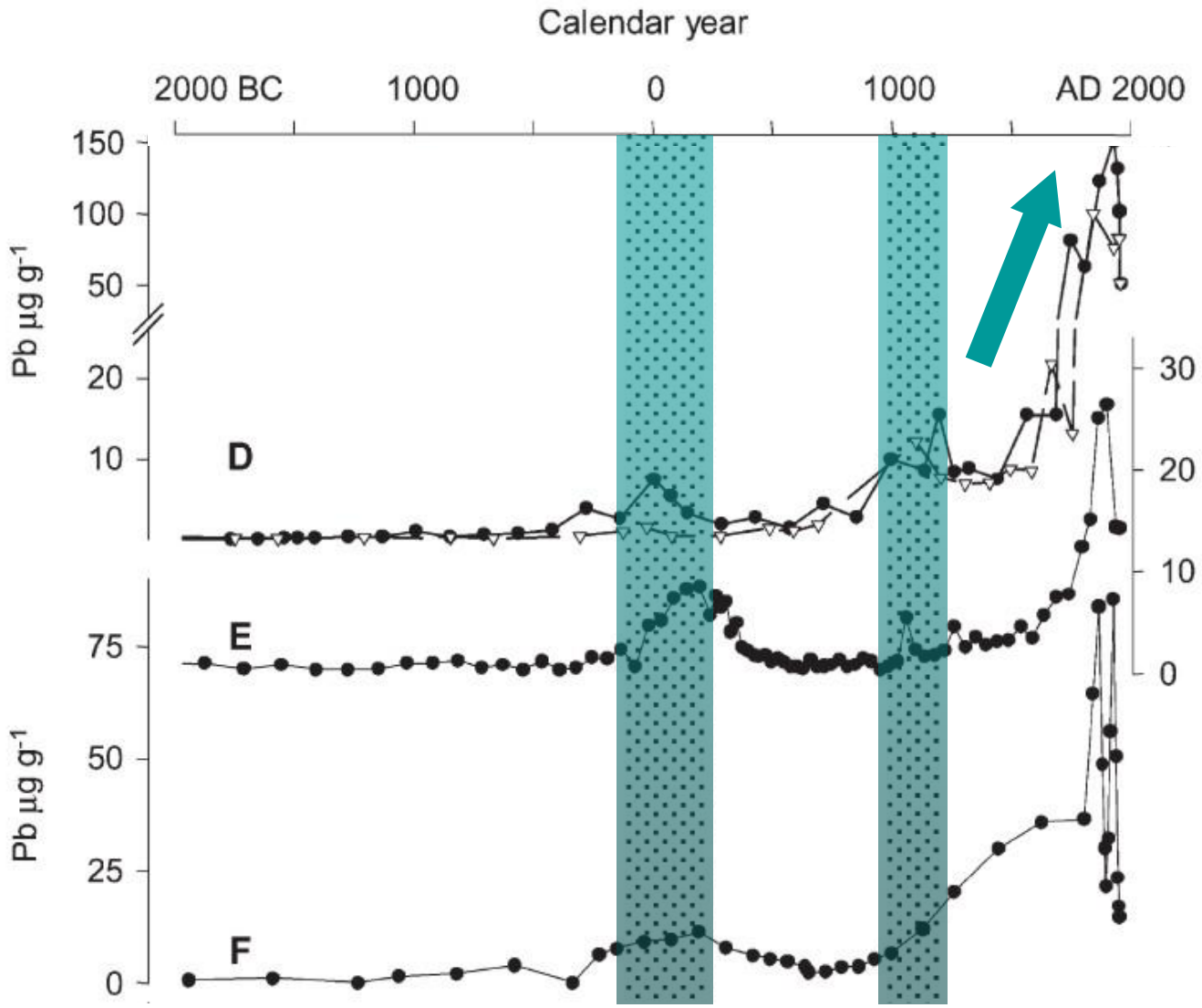






ILUSTRAČNÉ FOTO

Lead – global contaminant



Sweeden

Spain

Swiss

Renberg et al. Holocene, 11, 511-516

Introduction

- Total concentration and mineralogical form is not sufficient for evaluation of contamination
- Tracing of sources (local, global), kinetics of processes, residence time are of great concerns
- Convenient approach provides isotopic study

Pb isotopes

I. Short lived radionuclides

^{210}**Pb** ($t_{1/2}$ = 22 years) ^{212}**Pb** ($t_{1/2}$ = 10 hours)

^{214}**Pb** ($t_{1/2}$ = 26.8 min)

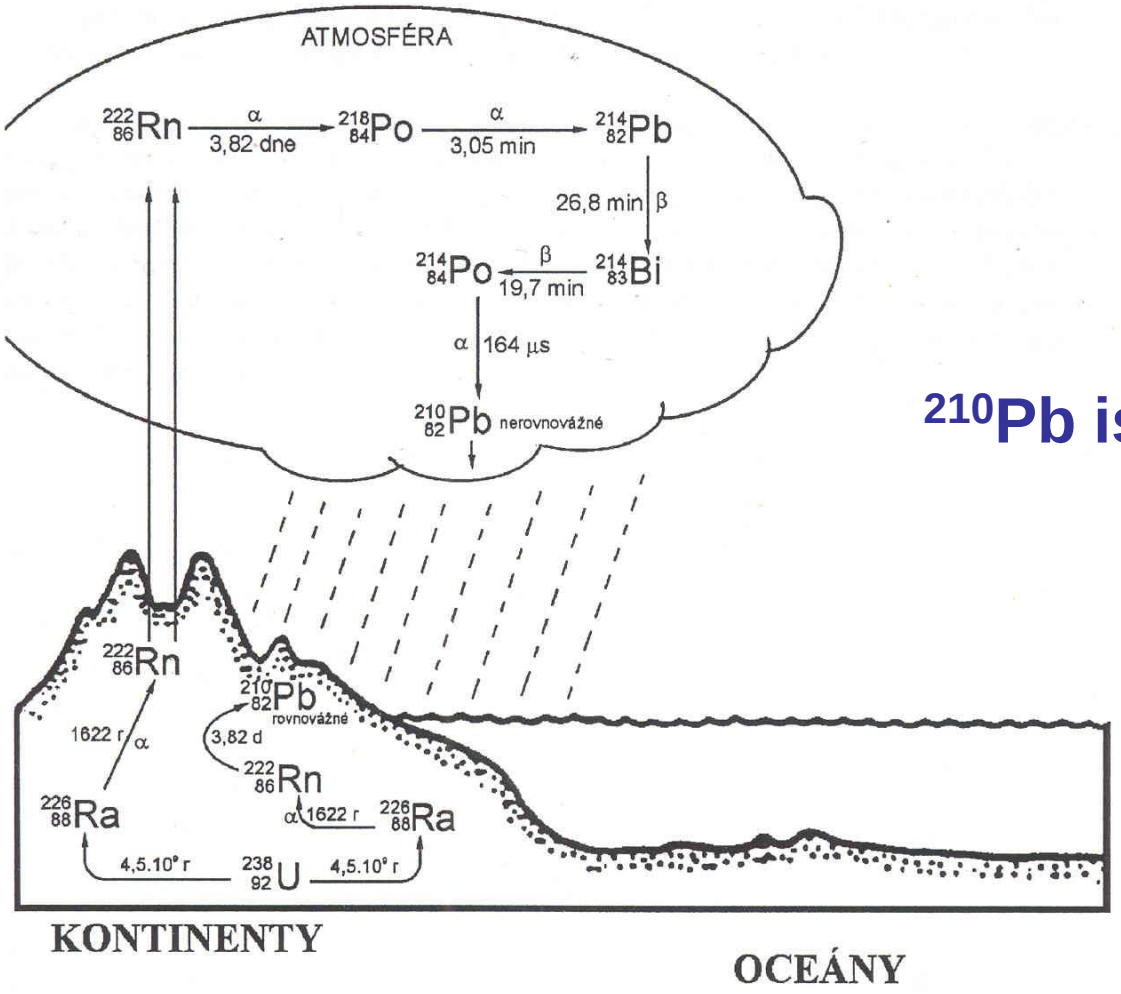
II. Products of U and Th decay

^{206}Pb, ^{207}Pb a ^{208}Pb

parent isotope	Pb isotope	decay half time (years)
^{238}U	^{206}Pb (24%)	4,466 x 10^9
^{235}U	^{207}Pb (23%)	0,704 x 10^9
^{232}Th	^{208}Pb (52 %)	1,401 x 10^{10}

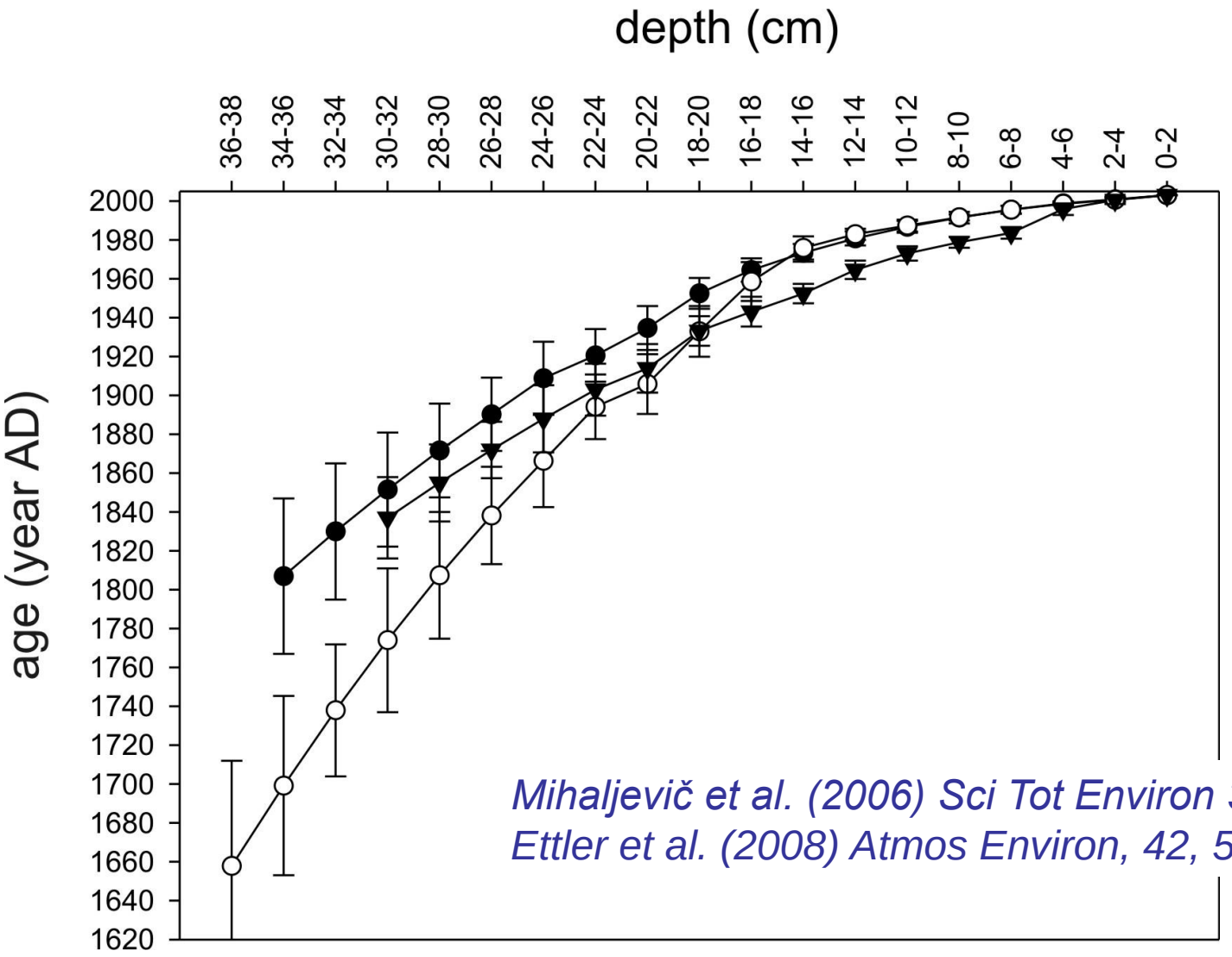
III. ^{204}Pb (1%) stable, non radiogenic , primordial, constant abundance on Earth in time

^{210}Pb cycle



^{210}Pb is decay product of ^{222}Rn

Dating of young sediments, peat deposit (~ 200 years)



Mihaljevič et al. (2006) Sci Tot Environ 372, 334-344.
Ettler et al. (2008) Atmos Environ, 42, 5968-5977.

^{206}Pb, ^{207}Pb, ^{208}Pb a ^{204}Pb isotopes

Origin of Pb Isotopic signature of geomaterials depends on

- **age of U, Th source**
- **separation of Pb (or U, Th) from the source**

I. separation of U a Th phases, which produce highly radiogenic ratio

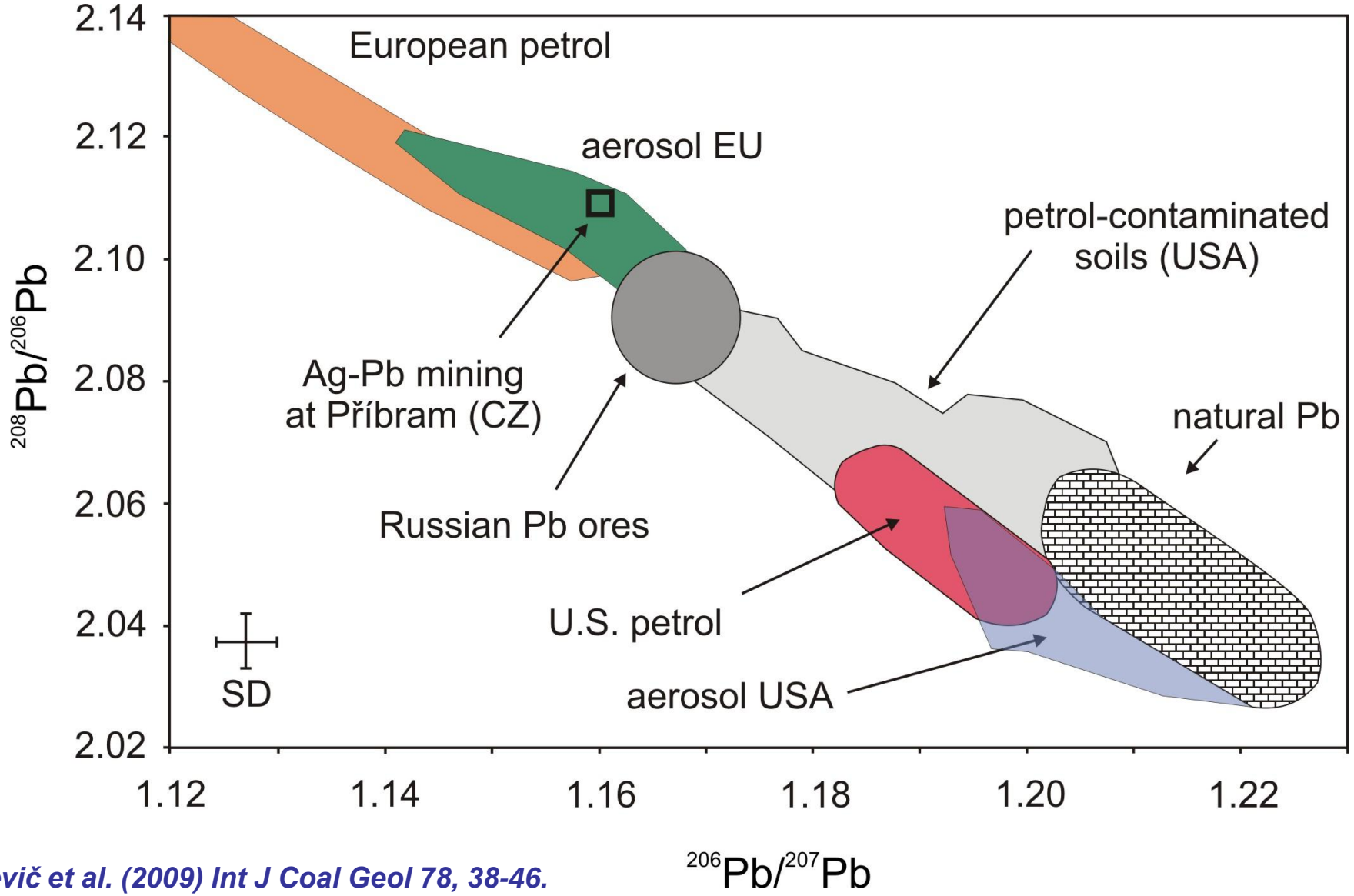
II. separation of Pb (sulphides) or phases containing low amount of U, Th)

III. separation of Pb simultaneously with U a Th

Origin of environmental Pb signature

- one important source of Pb (eg. lithogical, ore)
- mixing of different sources
- combination of Pb and parent isotopes of U and Th
- isotopic composition of the most important sources

A three-isotope plot



Mihaljevič et al. (2009) Int J Coal Geol 78, 38-46.
Ettler et al. (2004) Anal Bioanal Chem 378, 311-317.
Komárek et al. (2008) Environ Int 34, 562-577.

Material and methods



peat profiles


sedimentary profiles


soils


tree ring

soil and atmospheric waters





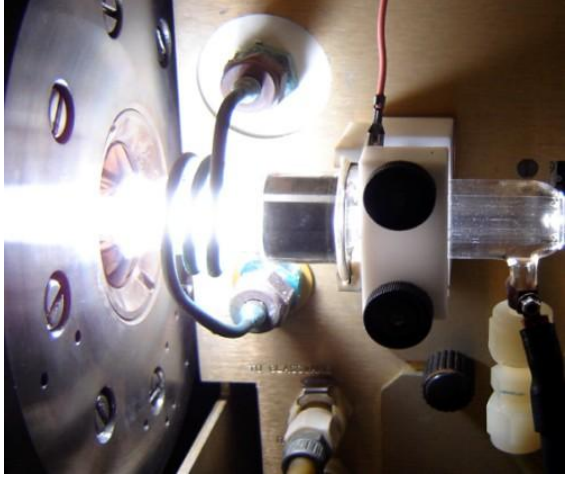


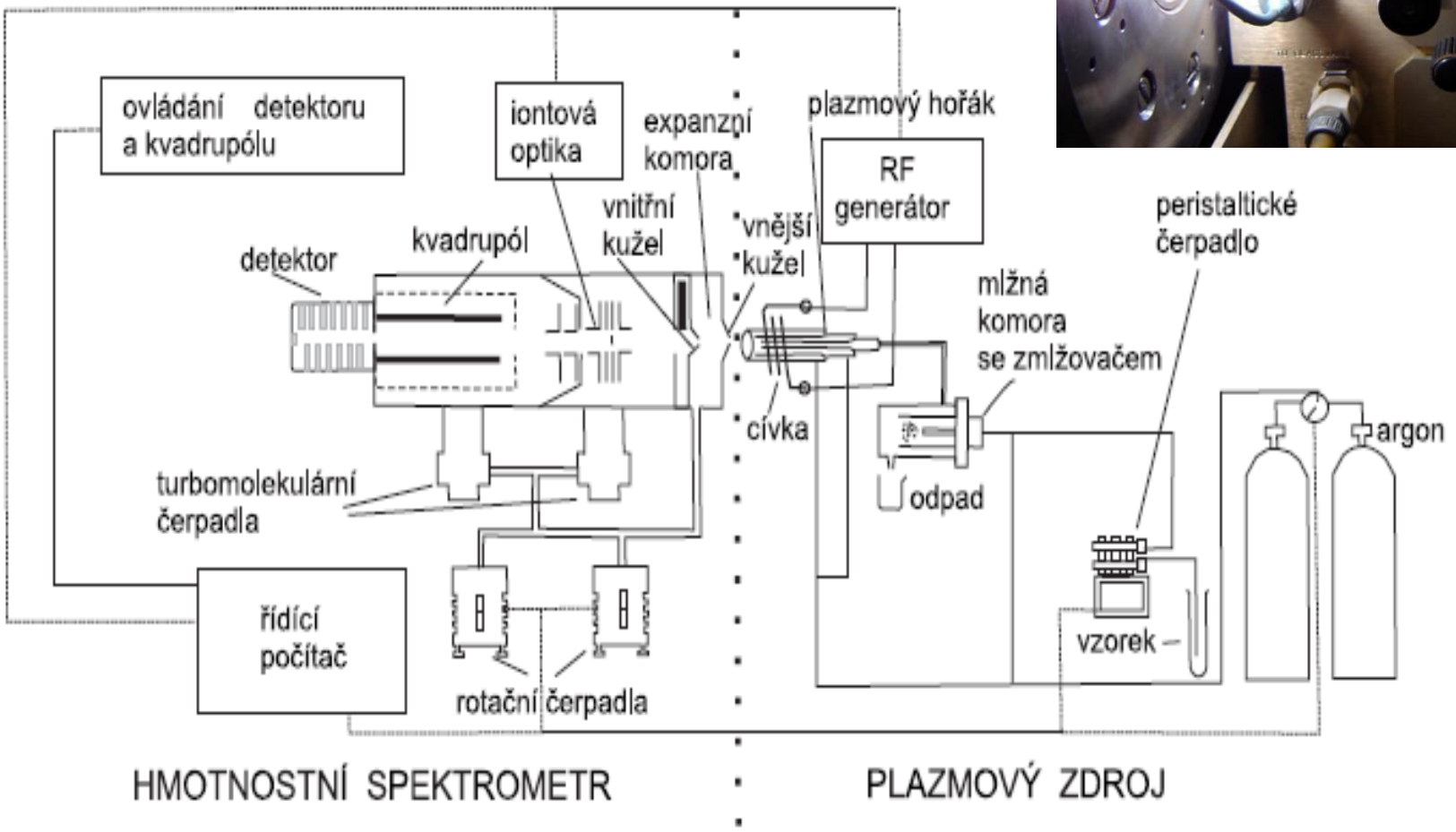
soils *vs.* biomass





Measurement of Pb isotopic composition

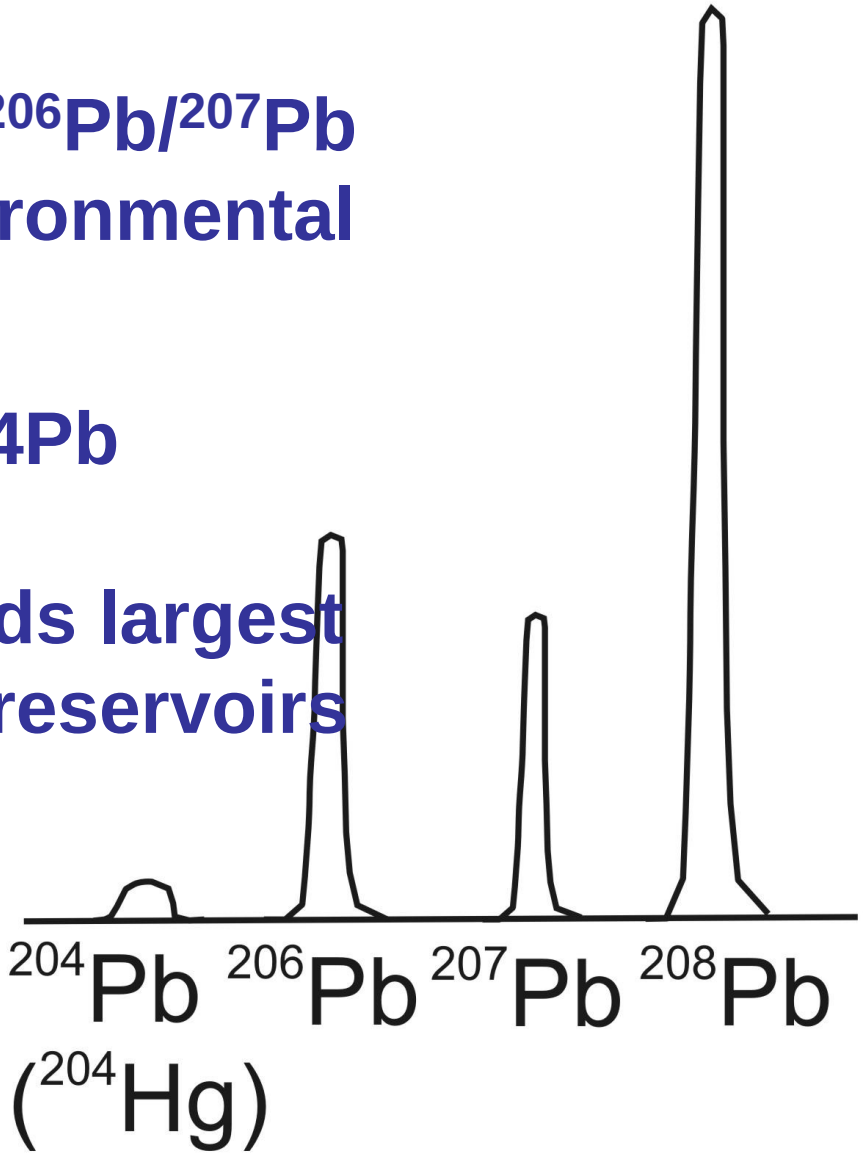




Quadrupole based ICP MS (VG Elemental PQ3)

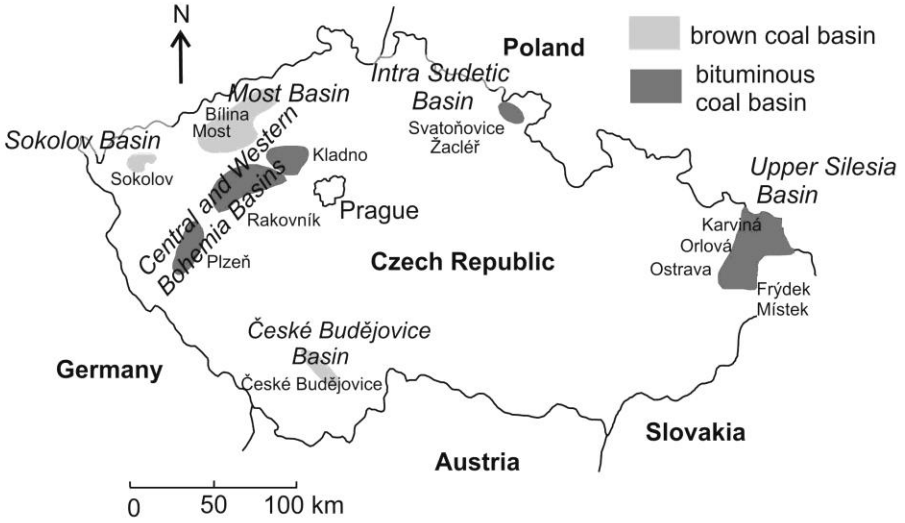
Pb mass spectrum

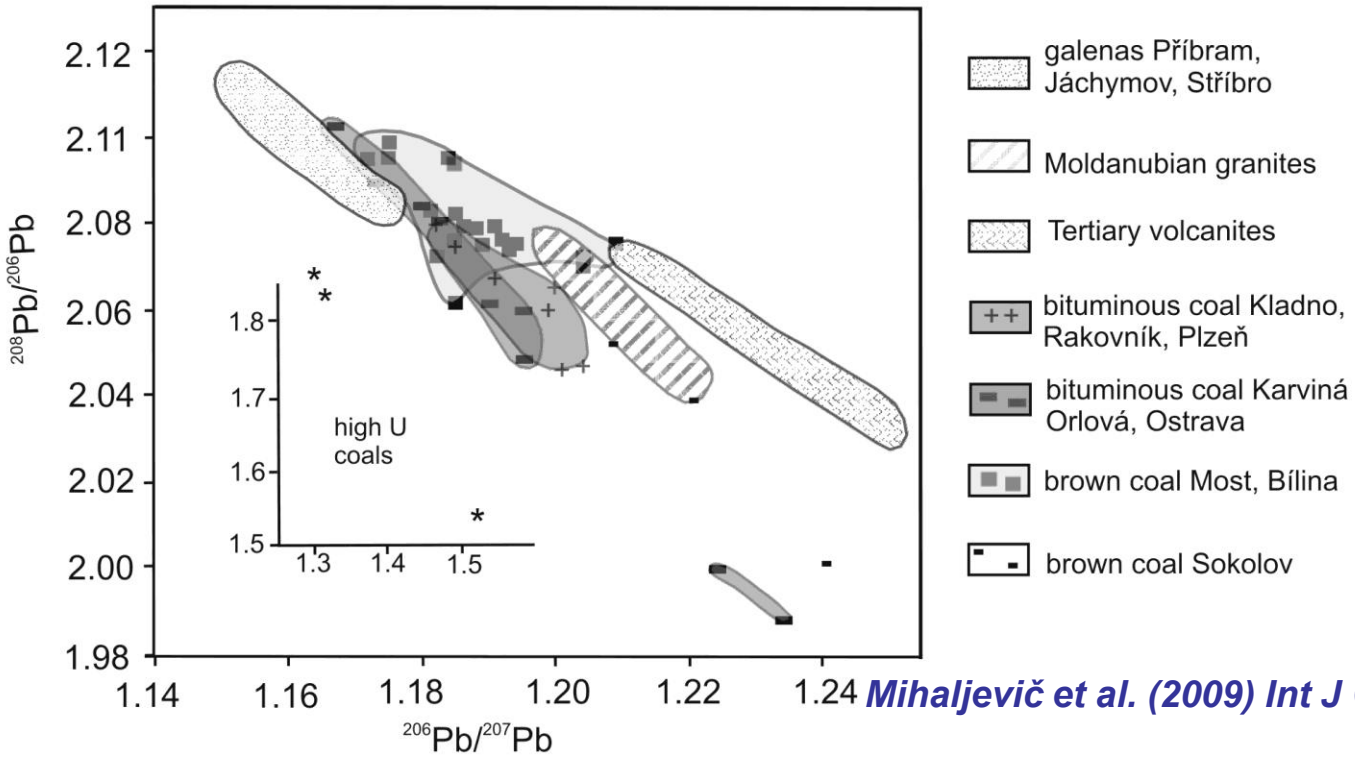
- the most preferred $^{206}Pb/^{207}Pb$ ratio is used in environmental science
- normalisation to 204Pb (206Pb/204Pb, 207/Pb204Pb...) yields largest variability between reservoirs



Coals

- important source of Pb
- different isotopic composition
- depends on Pb source and U content

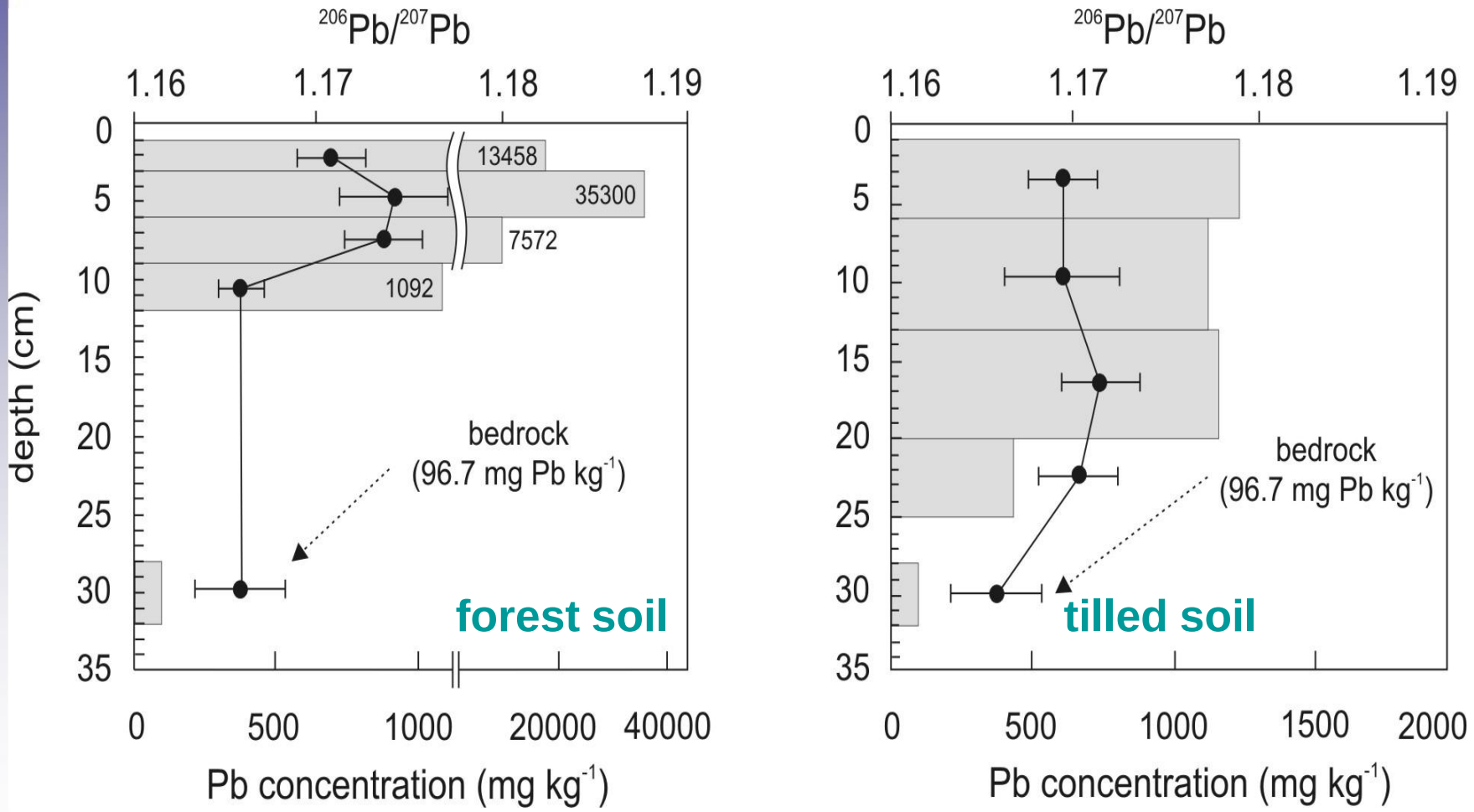




Mihaljevič et al. (2009) Int J Coal Geol 78, 38-46.

Soils

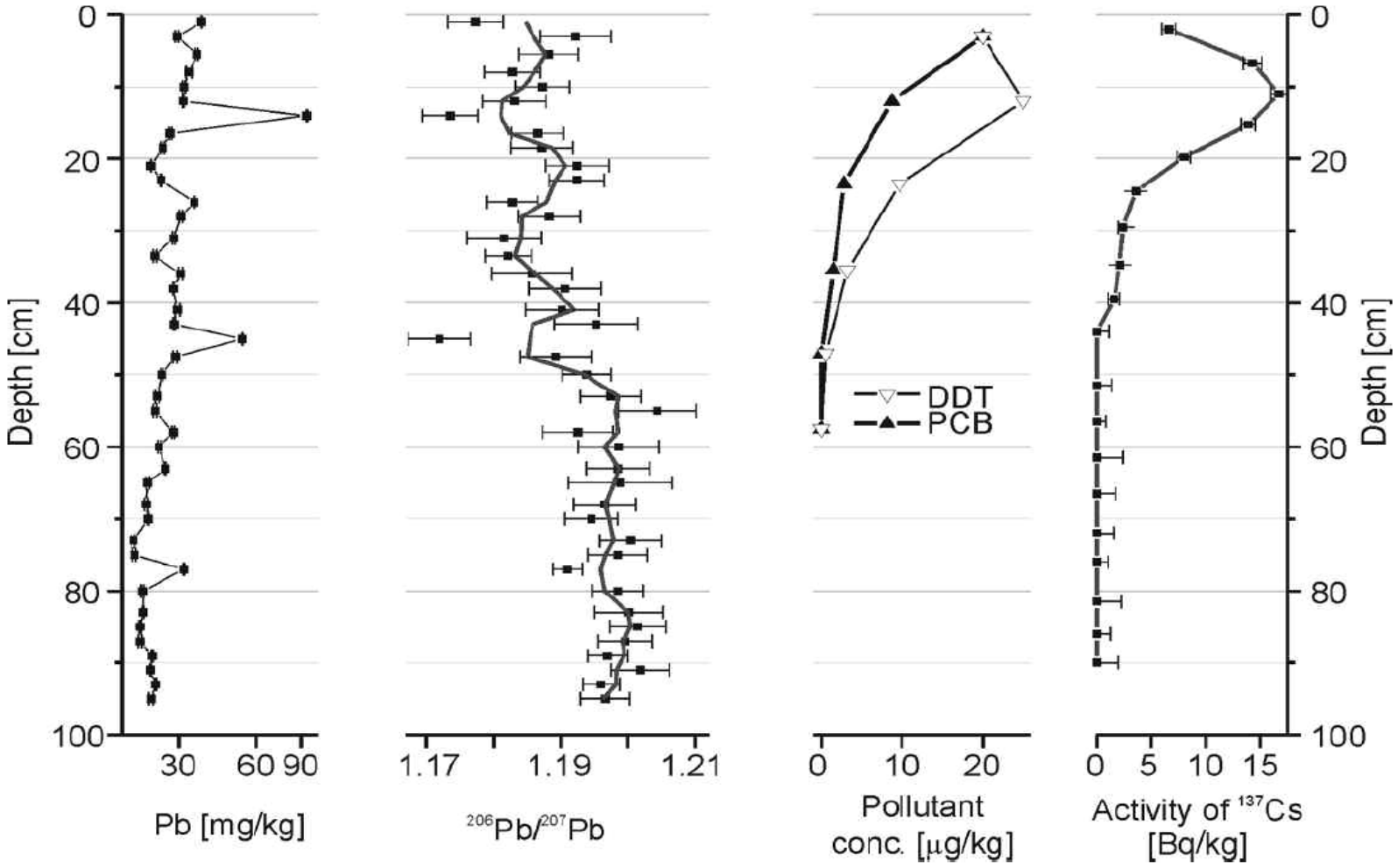
- source determination, mixing of sources
- determination of Pb penentration rate



Ettler et al. (2004) Anal Bioanal Chem 378, 311-317.

Sediments

- changes in Pb source

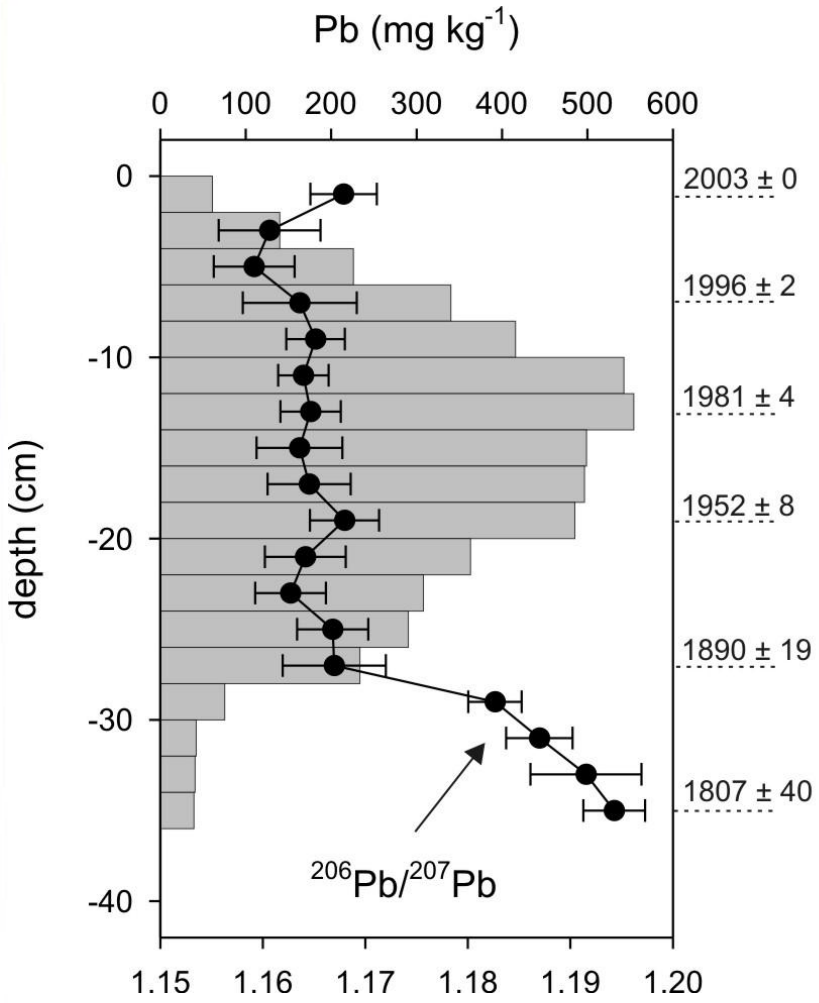


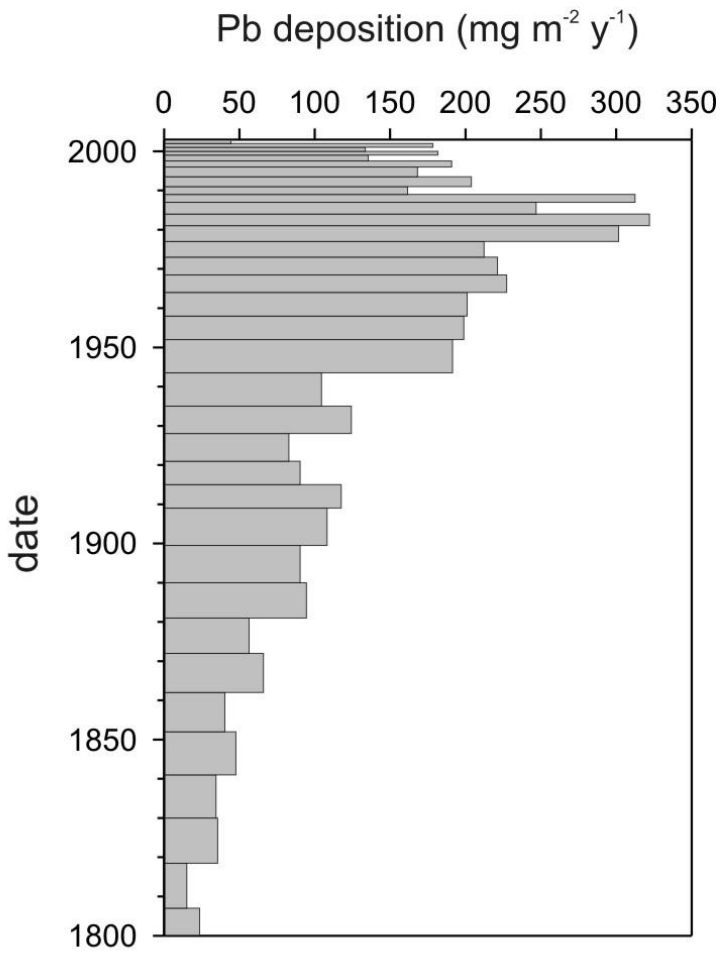
Morava River floodplain

Kadlec et al. (2009) Holocene, 19, 499-509

Peat deposits

- source identification in industrial and remote areas
- deposition rates calculation

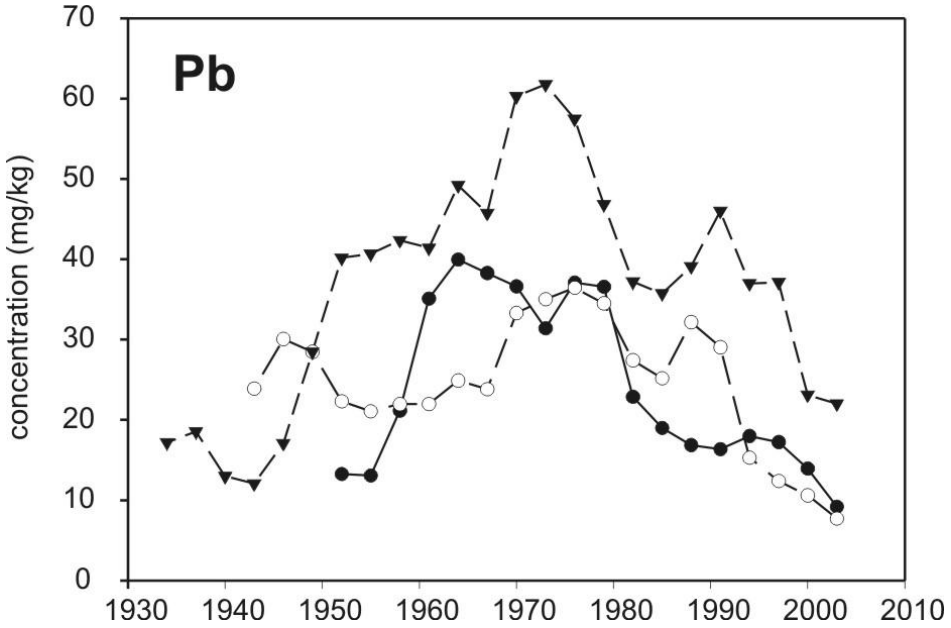


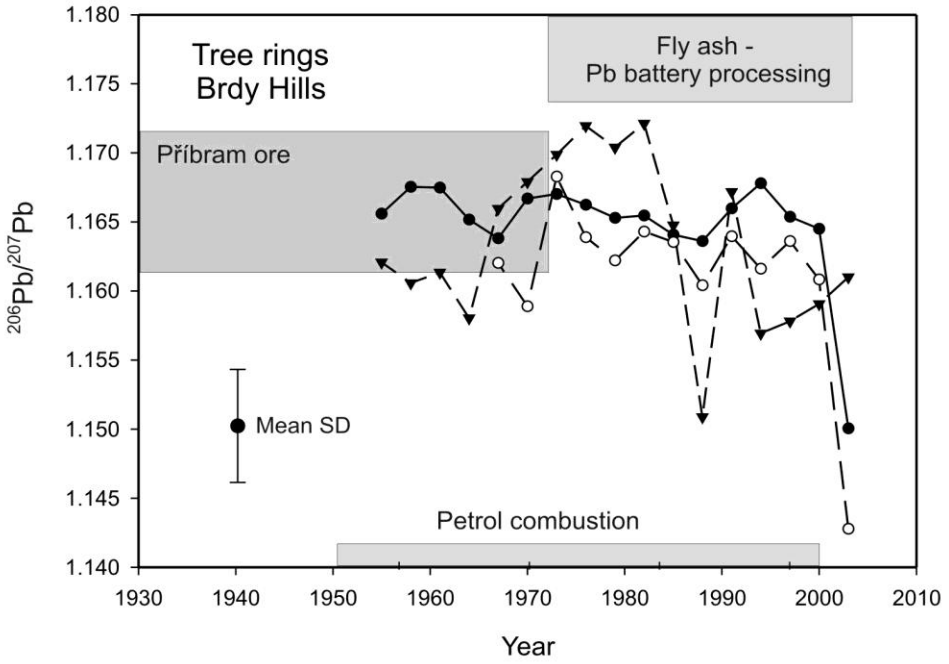


Mihaljevič et al. (2006) Sci Tot Environ 372, 334-344.

Tree rings

- trees in temperate climate have visually distinguishable tree rings
- Pb is a suitable element for dendroanalyses
- Pb source identification by isotopic study

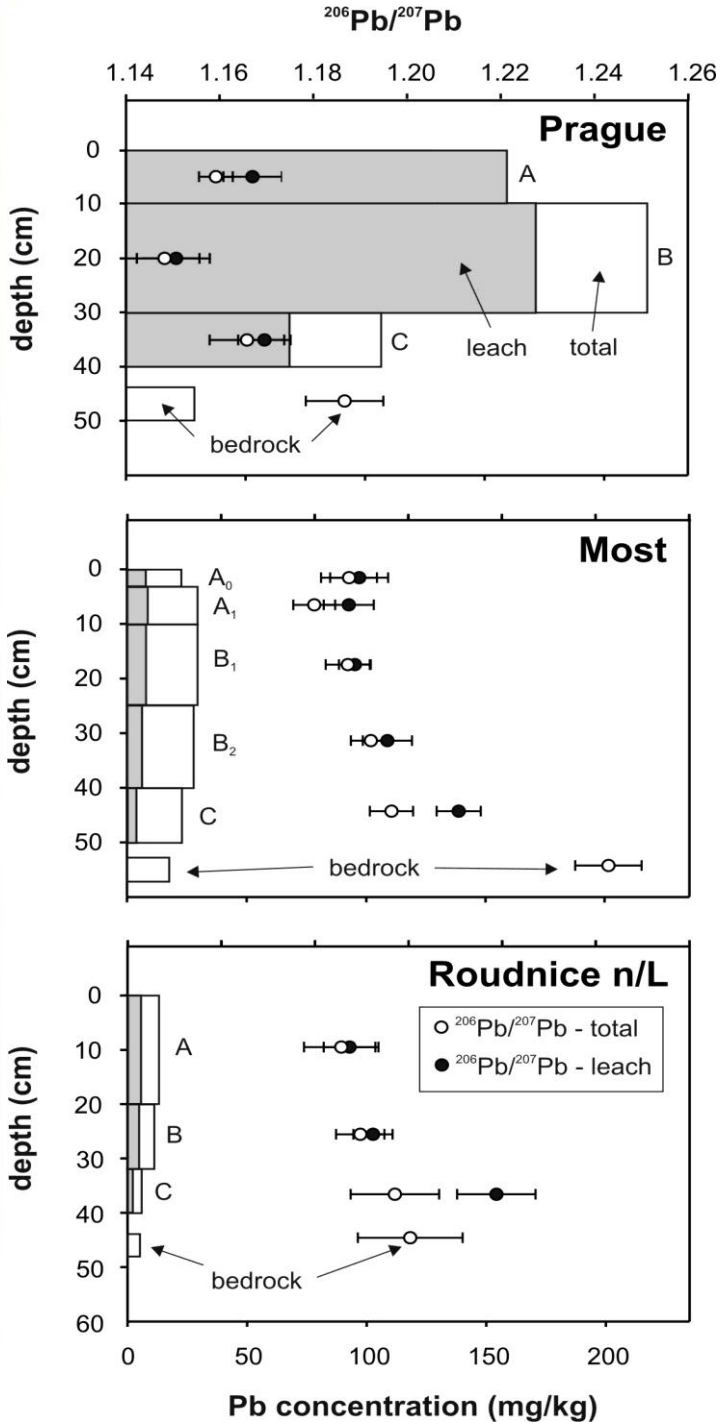


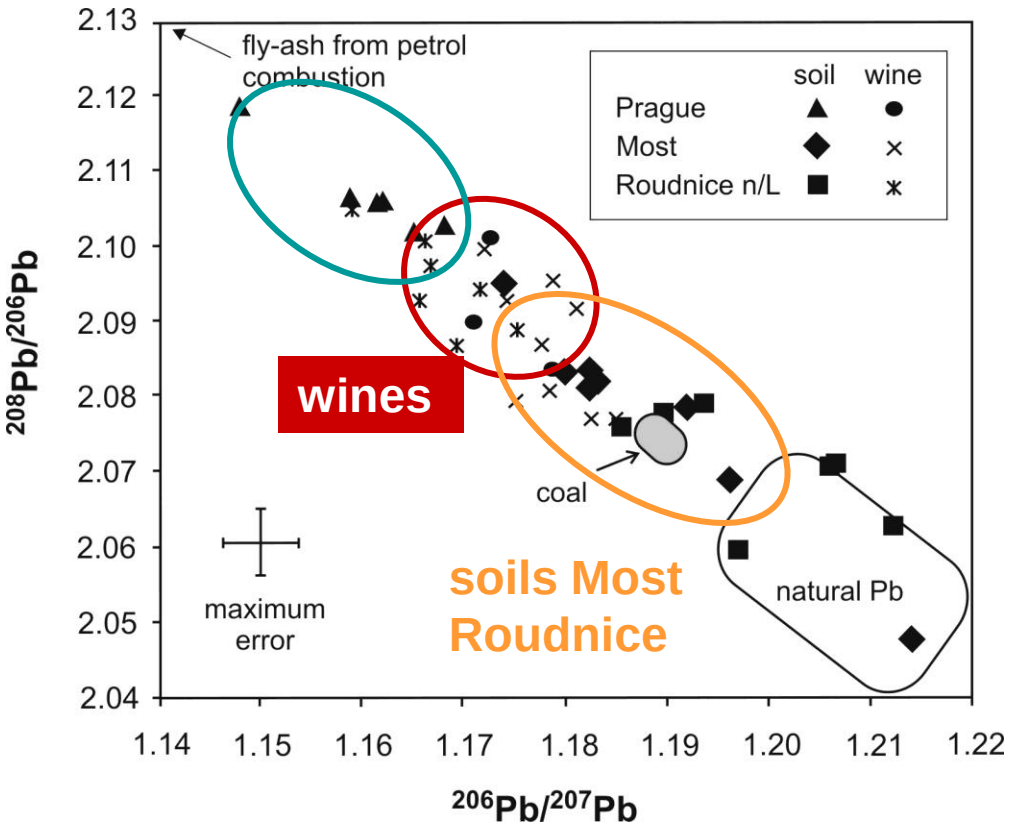


Mihaljevič et al. (2008) WASP 188, 311-321.

Plants- products

- source of Pb
- root uptake/interception

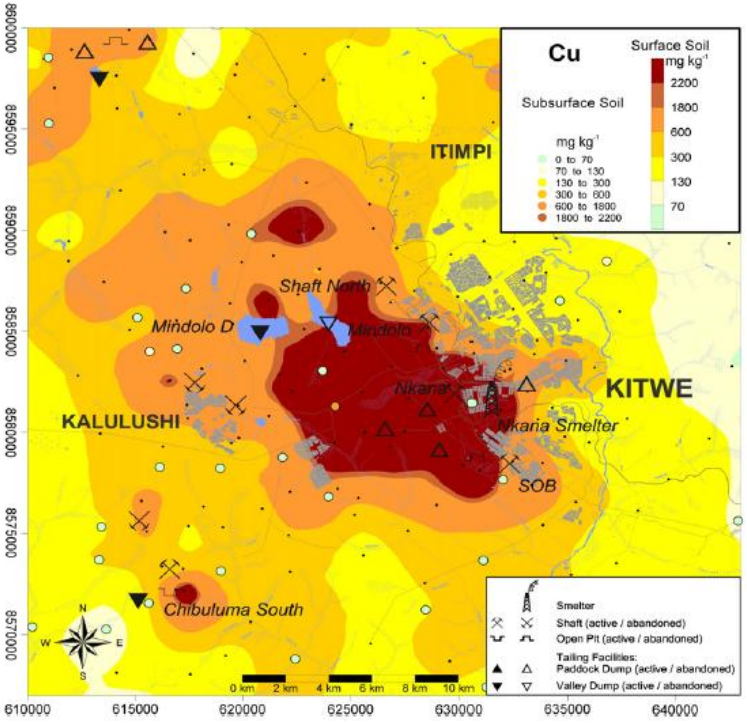


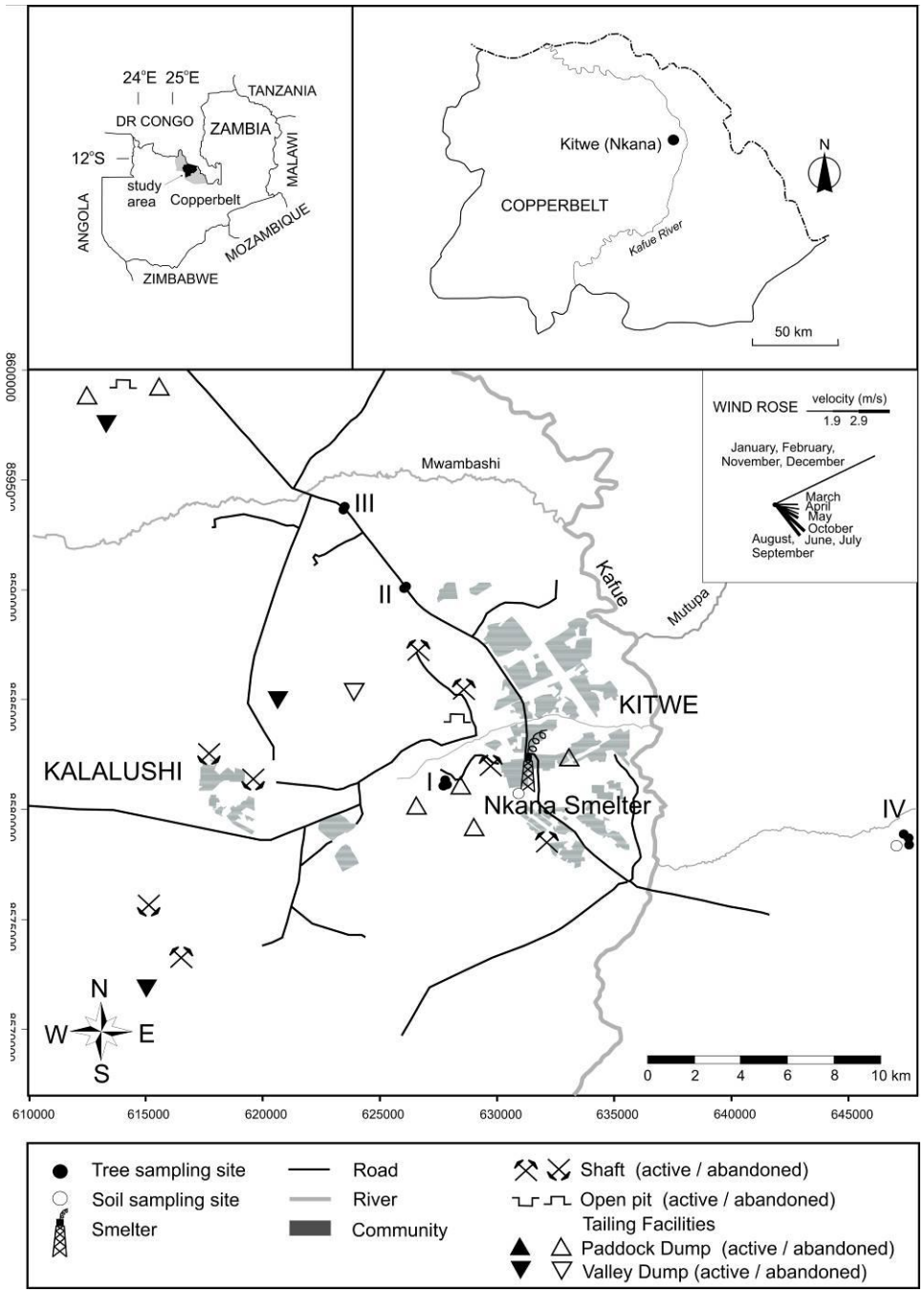


Mihaljevič et al. (2006) J Geochem Explor 88, 130-133

Zambia Copperbelt

Cu, Co ores metallic and SO2 pollution







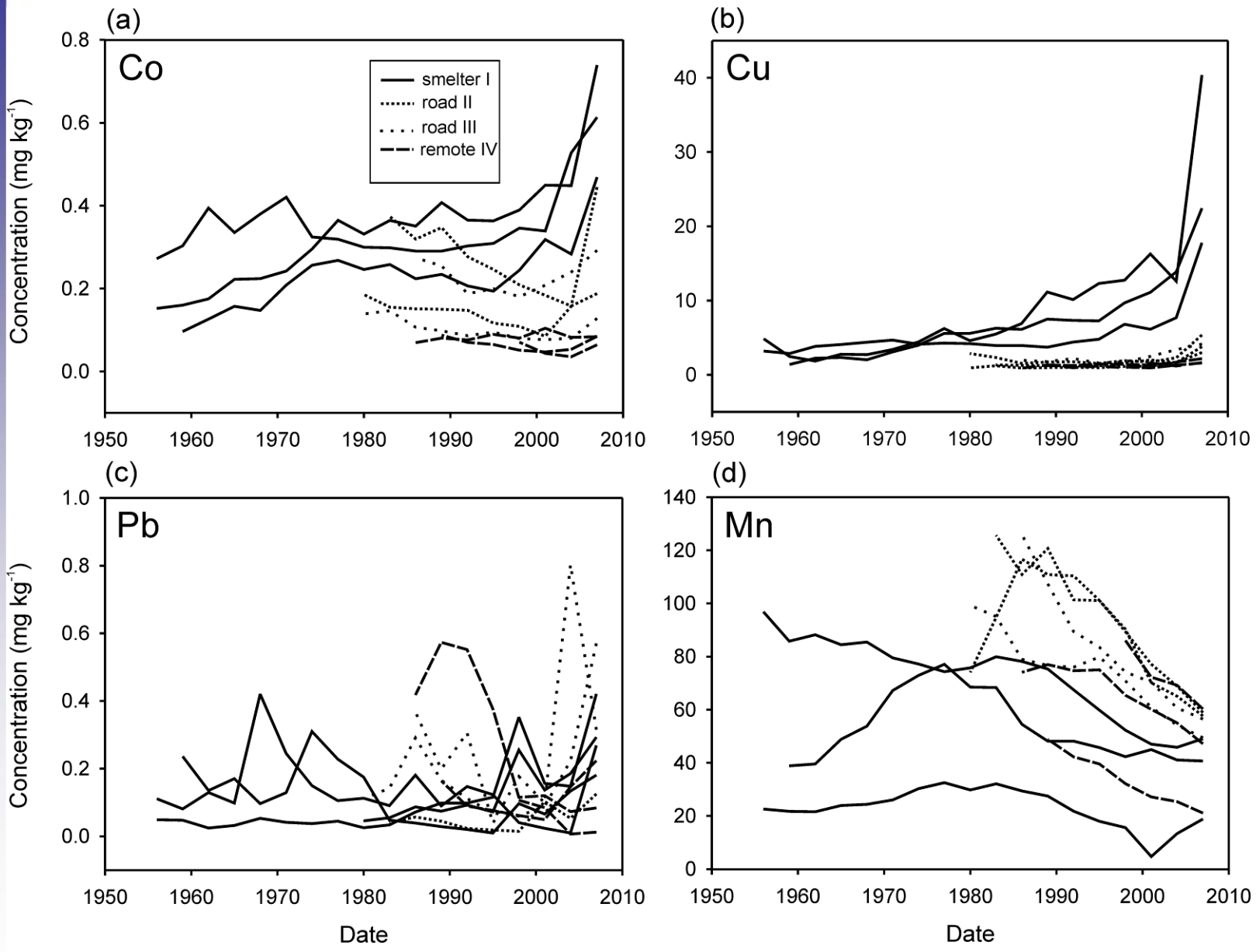


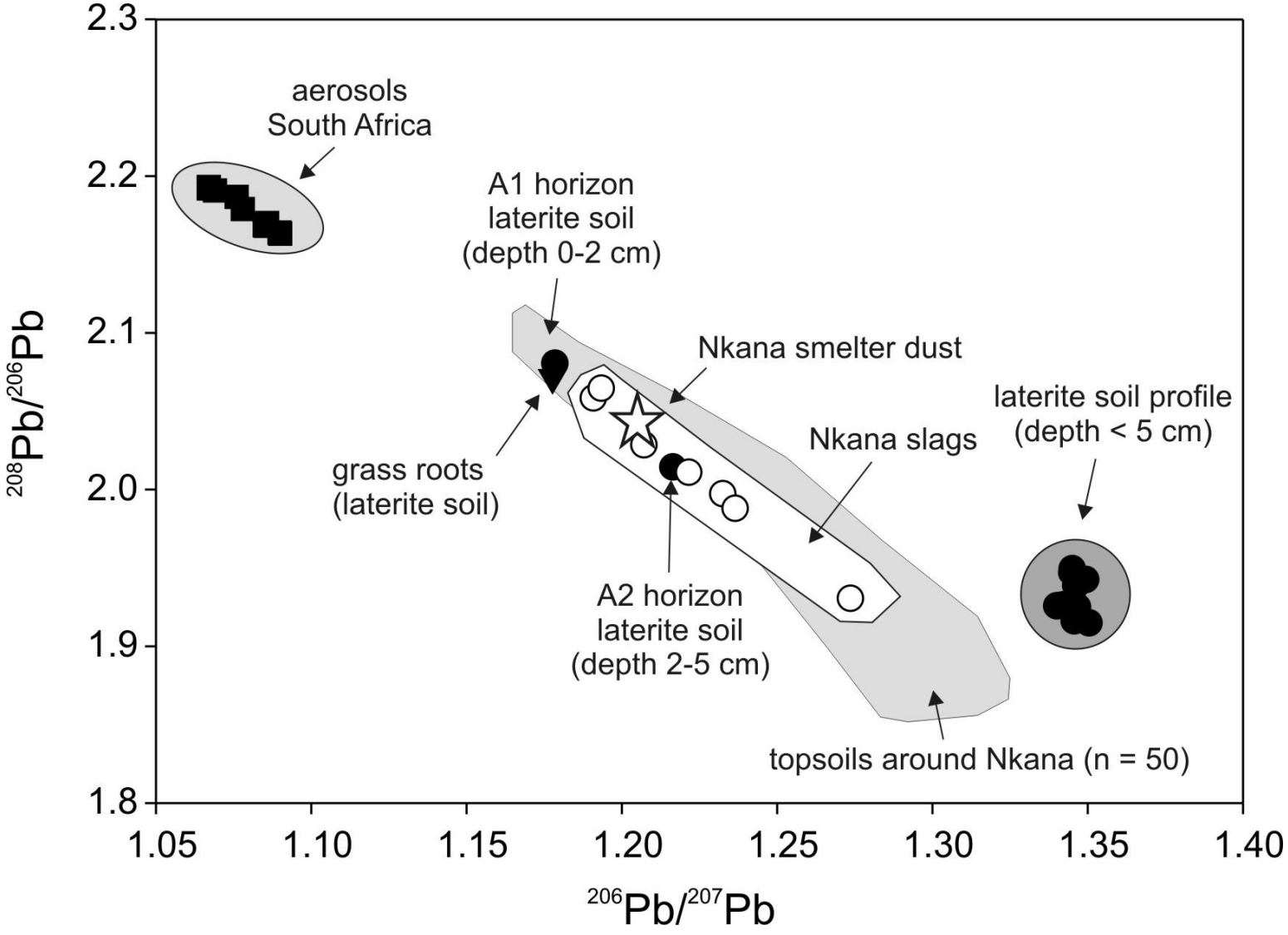




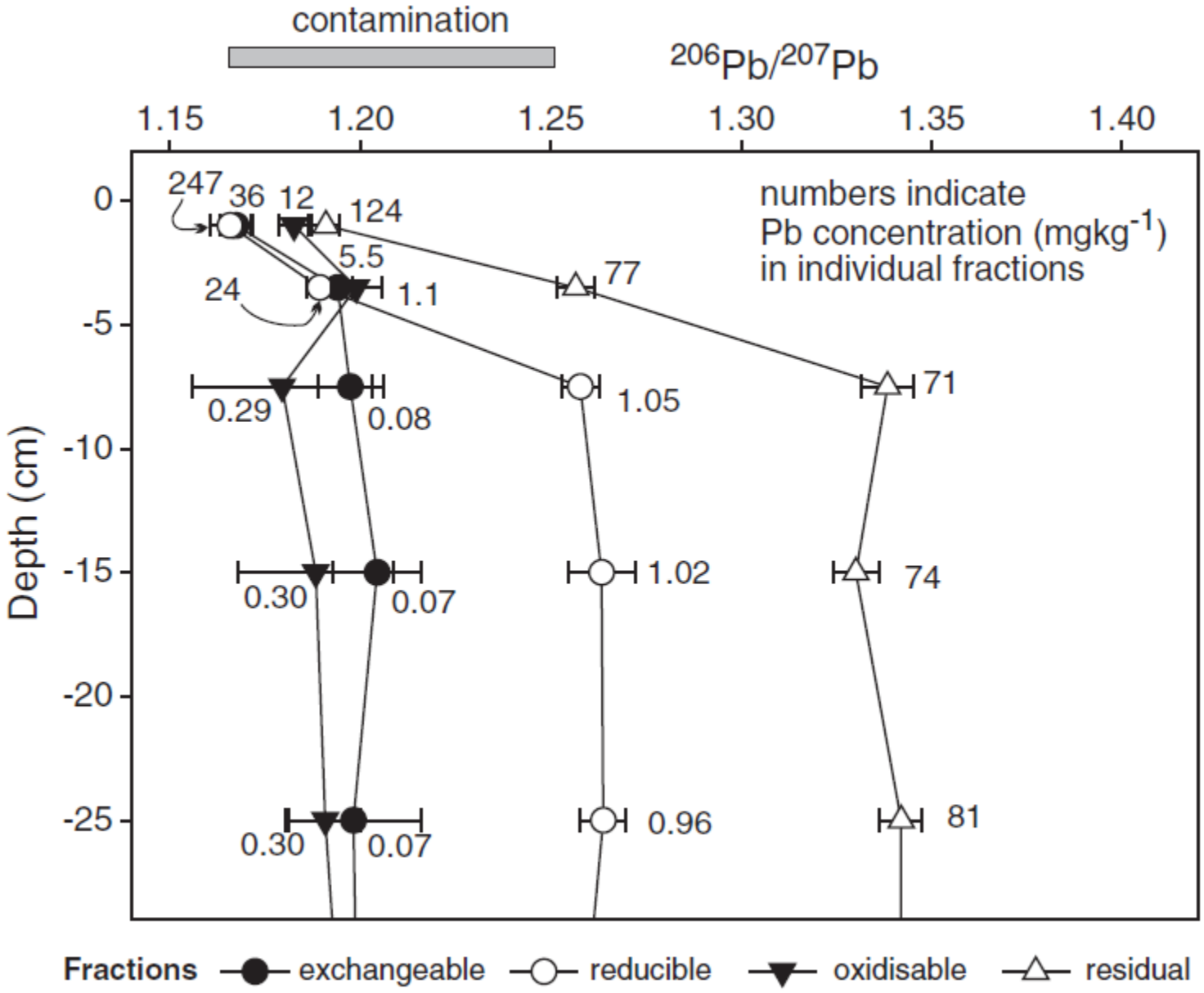




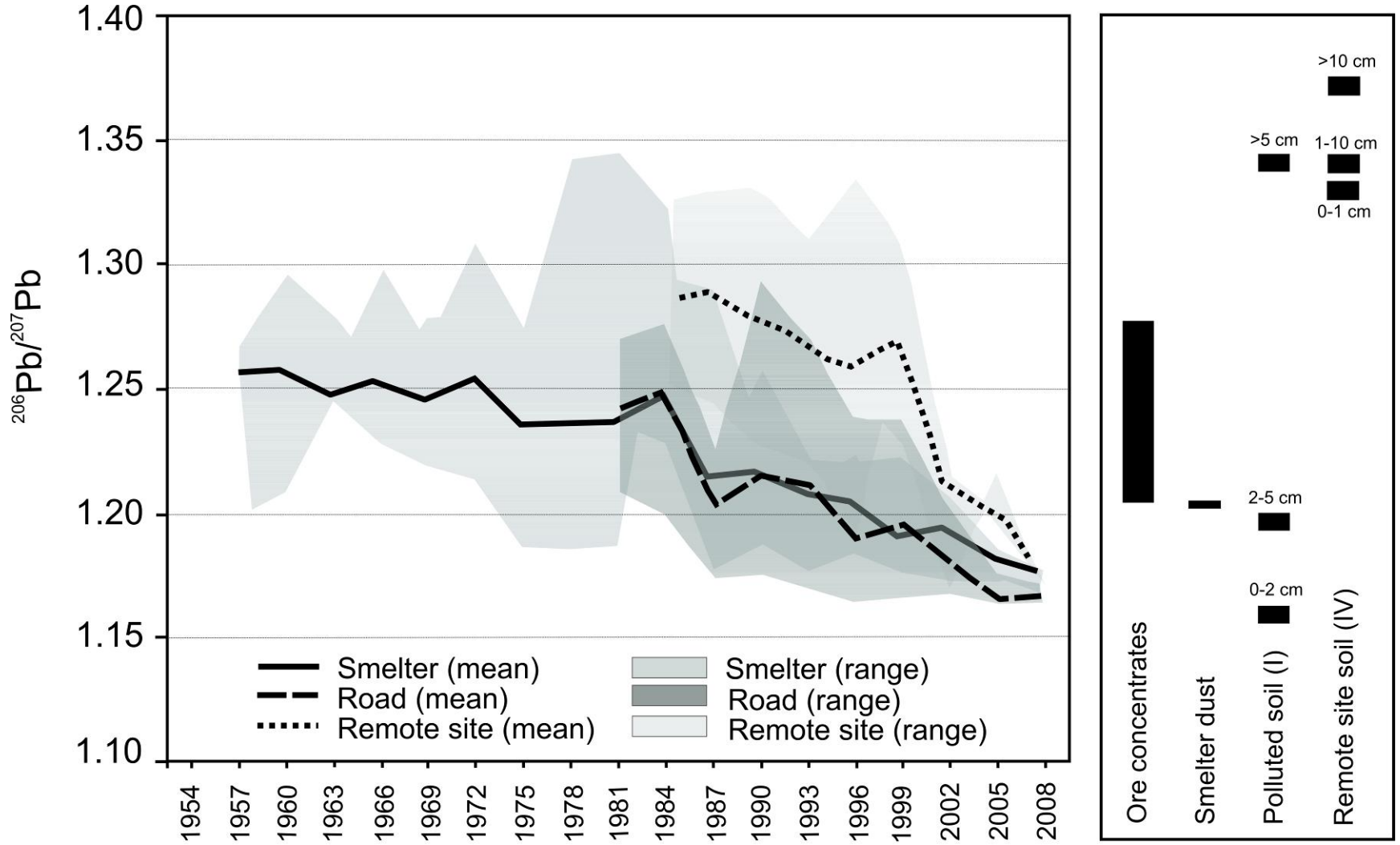

(a)
Co
smelter I
road II
road III
remote IV
Concentration (mg kg-1)
0.8
0.6
0.4
0.2
0.0
1950
1960
1970
1980
1990
2000
2010
(b)
Cu
40
30
20
10
0
(c)
Pb
1.0
0.8
0.6
0.4
0.2
0.0
Date
(d)
Mn
140
120
100
80
60
40
20
0
Date



Ettler et al. Geoderma 164



Ettler et al. Geoderma 164


1.40
1.35
1.30
1.25
1.20
1.15
1.10
$^{206}Pb/^{207}Pb$
1954
1957
1960
1963
1966
1969
1972
1975
1978
1981
1984
1987
1990
1993
1996
1999
2002
2005
2008
Smelter (mean)
Road (mean)
Remote site (mean)
Smelter (range)
Road (range)
Remote site (range)
>10 cm
>5 cm
1-10 cm
0-1 cm
2-5 cm
0-2 cm
Ore concentrates
Smelter dust
Polluted soil (I)
Remote site soil (IV)



Copper











Cu

essential micronutrients
(enzymes, proteins)
also pollutant

Stable 63Cu (69.17 %) and 65Cu (30.83 %)
(27 radioisotopes)

Analytical techniques

Shields et al 1964, 1964 first measurement of Cu isotopic ratio

First precise measurement of Cu Merechal et al (1999) Chem Geol

$$\delta^{65}\mathrm{Cu}(‰) = \left[\frac{\left(^{65}\mathrm{Cu}/^{63}\mathrm{Cu}\right)_{\mathrm{sample}}}{\left(^{65}\mathrm{Cu}/^{63}\mathrm{Cu}\right)_{\mathrm{NIST976}}} - 1 \right] \times 1000$$

Separation of Cu

- **basic anion exchange resin**

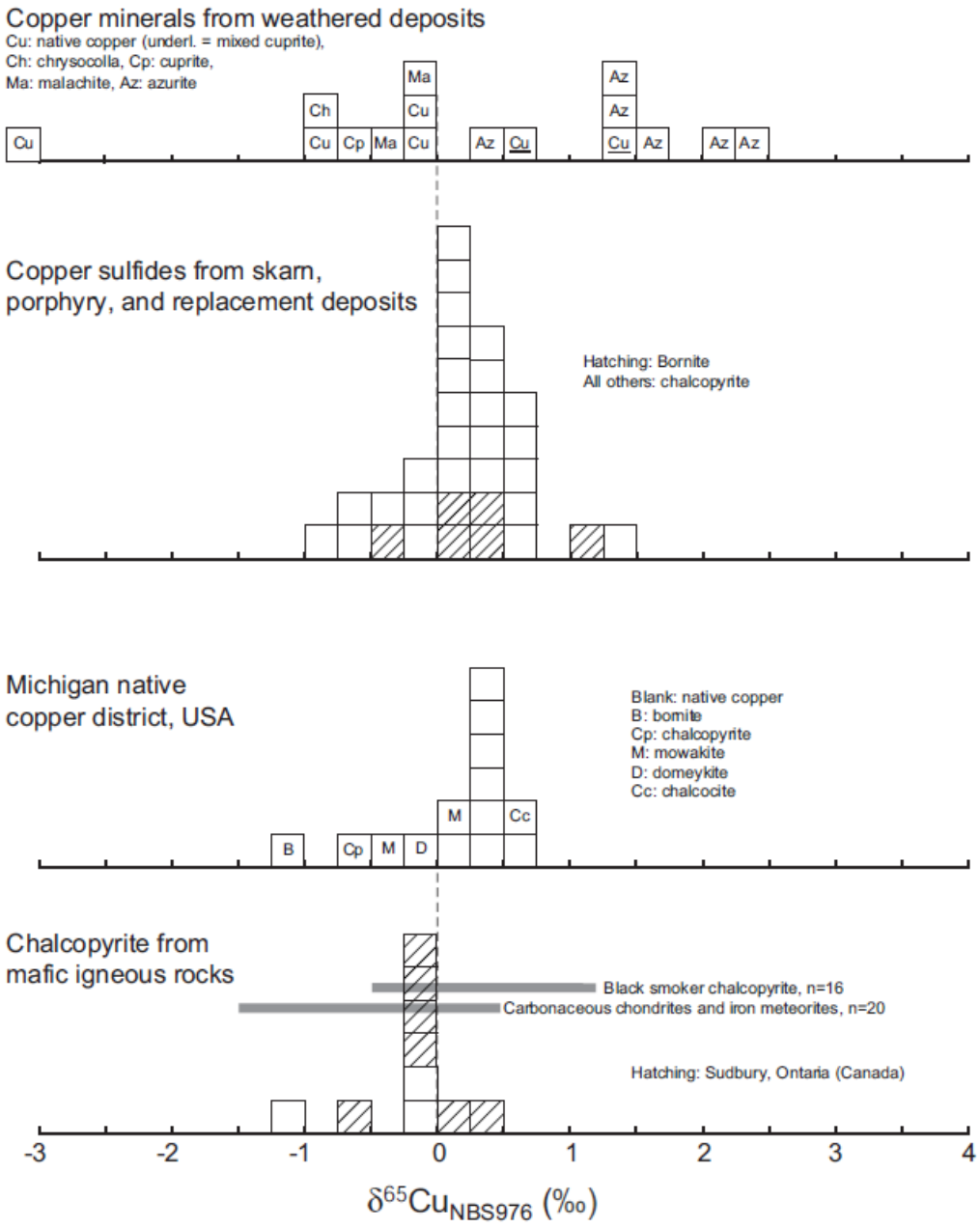
(BioRad, AG1-X) the separation of Cu from matrix in Cl forms

Measurement

MC ICP MS with magnetic sector analyser

Standard NIST 976

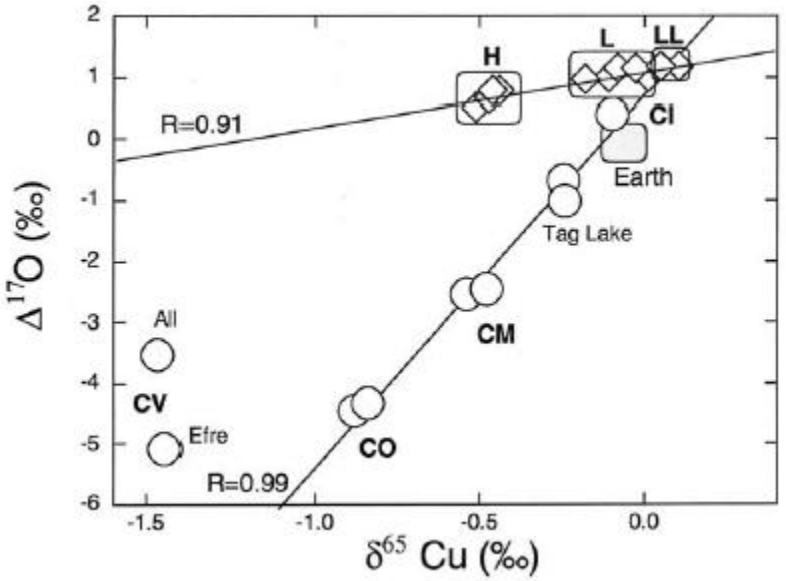
bracketing or interelement (62Ni, 60Ni) correction



Cu isotopic Composition of Cu minerals

Albarede (2004)

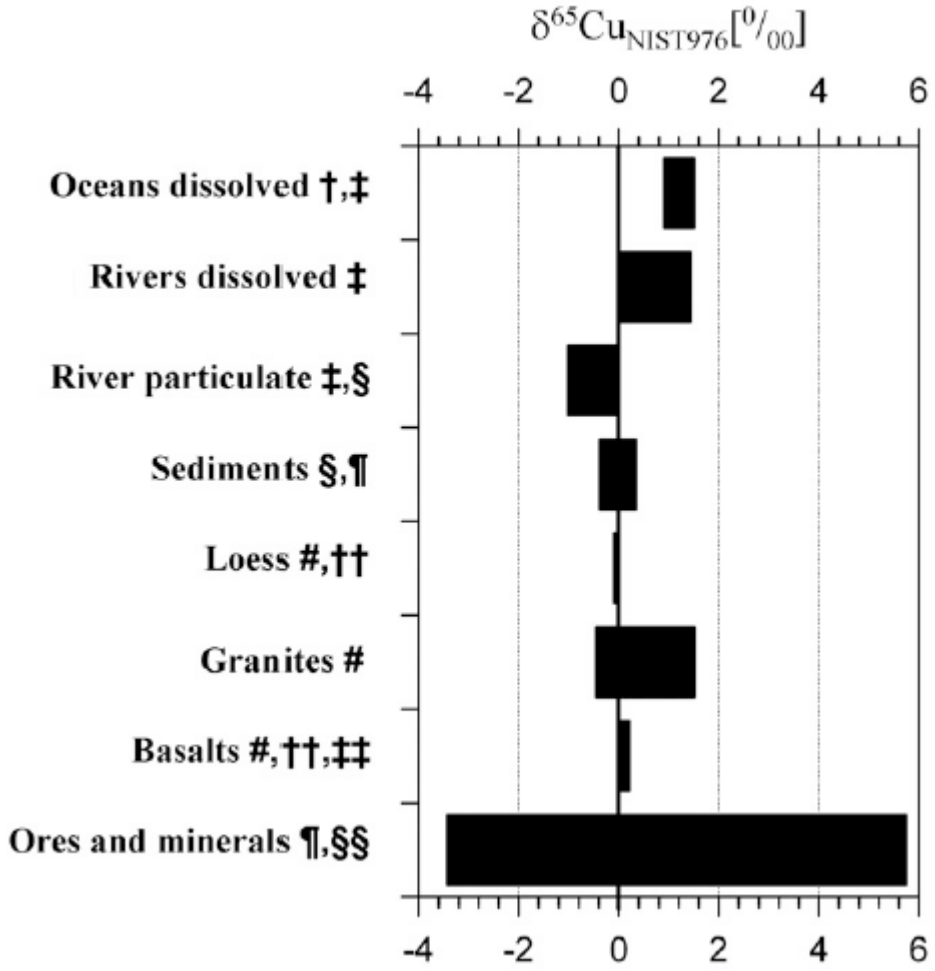
Meteorites – Luck et al (2004)
3 Cu reservoirs i) Earth like reservoir,
ii) Carbonaceous chondrites
iii) Mixture of i) and ii)



Luck et al GCA (2004)

Rocks
MORB, OIB – igneous processes are inefficient in Cu fractionation

Sediments
Deep sea clays 65Cu -0,9 to – 3 ‰ preferential reductive dissolution of light Isotope
Manganese nodulese preferential sorbtion of heavy 65Cu



The 65Cu of natural materials

Bigalke et al SSSAJ 2010

Adsorption on oxy(hydr)oxides, abiotic
Δ(oxy(hydr)oxide-solution) †,‡,§

Binding on bacteria surface
Δ(bacteria-solution) §,¶,#

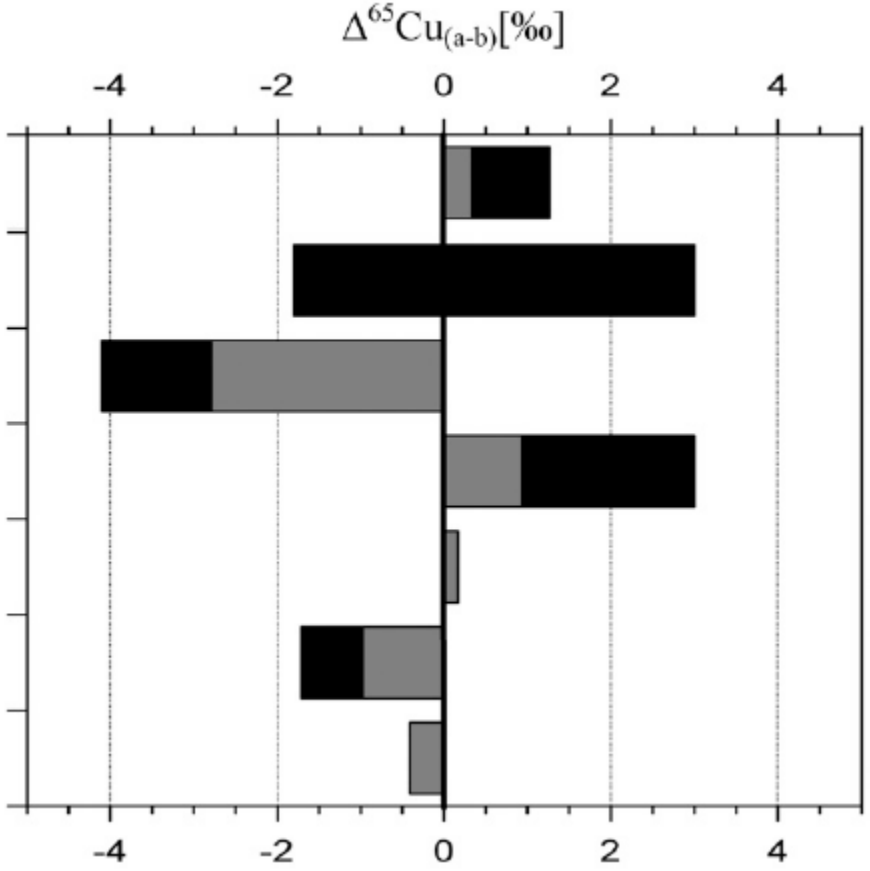
Copper reductive precipitation, abiotic
Δ(Cu(I)-Cu(II)) ††,‡‡

Copper oxidative leaching, abiotic
Δ(Cu(II)-Cu(I)) #,§§

Crystallization
Δ(crystall-solution) ¶¶

Incorporation into protein
Δ(protein-solution) ‡‡

Translocation in plants
Δ(shoots-roots) ##



Fractionation of Cu isotopes

Bigalke et al SSSAJ 2010

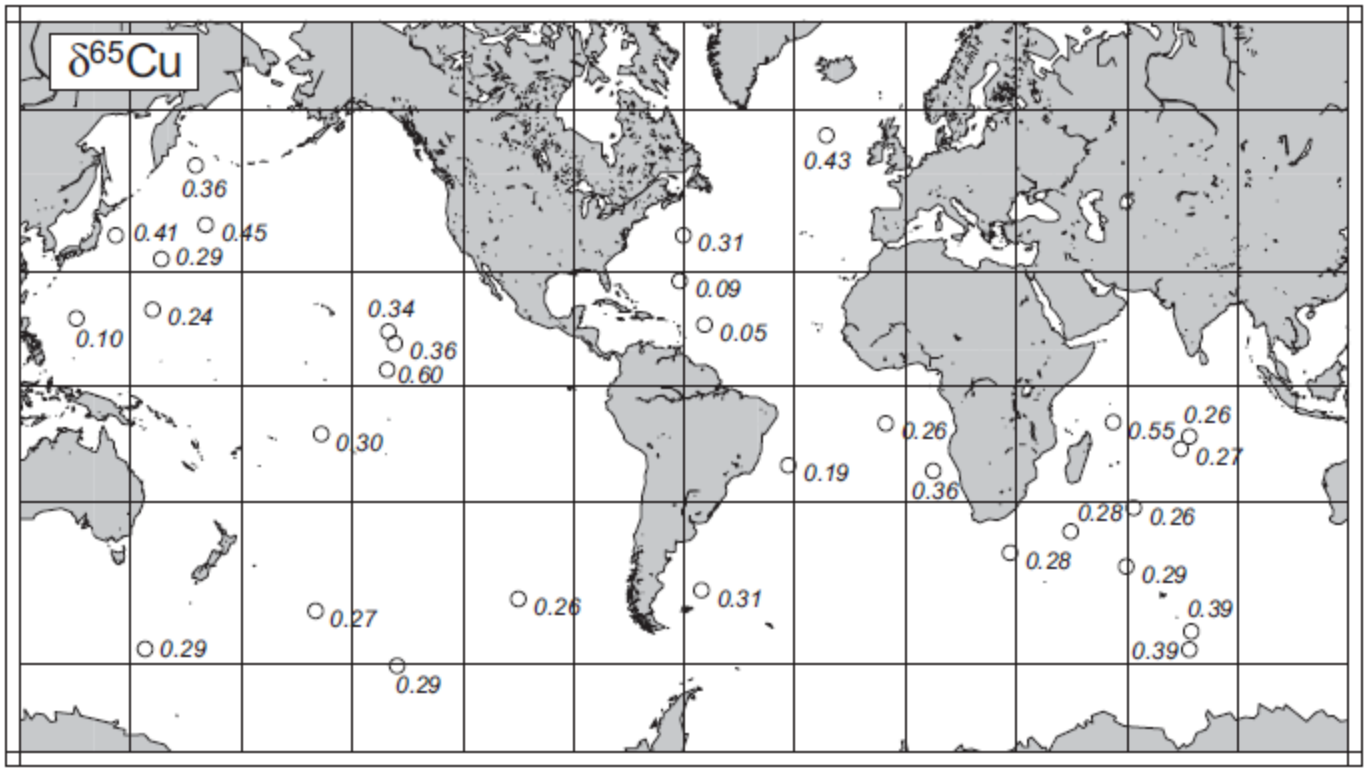
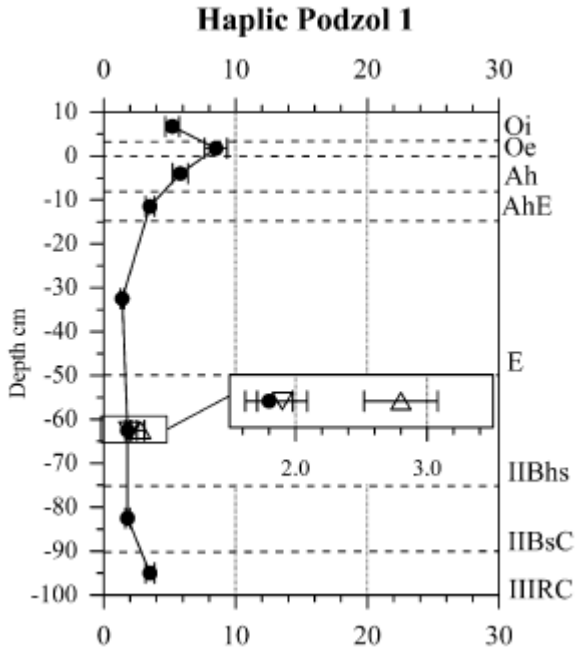
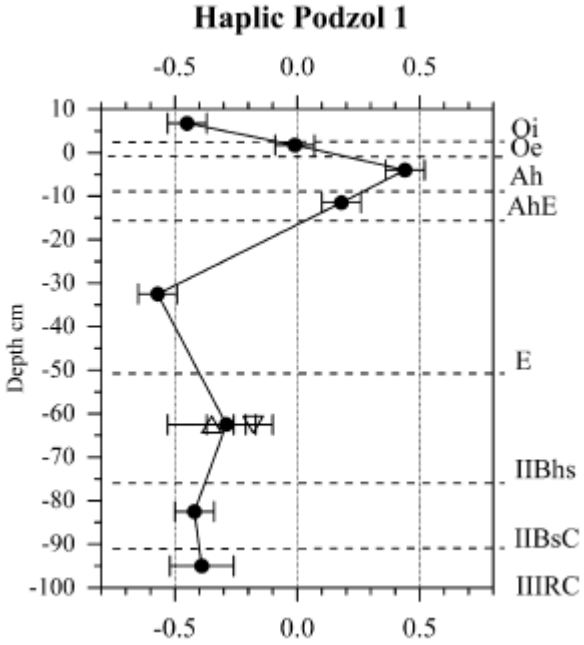


Figure 8. Map of δ^{65}Cu (‰) in the surface layer of FeMn-nodules (Albarède unpub. data). In contrast to Zn (Fig. 7), Cu in nodules is isotopically homogeneous.

Albarede (2004) Rev Geochem Min

Soils



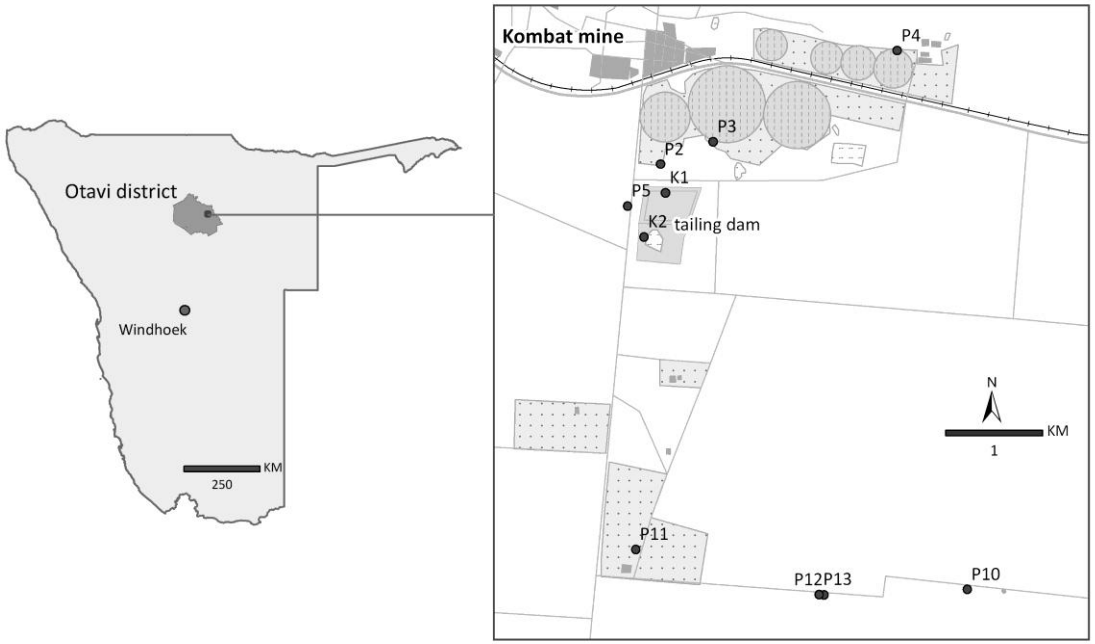


Cu mg/kg **65Cu**

Organic horizons are enriched in Cu, and 65Cu

Bigalke et al. GCA 2010

Pb and Cu isotopic study in Kombat





Kombat

Cu, Pb and Zn deposit
bornite chalcopyrite, galena, sphalerite, tennantite, pyrite and,
chalcotite, digenite, malachite, covellite, cuprite, native Cu and Ag

Closed in 2008, problems with flooding
Tailing dam 213 000m^2

Tailing material

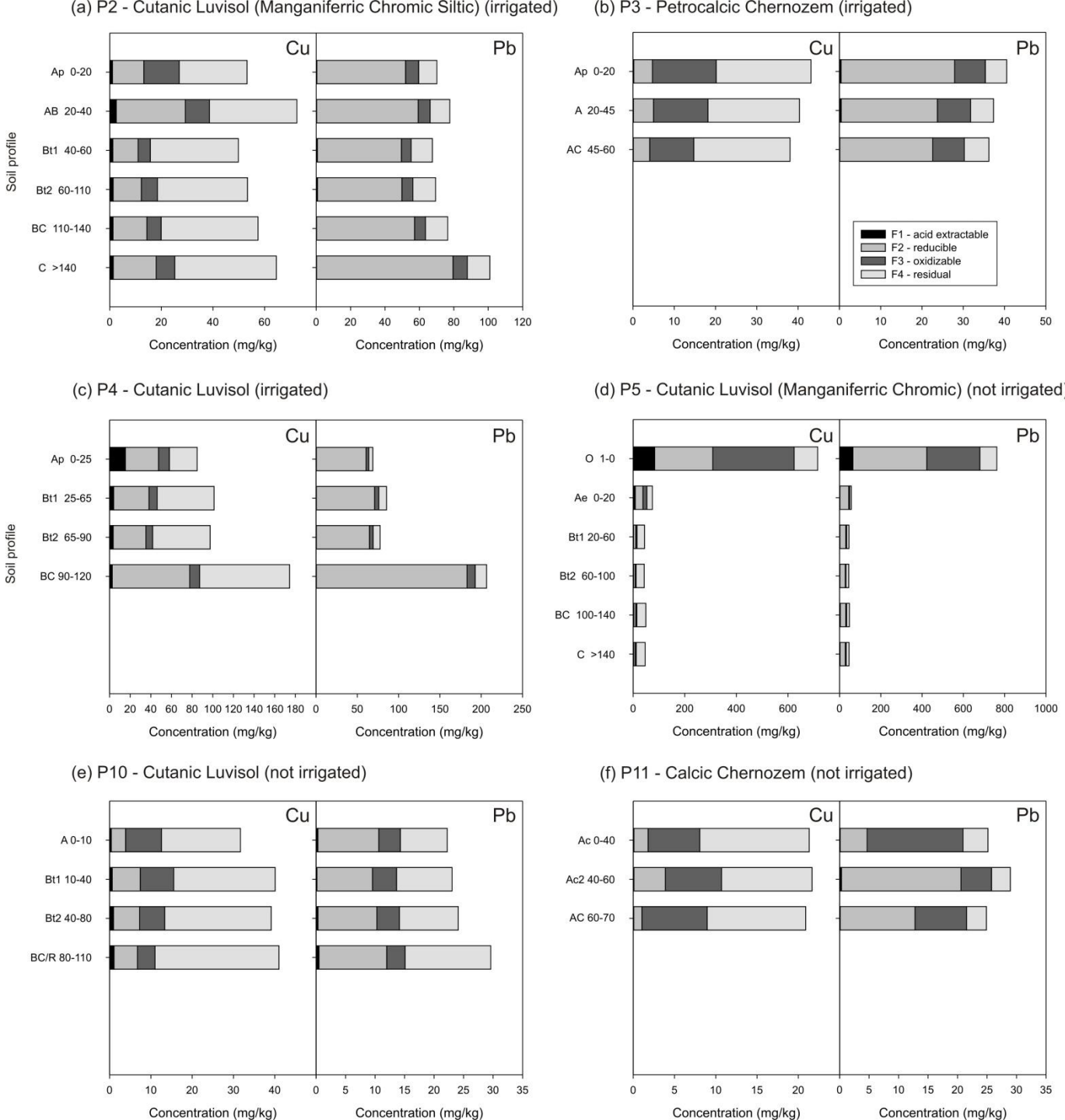
Sample	Depth (cm)	Fe tot (mg kg^{-1})	Mn tot (mg kg^{-1})	Cu (mg kg^{-1})	d65Cu (‰)	SD	Pb (mg kg^{-1})	$^{206}Pb/^{207}P$b	SD	$^{208}Pb/^{206}P$b	SD
K1 wet	0-20	4174	3811	1711,0	0,667	0,007	552,0	1,152601	0,002665	2,112931	0,007179
	40-60	4452	5335	2625,0	0,820	0,006	827,0	1,151611	0,003431	2,107413	0,005186
	160-180	13365	4038	4794	0,377	0,023	1904	1,151019	0,002969	2,10715	0,006333
K2 dry	0-20	7965	4349	1851	0,678	0,001	989	1,147687	0,003487	2,113504	0,008791
	40-60	5670	2810	1199	0,612	0,008	689	1,150223	0,003994	2,118687	0,006194
	160-180	4921	3664	2915	0,144	0,011	1120	1,14847	0,003902	2,11896	0,004147

Sample	Depth (cm)	TC (%)	TS (mg kg^{-1})	Mineralogy
K1 wet	0-20	9,37	<100	Fe-dolomite, calcite, quartz, apatite, malachite, hematite rutile, muscovite
	40-60	10,20	<100	Fe-dolomite, calcite, quartz, goethite, malachite, hematite, muscovite
	160-180	10,11	<100	goethite, apatite, malachite, Fe-dolomite, calcite, quartz, hematite, rutile, muscovite
K2 dry	0-20	10,32	200	Fe-dolomite, calcite, goethite, apatite, malachite, quartz, hematite, muscovite
	40-60	8,97	100	Fe-dolomite, apatite, calcite, goethite, quartz, rutile, malachite, hematite, muscovite, cerusite
	160-180	9,23	300	fe-dolomite, apatite, calcite, quartz, rutile, cerusite, goethite, malachite, hematite, muscovite,





Cutanic luvisol **Petrocalcic Chernozem**


(a) P2 - Cutanic Luvisol (Manganiferric Chromic Siltic) (irrigated)
(b) P3 - Petrocalcic Chernozem (irrigated)
(c) P4 - Cutanic Luvisol (irrigated)
(d) P5 - Cutanic Luvisol (Manganiferric Chromic) (not irrigated)
(e) P10 - Cutanic Luvisol (not irrigated)
(f) P11 - Calcic Chernozem (not irrigated)
Cu
Pb
Soil profile
Ap 0-20
AB 20-40
Bt1 40-60
Bt2 60-110
BC 110-140
C >140
A 20-45
AC 45-60
Ap 0-25
Bt1 25-65
Bt2 65-90
BC 90-120
O 1-0
Ae 0-20
Bt1 20-60
Bt2 60-100
BC 100-140
C >140
A 0-10
Bt1 10-40
Bt2 40-80
BC/R 80-110
Ac 0-40
Ac2 40-60
AC 60-70
F1 - acid extractable
F2 - reducible
F3 - oxidizable
F4 - residual
Concentration (mg/kg)

Cu and Pb speciation in tailing water
$CuCO_3aq$ (82 %), $Cu(OH)aq^+$ (6.5%), Cu^{2+} (5.5 %), $CuSO_4aq$ (3 %), $Cu(CO_3)_2^{2-}$, $Cu(OH)_2$ (0.6%), $CuHCO_3^+$ (0.4 %).
uncharged Cu complexes (85.7%)

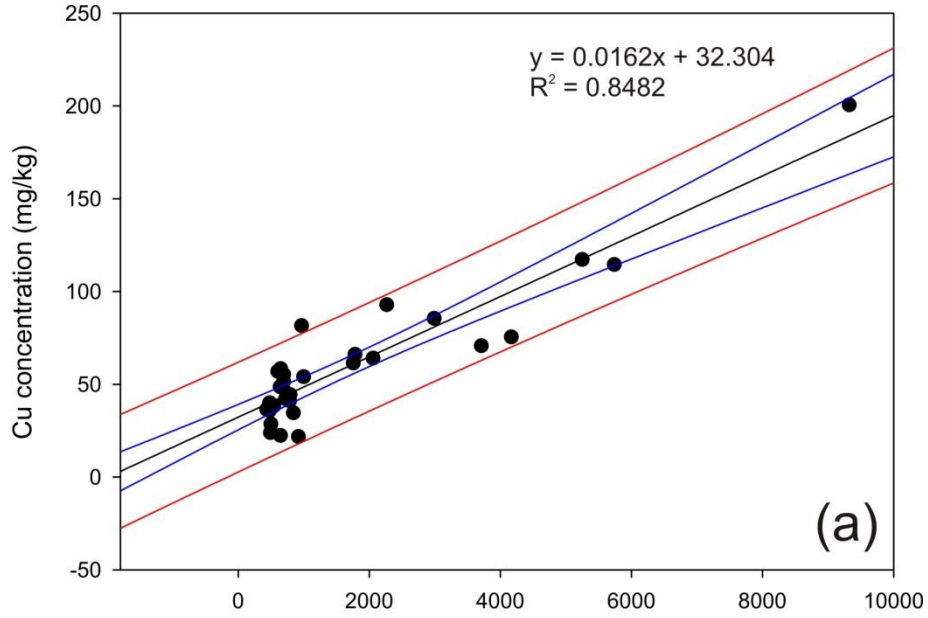
$PbCO_3$ (64.2 %), $PbSO_4$ (9.9 %), Pb^{2+} (8.374 %), $PbOH^+$ (8.1 %), $PbHCO_3^+$ (7.11), $Pb(SO4)_2^{2-}$ (0.5 %) and $Pb(OH)_2$ (0.12 %) uncharged complexes 75% of all forms of Pb

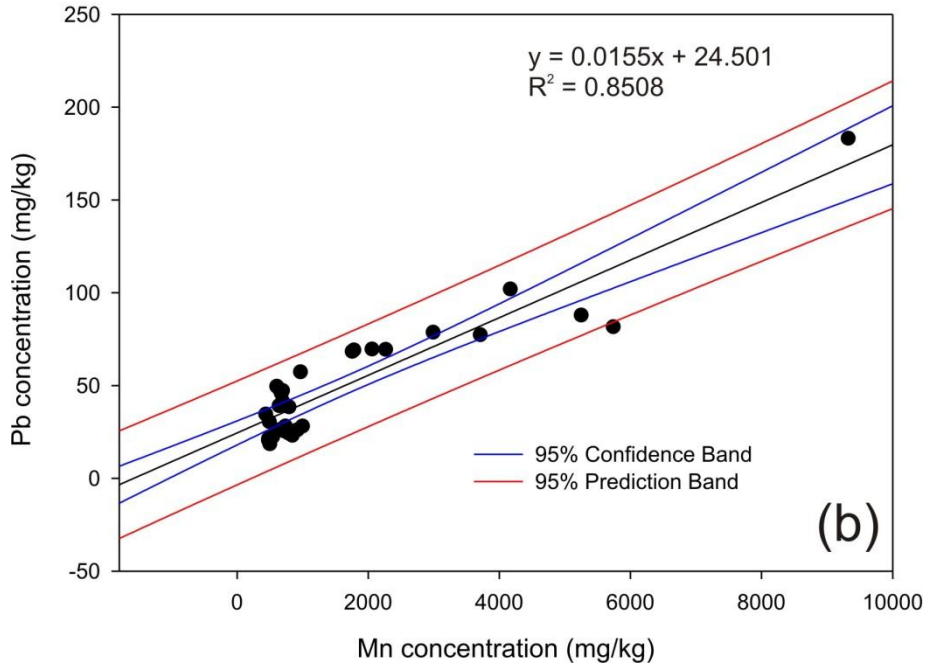
Leachate solution Lin STOTEN (1997)

Model equilibration with soil particles (quartz, kaolinite, illite and hematite)
no data for SOM or Mn oxides

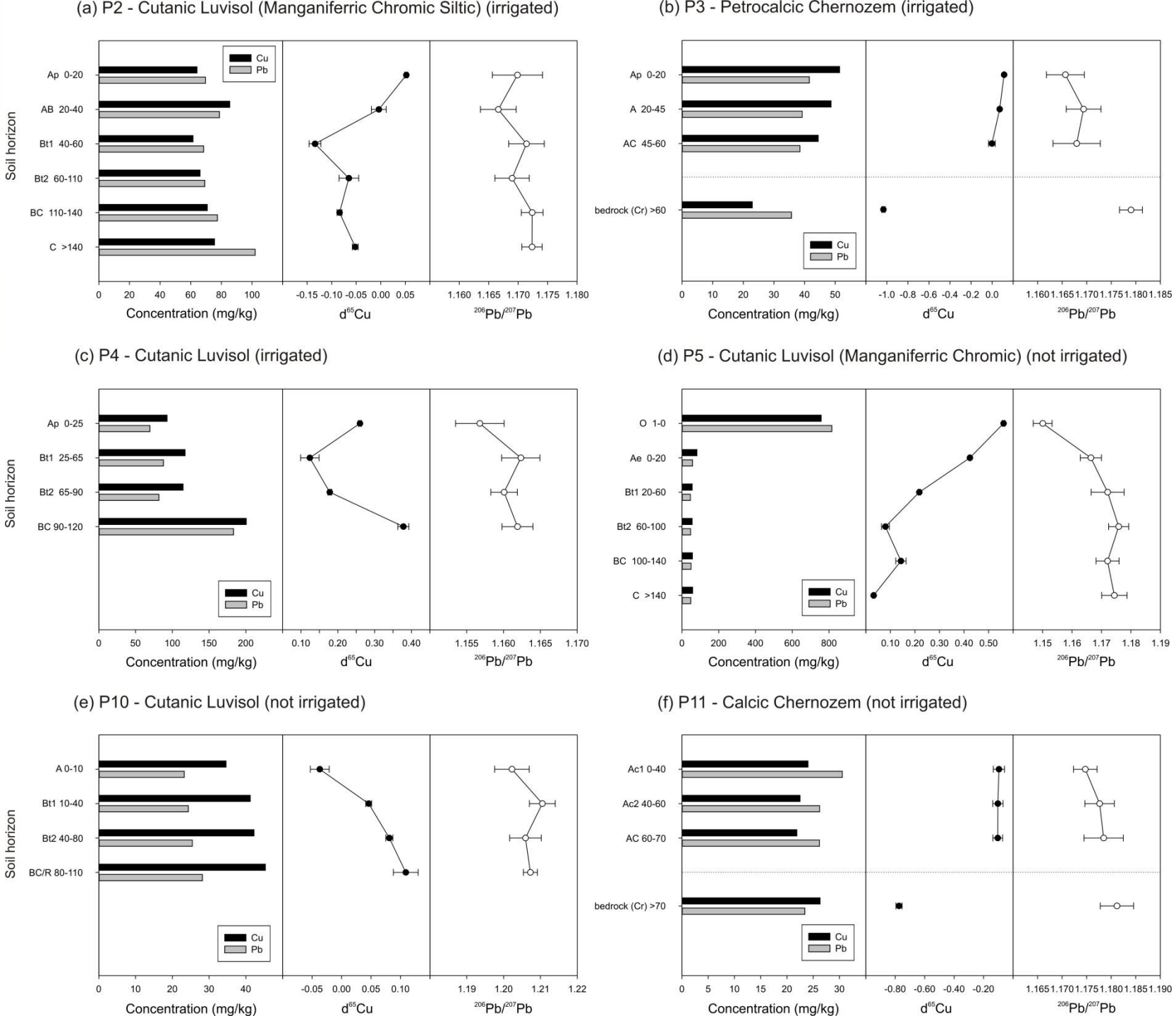
Cu in solution
< 3% Pb in solution

Soils contain birnesite and todorokite and 1,75-44 g/kg TC





Cu and Pb correlation with Mn contents in soils


(a) P2 - Cutanic Luvisol (Manganiferric Chromic Siltic) (irrigated)
(b) P3 - Petrocalcic Chernozem (irrigated)
(c) P4 - Cutanic Luvisol (irrigated)
(d) P5 - Cutanic Luvisol (Manganiferric Chromic) (not irrigated)
(e) P10 - Cutanic Luvisol (not irrigated)
(f) P11 - Calcic Chernozem (not irrigated)
Soil horizon
Concentration (mg/kg)
d65Cu
206Pb/207Pb
Cu
Pb
Ap 0-20
AB 20-40
Bt1 40-60
Bt2 60-110
BC 110-140
C >140
A 20-45
AC 45-60
bedrock (Cr) >60
Ap 0-25
Bt1 25-65
Bt2 65-90
BC 90-120
O 1-0
Ae 0-20
Bt1 20-60
Bt2 60-100
BC 100-140
C >140
A 0-10
Bt1 10-40
Bt2 40-80
BC/R 80-110
Ac1 0-40
Ac2 40-60
AC 60-70
bedrock (Cr) >70

- metals are more mobile in luvisols compared to chernozem
- Cu is more mobile than Pb
- basement rocks have negative ^{65}Cu values, the flotation waste of the tailing material has positive ^{65}Cu values
- the transformation of Cu to mobile forms $^{65}Cu \downarrow$
- bonding to Mn oxides in deeper parts $^{65}Cu \uparrow$
- plant activity $^{65}Cu \downarrow$

Conclusion I

- The higher accesibility of ICP MS has led to higher number of isotopic studies
- Pb isotopic composition were succesfully used in environmantal studies as a tracers
- Geochemical archives are powerful tool for studying polution history
- Decline of Pb deposition since sewenties

Conclusion II

- Determination of fractionation of non-traditonal isotopes (Cu) are dependent on very good resolution of MS

- Cu isotopic composition are succesfully used in environmantal studies.

- Cu iso can serve as tracer of source material
- Cu isotopes are successfully used for Identification of biogeochemical cycling

Acknowledgements

Colleagues
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Students
Funding GAČR, GAUK, Phare, Ministry of Education...

Thank you for your attention

4. SIMPLIFIED RISK ASSESSMENT

4.1 Simplified Risk Assessment for Safety

4.1.1 General Aspects

The Simplified Risk Assessment (SRA) for Safety in a SD/AMS enables the identification and assessment of Hazard Scenarios that could threaten the safety of individuals, the physical integrity of the environment or the pursuit of economic activities.

There are two groups of Hazard Scenarios related to safety:

- Hazards related to individuals accessing the site.
- Hazards due to the failures in deposits of large scale mining waste.

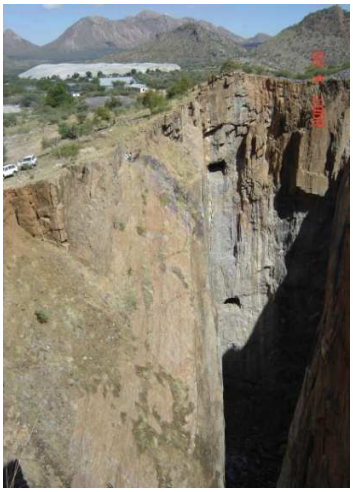


Plate 4.1: Hazard Scenario relating to an unprotected open pit (Oamites Mine)



Plate 4.2: Hazard Scenario relating to an unstable tailings dam slope with deep erosion gullies (Oamites Mine)

Each Hazard Scenario involves a risk, the magnitude of which depends on the Likelihood of Occurrence (Probability) and the Severity of Consequences.

For scenarios involving access to abandoned mine sites, ***Probability*** or **Likelihood of Occurrence** is based on the frequency of people entering the site and the dangers present therein (uncapped mine shafts, rock fall, presence of sharp objects, presence of hazardous/potentially toxic substances, etc.).

In the second group — Hazard Scenarios related to failures in waste deposits — the **Likelihood of Occurrence** is determined by assessing the stability of retaining walls or the potential for the sudden, massive release of tailings. This Handbook will address each of these to enable calculation of the Likelihood of Occurrence.

The second variable that determines the magnitude of risk is the ***Severity of Consequences.*** This will depend on the number of people affected and the seriousness of any injury or harm that could result from the Hazard Scenario. For environmental and economic receptors, it will depend on the number of hectares that could be affected, the number of individuals injured/killed, or the degree to which an economic activity is jeopardised.

To reiterate, the purpose of a SRA is to determine in a short period of time whether the risks present are significant or not. Only where there is uncertainty about this determination is a Detailed Risk Assessment (DRA) (see Chapter 5) called for, to ensure the site is correctly classified as a MEL or non-MEL. Otherwise, the simplified methodology is sufficient to fulfill the established objectives.

4.1.2 SRA Process for Safety Risks

The SRA for Safety is composed of four main steps (Figure 4-1).

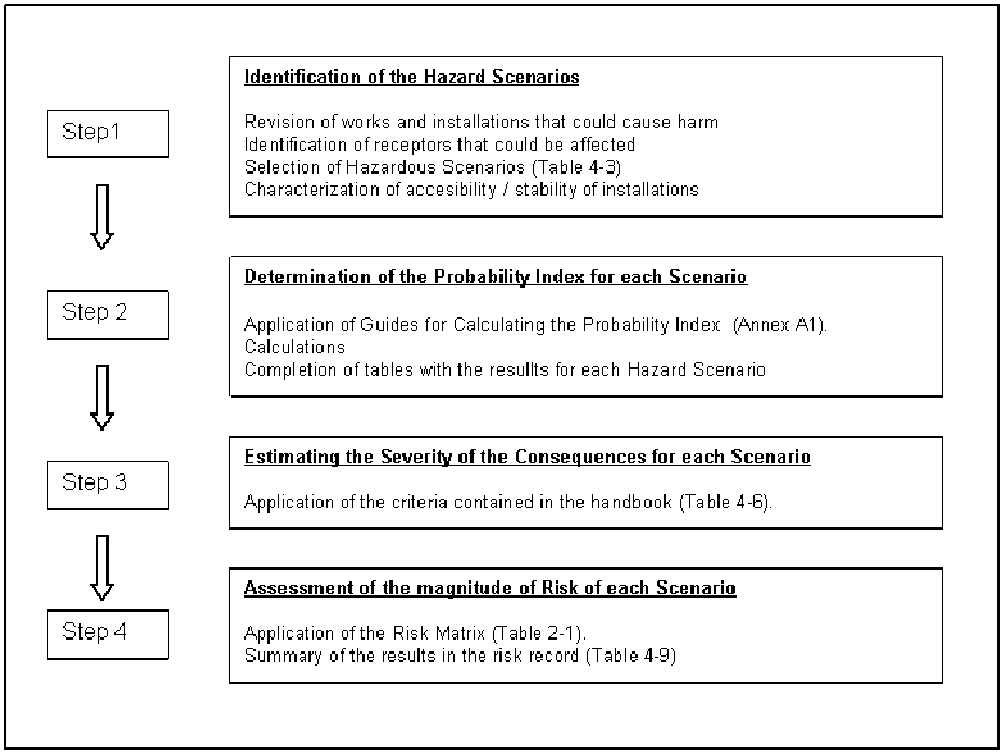
Step 1: identification of the **Hazard Scenarios** present at the SD/AMS. The Assessor must identify hazardous situations present at a SD/AMS that could cause harm, and identify possible receptors (people, environments and/or economic activities) that could be affected. Hazard Scenarios that may be present in the installations, deposits and/or works of a SD/AMS are enumerated in Table 4-3.

Step 2: Determination of the **Probability Index** for each Hazard Scenario. To determine this the Handbook offers “Guides for Calculating the Probability Index for Safety Risks” (Annex A1).

Step 3: Estimating the **Severity of the Consequences**, based on information collected in the field and available cartographic data. This information is obtained by applying the criteria established by experts in the field, which are set out in Table 4-6.

Step 4: Assessing the magnitude of risk, a process that is carried out using the **Risk Matrix**. The simplified assessment concludes with the summary of all results in a table, including risk magnitudes associated with each Hazard Scenario.

Figure 4-1: SRA process for Safety Risks



4.1.2.1 STEP 1: Identification of Hazard Scenarios

a. Logging installations, deposits and works

The Assessor's first task at this stage is to conduct a complete inspection of the site, confirming in person all installations, deposits and/or works. Each element identified will be assigned a unique identifying code and a description of the most important safety-related features and properties should be prepared. This information will be recorded in the Record Form (RARF), which can be found in Annex E of this Handbook. To save time on site, it is recommended that as much of this information as possible should be recorded from the MIDS and RABM prior to going to site. Once on site the pre-recorded inventory can be checked and augmented.

The identification code assigned to each element should consist of a letter and a number. The letter will represent an abbreviation identifying the component in question, as follows:

- Mine - M
- Plant - P
- Large Scale Mining Waste - LW
- Small Scale Industrial Waste - SW
- Associated Infrastructure - I



Plate 4.3: The first task is to conduct a site walkover and identify each installation, deposit or working

The number identifies specific installations, deposits and/or works at a given site. Therefore, the first element described for a certain kind of component (for example, a mine) will have the number '1', the second of these elements will be '2', and so on.

As an example, if three underground mine shafts are identified at the same abandoned mine site, these will be coded M1, M2, M3. In this case, the abbreviation 'M' indicates the 'Mine' on the site, while the numbers 1, 2 and 3 identify the individual shafts or open pits.

The description of each installation, deposit or work should include:

- its **name** (where applicable);
- **geographic coordinates** and altitude from a central point or point close to the unit;
- a **general description** of the safety status of the element and its parts;
- a **more precise description** of its physical dimensions, geographic location and, where applicable, composition of the waste present.

The **name** of each installation, deposit or work should be the same as the one it had when in operation. Such names shall only be recorded when they are known with certainty or when individuals living nearby can provide it. If uncertain, it is best that the Assessor gives a new descriptive name e.g. 'main pit', 'north waste rock dump' and clearly records these names on the base map.

The **geographic coordinates** need to be taken by GPS. The grid to be used shall be that established by the Department of Surveys and Mapping. The degree of error in this measurement must not exceed 15m. **Altitude** should be recorded using an altimeter or a properly calibrated GPS, or by consulting official topographic maps.

The **general description** consists of a summary text in which the Assessor will report the kind of installation, deposit or work in question. This description will at least explain clearly the purpose of the unit (product produced in the plant, process used, etc.), and should also indicate the main elements of the item (drainage system, retaining wall, etc.)

Finally, the information required to provide the **more precise description** of each element will vary, depending on the type of component identified. In general, this description will include basic dimensions and the most important features related to stability (slope, altitude, presence of major cracks, etc.). Table 4-1 provides general guidelines for building this description in each case.

Table 4-1: Characterization of site components.

Component	Characterization of Site Components
Mine	Underground mines: Location of entrance, depth, dimensions of entrance, other safety-related aspects, etc. Open pits: Dimensions of pit, bench heights, condition of side walls and haul roads, rehabilitation and backfill, and other safety-related aspects, etc. (Plates 4.1 and 4.3)
Plants	Type of plant, area, main components, safety-related aspects, etc.
Large scale mining waste	Type of waste stored, dimensions of deposit, method of disposal, features of the deposit, degree of erosion, safety-related aspects, etc. (Plate 4.2)
Small scale industrial waste	Type of waste stored, dimensions, method of containment, features of the deposit, safety-related aspects, etc.
Associated infrastructure	Type of mine work or installation, dimensions, safety-related aspects, third party usage, etc.

=> The RARF (Cover Page 2) (Annex E) should contain all information required to characterize each installation, deposit and/or work identified in the abandoned mine site. This information should be collected in the field in written form and backed up by photographs.

By way of example, the table below offers information on how to identify and describe the safety risks of a SD/AMS following Handbook guidelines (Table 4-2). The 'site' used in this example, is the Abenab abandoned mine site. The description of each unit is based on field observations made by a

risk assessment team during the pilot phase of the development of this manual (see section 1.1). The completed sheets are included in Annex E.

Table 4-2: Sample information identifying and describing the installations, deposits and works of a SD/AMS.

Component	Type of installation, deposit or works	Name	Facility code	General description	Description of safety risk factors	Co-ord south	Co-ord east	Elev
Mine	Open pit mine	Breccia pipe	OP1	Roughly circular pit approx 120m in diameter. Almost vertical walls covered in vegetation; some benches still apparent. Filled with water at a depth of 80-100m	Fenced off, but still several access points and steps leading down to last bench above water	-19.283	18.083	
Plant	Process plant	Concen-trator plant	P1	Large number of dilapidated buildings from top of slope to foot of hill. Unsafe structures, high walls, open tanks, pits and sumps	Open access to all areas. Plant area includes: concentrator area, analytical lab, workshops, storage areas etc			
Large-scale mine wastes	Tailings dumps (dry)	Tailings dump	LW2	Two main areas of tailings disposal: approx 500m to NW; and slurried out from the plant on top of waste rock, covering an area of about 18ha	Highly eroded and widely dispersed. Good growth of vegetation over parts, especially on NW dump			
Infra-structure	Water reservoirs and pipelines	Plant area	I1	Concrete water tank 20mx6mx4m deep divided into two. Vertical sides; no escape route; contains water of 1-2m depth	Dead bird and fish visible. Many small live fish visible. Water green in colour with abundant algae; no apparent use			

b. Identification of Hazard Scenarios

Once the components of the SD/AMS being assessed are identified and characterized, the Hazard Scenarios (HS) related to safety risks for each of the elements listed in the table above should be identified. Table 4-3 lists the HS related to safety that could be present in the installations, deposits and/or works of a SD/AMS. The Assessor can use the table as a checklist to gather the information necessary.

Table 4-3: Safety-related Hazard Scenarios

Component	Installations Deposits Works	Code	Safety Hazard Scenarios	Cause	PI Estimation Guide
MINE	Underground workings	SHS 1	Development of major cracks, dolines or sink holes that could affect people, the environment or economic activities.	Seismic movements, underground mine structural instability, or water entry.	GUIDE 1
		SHS 3	Asphyxiation of people entering the mine due to the presence of toxic gases.	Open access to abandoned mine.	GUIDE 7
		SHS 4	Drowning in underground pools.	Open access to abandoned mine.	GUIDE 7
		SHS 12	Falling into underground workings (people, stock, game animals).	Open access to abandoned mine.	GUIDE 7
		SHS 13	Rocks, unsafe remnant structures or elements falling on people.	Open access to abandoned mine.	GUIDE 7
	Open pits, trenches and other surface workings	SHS 2	Collapse of the pit or surface works that could affect people, the environment and/or economic activities.	Seismic movements, water erosion, or surface faults.	GUIDE 2
		SHS 4	Drowning in pool at bottom of pit.	Open access to abandoned mine.	GUIDE 7
		SHS 12	Falling into open pit or trench (people, stock, game animals).	Open access to abandoned mine.	GUIDE 7
PLANTS	Processing Plants	SHS 4	Drowning in tanks and ponds.	Open access to abandoned plant site.	GUIDE 7
		SHS 12	Risk of falling from elevated unsafe structures.	Open access to abandoned plant buildings.	GUIDE 7
		SHS 13	Rocks, unsafe remnant structures or other elements falling on people.	Open access to abandoned plant buildings.	GUIDE 7

Component	Installations Deposits Works	Code	Safety Hazard Scenarios	Cause	PI Estimation Guide
LARGE SCALE MINING WASTE	Tailings Dams	SHS 5	Dam failure that could cause a sudden release of tailings slurry that could affect people, the environment and/or economic activities.	Poor construction, seismic movements, rise in water table, overflow of dam, erosion of side walls.	GUIDE 3
		SHS 12	Risk of falling into tailings pond or from dam walls.	Open access to abandoned tailings dam.	GUIDE 7
		SHS 4	Drowning in tailings pond.	Open access to abandoned tailings dam.	GUIDE 7
	Tailings deposits dry-stacked or in other form	SHS 7	Failure of slopes of dry stacked or other tailings deposit that could affect people, the environment and/or economic activities.	Seismic movements, water erosion, poor construction, undermining of toe	GUIDE 5
		SHS 12	Risk of falling down steep slopes.	Open access to tailings impoundment.	GUIDE 7
	Heap leach waste dump	SHS 8	Failure of heap leach waste dumps that could affect people, the environment and/or economic activities.	Seismic movements, water erosion, poor construction.	GUIDE 5
		SHS 12	Risk of falling down steep slopes.	Open access to abandoned heap leach facility.	GUIDE 7
	Dumps for waste rock, low grade ore	SHS 9	Failure of slopes of dumps containing waste rock or low grade ore that could impact people, the environment or economic activities.	Seismic movements, water erosion, undermining of toe	GUIDE 6

Component	Installations Deposits Works	Code	Safety Hazard Scenarios	Cause	PI Estimation Guide
LARGE SCALE MINING WASTE	Dumps for waste rock, low grade ore	SHS 12	Risk of falling down steep slopes.	Open access to abandoned mine site.	GUIDE 7
	Slag heap	SHS 12	Risk of falling down steep slopes.	Open access to abandoned mine site.	GUIDE 7
SMALL SCALE INDUSTRIAL WASTE	Industrial waste deposits	SHS 14	Physical contact with unsafe remnant structures or other elements that may cause injury or damage.	Open access to abandoned mine site.	GUIDE 7
ASSOCIATED INFRASTRUCTURE	Explosives magazine	SHS 10	Incorrect and/or unprotected storage of explosives which could result in an explosion causing injury.	Open access to explosives magazine.	GUIDE 7
	Offices, camps, workshops and storage areas	SHS 12	Risk of falling in unsafe areas.	Open access to abandoned mine site.	GUIDE 7
		SHS 13	Falling of unsafe remnant structures or other elements onto people.	Open access to abandoned mine site.	GUIDE 7
		SHS 14	Physical contact with unsafe remnant structures or other elements that may cause injury or damage.	Open access to abandoned mine site.	GUIDE 7
	Water systems and tanks	SHS 4	Drowning in tanks.	Open access to abandoned mine site.	GUIDE 7

Component	Installations Deposits Works	Code	Safety Hazard Scenarios	Cause	PI Estimation Guide
ASSOCIATED INFRASTRUCTURE	Water systems and tanks	SHS 12	Risk of falling from elevated unsafe structures.	Open access to abandoned mine site.	GUIDE 7
		SHS 13	Falling of unsafe remnant structures and other elements onto people.	Open access to abandoned mine site.	GUIDE 7
	Power lines and substations	SHS 12	Risk of falling from elevated, unsafe structures.	Open access to abandoned mine site.	GUIDE 7
		SHS 14	Physical contact with high voltage cables and other electrical installations that may cause injury or electrocution.	Open access to abandoned mine site.	GUIDE 7
	Roads and bridges	SHS 11	Vehicle accidents due to roads and/or infrastructure (e.g. bridges) in poor condition.	Open access to abandoned mine site.	GUIDE 7
		SHS 12	Risk of falling from elevated unsafe structures.	Open access to abandoned mine site.	GUIDE 7

Note: there is no Guide 4 in the Namibian version of the Manual as this addresses Safety Hazard Scenario 6, which does not exist in the Namibia situation.

As observed in Table 4-3, a single component of a site may often present various Hazard Scenarios. For example, a quarry has the potential to harm people, the environment or economic activities due to rockslides, and could also cause major accidents from rocks falling on people, or people falling from heights. As a result, the same mine presents different Hazard Scenarios, the first associated with rockslide, the second from rock fall and the third from people falling from elevation.

The following pages offer a description of these Safety Hazard Scenarios so users of this Handbook have standard criteria for identifying them.

c. Description of Safety Hazard Scenarios (SHS)

SHS 1: Subsidence that could provoke major cracks, dolines or sink holes that could affect people, the environment and/or economic activities on the surface.

Underground extraction of mineral ore usually requires the excavation of large volumes of material. Once the mine ceases operation, these empty spaces could provoke settling of the mine, leading to subsidence in the form of cracks, dolines or sink holes on the surface. This could generate impacts on productive land, changes in water drainage patterns, or risks to human safety or building integrity.

BOX 2

Ministry says Klein Aub community should not be worried about collapsed section of ground
– by Rhyn Tjituka
NBC News Report Published: February 3rd, 2010

The Ministry of Mines and Energy says the Klein Aub community should not be worried about a section of the ground that collapsed, opening a hole of seven meter diameter above an old copper mining tunnel at the settlement recently.
The Ministry's Inspector of Mines, Samson Nghiteeka says the collapse took place inside an area that was already declared risky years ago.
This hole at the settlement of Klein Aub opened on Friday, the 22nd of January following a night of heavy rains.
Ministry of Mines and Energy officials arrived here and inspected the site with the help of a map showing old mining activities.
They found that the collapse was in an area the former mining company found risky and fenced off. In that area, mining came to about 25 to 30 meters below the surface according to the Mines and Energy Ministry's report. Mines Inspector Samson Nghiteeka says there should not be any fear.
The team of inspectors erected this sign to warn the community to stay away from the fenced off area. Only this portion of land in Klein Aub poses a danger of collapsing but infrastructure everywhere else is on solid ground above the tunnels that are up to 300 meters deep from the surface.
The Ministry says the humidity from water in the tunnels and the saturation of the surface from heavy rains may have caused the collapse of the portion of land.
The Ministry of Mines and Energy's findings suggest that the seven meter diameter hole in the ground will not pull Klein Aub with it.

SHS 2: Collapse of the open pit or surface works that could affect people, the environment and/or economic activities.

Open pit mines could present risks associated with the collapse of its walls. The loss of stability between benches often occurs and is not usually a major problem; however, if the slope of the pit walls is pronounced and the entire pit collapses, adjoining lands could be affected.



Plate 4.4: Overhanging loose rocks in the pit wall at Kombat

SHS 3: Asphyxiation of people entering the mine.

Entry of people into abandoned mines without proper personal protection can cause serious injury and even death from oxygen deprivation and/or toxic gases.

SHS 4: Drowning.

Open pit mines and structures such as lined ponds and tanks can sometimes accumulate water from rain or water table seepage, making abandoned mines attractive for swimming. If the installation does not have suitable safety measures in place for such uses, bathers may drown. Children are at special risk for drowning, especially when not supervised by an adult. Water also frequently accumulates in the shafts and galleries of abandoned underground mines, resulting in a risk of drowning after a fall.



Plate 4.5: Water collecting at the base of this tank at Abenab poses a potential drowning hazard as there are no escape routes and the area is not fenced off

SHS 5: Dam failure that could cause a sudden release of tailings slurry that could affect people, the environment and/or economic activities.

This Hazard Scenario could include a dam failure where massive volumes of tailings slurry from the dam could impact different receptors. In Namibia, this could be caused by a 1:100 year storm event, long-term erosion of the tailings dam walls, or poor original construction.

Note: SHS5 and SHS6 in the original manual for Chile differentiated between tailings deposited in a pond (SHS5) and a reservoir (SHS6). There is no distinction between these two types of tailings disposal in Namibia and therefore SHS6 has been omitted.



Plate 4.6: The results of the failure of the tailings dam at the Namib lead Mine

SHS 7: Failure of dry stacked tailings slopes that could affect people, the environment and/or economic activities.

At some mines, tailings are dewatered prior to disposal on the tailings dump where they are dry stacked in a single dump, or co-disposed with waste rock and contain massive volumes of material. Depending on the procedure used, the slopes of these deposits can be very high, with a steep angle of repose, and unstable. If such a slope failed its material would slide, covering surrounding lands and negatively impacting receptors in the Area of Study. This type of failure could be caused by water erosion or by people excavating material from the toe of the dump, thus undermining the slope.

SHS 8: Failure of heap leach waste dumps that could impact people, the environment and/or economic activities.

This scenario addresses an event similar to that described in SHS 7, for large scale mining waste composed of waste from leach heaps.

SHS 9: Failure of slopes of dumps containing waste rock or low grade ore that could impact people, the environment and/or economic activities.

Covers events similar to that described in SHS 7 for mining waste composed of waste rock or low grade ore.

SHS 10: Explosion causing injury.

This point addresses the potential scenario in which the abandoned or shut down mine site contains explosives in poor condition or which are stored in unlocked areas. An explosion could result if a visitor handles such material improperly or ignores basic safety measures by lighting a fire, for example.

SHS 11: Vehicle accidents due to roads and/or infrastructure (e.g. bridges) in poor condition.

Access roads or tracks to SD/AMS usually have not been closed properly and have not been maintained since the mine ceased operations. Vehicles using these roads risk accidents due to a number of causes, including lack of road signs, rocks on the road, large potholes, a road that has become too narrow from erosion, low visibility from suspended dust during transit, etc. In other cases, bridges may have been washed away or are impassable to vehicles.

SHS 12: Risk of falling from elevated, unsafe structures

A SD/AMS may have uncapped mine workings or other uncovered or unprotected elements such as shafts, chimneys, pits, pools, deposits, ladders, walkways, walls in poor condition and/or other elements that visitors could fall into or fall from. This scenario covers falls from heights greater than 1.5 m.



Plate 4.7: Unsafe structures at the old Abenab Mine

SHS 13: Rock fall, falling of unsafe remnant structures and other elements.

Anyone can enter an abandoned underground mine if the access points have not been capped. The deterioration of underground installations and supporting structures over time can provoke rockslides inside that could affect people entering the mine. Surface mines can also experience rockslides on their pit walls.



Plate 4.8: This unsealed entrance to underground mine workings at Thorntree Mine represents a Safety Hazard Scenario

Remnants of processing plants or infrastructure at a SD/AMS can also present a safety risk to those visiting the site due to the deterioration and/or instability of components or structures that could fall or collapse unexpectedly, injuring persons nearby.

SHS 14: Physical contact with unsafe remnant structures, waste and any other elements which may cause injury or damage.

Old mine sites might contain dangerous elements such as broken glass, scrap metal, spikes, etc., which could cause injuries (Plates 4.7 and 4.8). Old sites may also contain abandoned electricity supply infrastructure such as high voltage cables, live wires, switch boxes, transmission towers and substations which represent a risk of electrocution to those who come into contact with them.

d. Record of Safety Hazard Scenario identification (on the Risk Assessment Record Form, RARF)

Hazard Scenarios identified in the SD/AMS are recorded on the RARF (*SHS Step 1*) (Annex E). Filling out this form includes:

- Selecting the SHS present on site from the list of options.
- Selecting the standard code representing each SHS.
- Selecting the standard definition corresponding to each SHS.
- Linking the code of the installation, deposit or work with the standard SHS code.

- Describing the Safety Hazard Scenario with explicit reference to receptors that could be affected and how the negative effect may occur.

  => *On the RARF (Form SHS Step 1 in Annex E) the Assessor will record each of the Hazard Scenarios identified, assign the corresponding code to each and provide a brief description of receptors and how the hazard could come about.*

For example, for an abandoned quarry, the identification code of the mine component will be 'M1'. If a 'risk of falling' hazard is identified, the respective scenario would have the standard code 'SHS12', meaning that the Hazard Scenario code for that risk would be 'M1-SHS12'. If there are three similar shafts in the same site with the same Hazard Scenario due to 'risk of falling', these will be identified as follows 'M2-SHS12', 'M3-SHS12', and 'M4-SHS12', respectively. As an example, Table 4-4 presents a sample record of Safety Hazard Scenarios for Abenab Mine (see Annex E for completed Data Sheet). Note the description of each scenario, which refers to potential receptors.

Table 4-4: Sample Record of Safety Hazard Scenarios

Name	Code	SHS standard code	SHS description (according to handbook)	SHS site code	SHS description
Breccia pipe	**OP1**	**SHS 12**	**Risk of falling from elevated unsafe structures or heights.**	**OP1-SHS12**	**Although the open pit is fenced, there are gaps in the fence and access is unrestricted. Very high vertical pit walls**
Concentrator plant	**P1**	**SHS 13**	**Falling of unsafe remnant structures and other elements onto people.**	**P1-SHS13**	**Dilapidated buildings with loose bricks, unsafe roof trusses**
Tailings dump	**LW2**	**SHS 12**	**Risk of falling from elevated unsafe structures or heights.**	**LW2-SHS12**	**Deep gullies in eroded tailings which were slurried onto waste rock dumps; evidence of frequent access**
Plant area	**I1**	**SHS 4**	**Drowning in pools, ponds, tanks.**	**I1-SHS4**	**Concrete water tank 20mx6mx4m deep divided into two. Vertical sides; no escape route; contains water of 1-2m depth**

The Assessor may identify one or more SHS that are not contained in Table 4-3, in which case he or she should add these to the RARF. The description of any new Hazard Scenario should include the following:

(1) Indicate the *Negative effect* that could occur.
(2) Indicate the *Receptor.*
(3) Assign a code with a successive number higher than 14 (e.g. M1-SHS15).

4.1.2.2 STEP 2: Assessing the Likelihood of Occurrence (Probability)

The Likelihood of Occurrence of each Hazard Scenario is assessed in the Probability Index (PI), a qualitative, non-dimensional value that is obtained by following the steps in the 'Probability Index Estimation Guide' (Annex A1). The PI will be assigned one of the following values: High, Medium, Low or Negligible.

Safety Hazard Scenarios include two kinds of situations: those related to people entering abandoned mine sites, and those related to unstable works or structures in mine installations which could affect receptors outside the AD/SMS. In the first case, a 'Negligible' probability corresponds to Hazard Scenarios with very limited access. Higher probabilities are assigned where access to the site increases and more factors come into play that increase the risk of harm (such as the absence of safety measures and evidence of previous events e.g. rockslides, fallen debris from buildings, etc.).

For situations related to mine installations, the Likelihood of Occurrence is a function of the stability of those installations and the presence of external forces that may activate an occurrence (wind, precipitation, runoff, corrosion, etc.). Therefore, a probability of 'negligible' would be assigned when all factors combined indicate that there is practically no chance that an unwanted event will occur. The Likelihood of Occurrence rises with the presence of factors that affect the stability of the installation, deposit or works and the presence of potential receptors.

It is possible that the Assessor may not be able to answer all questions set out in the Probability Index Estimation Guide for Safety Hazard Scenarios. This may occur, for example, when underground mine workings are buried under large scale mining waste. In those cases, the Assessor shall choose the most conservative estimation offered in the respective question, except where there is reason to choose another value. The following information should be recorded in the RARF:

- The number of the Guide used.
- The PI value obtained by applying the procedures in the aforementioned Guide.
- A brief rationale for the estimation arrived at.

> ***=>*** *The RARF (Form SHS Step 2)(Annex E) will display a record of the Likelihood of Occurrence value assigned for each of the Hazard Scenarios identified. This value will be obtained by following the steps outlined in the Guides included in Annex A-1.*

For example, Table 4-5 offers a probability value for each of the sample Hazard Scenarios identified in Table 4-4 above for Abenab Mine (see Annex E for completed table).

Table 4-5: Sample record of SHS Probability Indices

Name	SHS site code	SHS description	Applied guide	Probability index	Justification
Breccia pipe	OP1-SHS12	Although the open pit is fenced, there are gaps in the fence and access is unrestricted. Very high vertical pit walls	**Guideline 7**	**Medium**	**Although steep, walls appear quite stable around edges; access not on a daily basis**
Concentrator plant	P1-SHS13	Dilapidated buildings with loose bricks, unsafe roof trusses	**Guideline 7**	**High**	**Many dangerous structures; unrestricted access; appears to be daily access by adults and children**
Tailings dump	LW2-SHS12	Deep gullies in eroded tailings which were slurried onto waste rock dumps; evidence of frequent access	**Guideline 7**	**High**	**Steep gullies and slopes more than 1.5m high; daily access**
Plant area	I1-SHS4	Concrete water tank 20mx6mx4m deep divided into two. Vertical sides; no escape route; contains water of 1-2m depth	**Guideline 7**	**High** **Negligible**	**Unrestricted access to tank for people. Stock are unlikely to climb over wall**

4.1.2.3 STEP 3: Estimating the Severity of the Consequences

The Severity of the Consequences of Hazard Scenarios is related to the estimated number of receptors that could be affected by an unwanted impact of the HS, as well as to the severity of that impact. To estimate this, the Assessor will refer to the list of receptors present inside the Area of Study (drawn up as per 3.2.4).

The Severity of the Consequences will be determined by applying a series of criteria (Table 4-6), and will be rated on the following scale: Negligible, Low, Moderate, High, or Catastrophic.

The consequences of a HS are considered to be 'Negligible' to humans when the harm produced does not require medical treatment. Consequences for the environment or economic activities, for their part, are 'Negligible' when there are no receptors of this kind in the Area of Study. More serious consequences are assigned progressively higher ratings based on the number of receptors affected and/or the increased seriousness of the harm that could result. It is important to note that a rating of 'Catastrophic' is used only in cases of human receptors, while the highest rating for

impacts on the environment and economic activities is 'High'.

Table 4-6: Severity of the Consequences Scale – Safety Hazard Scenarios

		Severity of the Consequences				
		Negligible	**Low**	**Moderate**	**High**	**Catastrophic**
PEOPLE	Public safety (number of people)	Does not require medical treatment	Injuries that may require medical treatment, but not hospitalisation for one or two individuals	Moderate injuries requiring hospitalisation or reversible disability of <50% of a group of people	Death of 1 person; OR Severe irreversible disability of >50% of a group of people	Multiple fatalities or severe irreversible disability of more than 50 people
ENVIRONMENT	Terrestrial Fauna and Flora	Absent	< 10 ha	10 - 100 ha	> 100 ha	-
		No species injured or killed	1-4 individuals of one species injured or killed per year	5-10 individuals of one or more species injured or killed per year	>10 individuals of one or more species injured or killed per year	-
ECONOMIC ACTIVITIES	Crop Farming	No crop lands affected	<10% of an individual farm affected	10-50% of an individual farm affected	>50% of an individual farm affected	-
	Game farming and Livestock activity	No animals adversely affected	<10% of the herd injured or killed per year	5-10% of the herd injured or killed per year	>10% of the herd injured or killed per year	-
	Tourism	Does not require medical treatment	Injuries that may require medical treatment, but not hospitalisation for one or two individuals	Moderate injuries requiring hospitalisation or reversible disability of <50% of a tourist group	Death of 1 person; OR Severe irreversible disability of >50% of a tourist group	Multiple fatalities or severe irreversible disability of more than 50 people in tourist group
		No tour operators or tourist sites affected	1 tour operator or tourist site affected	2-5 tour operators or tourist sites affected	>5 tour operators or tourist sites affected	-

In practice, this stage of the process consists in determining the Severity of the Consequences for each Hazard Scenario identified and each receptor (people, the environment and economic activities). This will yield a series of values: one for each area in which negative impacts could occur.

Because the same Hazard Scenario can affect different receptors (for example, people, farming and livestock activities) with different levels of severity for each, each Hazard Scenario identification code needs to have a suffix added that clearly identifies the receptor affected. Receptor suffixes have been defined as follows:

- **'pe'** where the receptor is people
- **'tf'** where the receptor is Terrestrial Fauna and Flora
- **'aq'** where the receptor is Aquatic Life
- **'pa'** where the receptor is a Protected or Environmentally Sensitive Area
- **'ag'** where the receptor is farming
- **'ga'** in the case of game farming or livestock activities
- **'ac'** for aquaculture and fishing activities
- **'to'** for tourism.

The information to be recorded on the RARF is as follows:

- The Severity of Consequences value obtained as per Table 4-6.
- A brief rationale for the estimation arrived at.

> **=>** *The Severity of Consequences rating for each Hazard Scenario identified, and potentially affected receptors, will be recorded on the RARF (Forms SHS Step 3-1, SHS Step 3-2 and SHS Step 3-3* in Annex E*). This rating is obtained as per the criteria indicated in Table 4-6.*

For example, Tables 4-7 and 4-8 indicate the estimated Severity of Consequences ratings for people and livestock, respectively, for each of the sample Hazard Scenarios identified at the Abenab mine site (see Annex E for completed tables).

Table 4-7: Severity of the Consequences rating for People.

Name	SHS site code	SHS description	Severity of consequences for people	Justification
Breccia pipe	OP1-SHS12	Although the open pit is fenced, there are gaps in the fence and access is unrestricted. Very high vertical pit walls	**High**	**A fall from the edge of the pit will likely be fatal**

Name	SHS site code	SHS description	Severity of consequences for people	Justification
Concentrator plant	P1-SHS13	Dilapidated buildings with loose bricks, unsafe roof trusses	Low	Falls of loose building material unlikely to cause permanent disability
Tailings dump	LW2-SHS12	Deep gullies in eroded tailings which were slurried onto waste rock dumps; evidence of frequent access	Negligible	Slopes are not that high or steep to cause major injury
Plant area	I1-SHS4	Concrete water tank 20mx6mx4m deep divided into two. Vertical sides; no escape route; contains water of 1-2m depth	High	If someone were to fall into this tank, there is no way out. If the depth of water is greater than the person who has fallen in (e.g. a child), they will drown, unless rescued immediately

Table 4-8: Severity of the Consequences rating for Livestock.

Name	SHS site code	SHS description	Severity of Consequences	Justification
Breccia pipe	OP1-SHS12	Although the open pit is fenced, there are gaps in the fence and access is unrestricted. Very high vertical pit walls	Low	No reports of cattle falling into pit, but possibility exists
Concentrator plant	P1-SHS13	Dilapidated buildings with loose bricks, unsafe roof trusses	Negligible	Unlikely to cause injuries to stock
Tailings dump	LW2-SHS12	Deep gullies in eroded tailings which were slurried onto waste rock dumps; evidence of frequent access	Negligible	Unlikely to cause injuries to stock
Plant area	I1-SHS4	Concrete water tank 20mx6mx4m deep divided into two. Vertical sides; no escape route; contains water of 1-2m depth	Low	If stock were to fall in they would probably drown

4.1.2.4 STEP 4: Assessing the Magnitude of Risk

Once the Likelihood of Occurrence and Severity of the Consequences have been estimated, the Risk Matrices should be used to determine the magnitude of risk involved in each Hazard Scenario. The result of this assessment shall be recorded on the corresponding matrix.

This operation is carried out using the following procedure (Figure 4-2):

(1) For a given Hazard Scenario, the Probability Index assigned will be verified and the corresponding line in the Risk Matrix located.

(2) For the same Hazard Scenario the Severity of the Consequences assigned is verified for a receptor, followed by the corresponding column in the Risk Matrix.

(3) The row and column selected determine the magnitude of risk for the Hazard Scenario for this receptor (for example, people), and the magnitude of risk should be recorded by writing the respective Hazard Scenario code and receptor code ('pe') in the cell selected.

(4) Steps (2) and (3) are repeated for each receptor. In this way, the Scenario's risk to this new receptor can be determined and the respective code recorded in the corresponding cell (in the case of the Abenab example, OP1-SHS12ga).

All risks associated with the first Hazard Scenario are recorded in this way, considering each of the receptors that could be affected by it. The result of this assessment will be recorded on the Risk Matrices.

(5) The above steps should be repeated for each and every Hazard Scenario identified for the site under assessment.

4.1.3 Results of the Simplified Risk Assessment for Safety

Once the risk assessment has been completed for each Hazard Scenario identified in a given SD/AMS, the process concludes with the Risk Matrices of the SD/AMS, where each SHS is situated on the corresponding grid based on its Likelihood of Occurrence and Severity of Consequences for each receptor.

By way of example, Table 4-9 below presents a sample record of risks that from the SRA conducted for the Abenab Mine. Potential receptors in this worked example are people (pe) and livestock (ga). In this record of risks, each of the Scenarios occupies its corresponding position based on the Probability Index (Table 4-5) and Severity (Tables 4-7 and 4-8) ratings assigned during the assessment. As can been seen, the highest risk relates to the risk of people drowning in the water tanks (I1-SHS4pe), followed by the risks of people falling into the open pit (OP1-SHS12pe). There is a

high potential for people to injury themselves while walking/playing in the old plant area, but the injuries would mostly be cuts and bruises, not requiring hospitalization. The tailings dump does not pose a threat to people of stock.

Table 4-9: Sample record of safety risks

	SEVERITY OF CONSEQUENCES				
PROBABILITY INDEX	Negligible	Low	Moderate	High	Catastrophic
High	P1-SHS12ga	P1-SHS13pe		I1-SHS4pe	
Medium	LW2-SHS12pe LW2-SHS12ga	OP1-SHS12ga		OP1-SHS12pe	
Low					
Negligible		I1-SHS4ga			

=> *In the RARF (Form Matrix* in Annex E) *the risks assessed will be written onto the Risk Matrices, placing the Safety Hazard Scenario codes in the corresponding cells. Each of these will have a suffix for its potential receptor.*

4.2 Simplified Risk Assessment for Contamination

4.2.1 General Aspects

Simplified Risk Assessment (SRA) for contamination hazards enables the risks of a SD/AMS to be assessed when harmful chemical substances are present that could adversely affect the health of the population, the environment or economic activities.

The magnitude of risk is defined by the Hazard Scenario's Likelihood of Occurrence and Severity of the Consequences (Chapter 2). For contamination hazards, the following are the central elements:

- the **exposure pathway**, or the way in which a contaminant enters into contact with a receptor (ingestion, skin contact, inhalation).
- the **environmental medium** through which the contaminant moves in the environment (surface water, groundwater, air, soil).

The likelihood of a Contamination Hazard Scenario will be determined by the '**Probability Index'**, (PI) an indicator of the degree to which contamination associated with a particular Hazard Scenario will affect a given receptor. The PI of contamination for each Contamination Hazard Scenario (CHS) is

estimated in the field using simple criteria such as the distance between the pollution source and the receptor(s) or the approximate size of the source (hazardous waste deposits, remnant reagents, tailings, etc.). A series of Guides for Calculating the Probability Index can be found in Annex B1 of this Handbook for establishing the contamination PI for each Scenario.

Estimation of the **Severity of the Consequences** of chemical contamination uses the same principles as the Simplified Risk Assessment for Safety; i.e. it estimated the seriousness of the unwanted effects associated with a Hazard Scenario. If an environmental medium such as soil, air or surface water becomes contaminated, the unwanted impacts could affect all receptors located in the Area of Study specified for that Hazard Scenario. Because of this the Severity of Consequences is assessed conservatively based on the number of people or hectares within the Hazard Scenario's Area of Study.

Like that for safety, the SRA for chemical contamination is a procedure designed to establish in preliminary form whether there are grounds for designating the SD/AMS a MEL. In cases where the SRA results are highly uncertain and the site may be erroneously classified as a MEL (or vice versa), it is advisable to conduct a Detailed Risk Assessment (DRA, described in Chapter 6).

The Assessor should bear in mind that the tools and procedures offered for the SRA are relatively simple and seek to provide a method for quickly determining whether there are grounds to consider a given SD/AMS a MEL or not.

4.2.2 SRA Process for Contamination

The procedure for the SRA for chemical contamination includes 5 main steps (Figure 4-2), namely:

Step 1 – Formulation of the Problem. The first step in a SRA for contamination comprises a preliminary identification of the causes of contamination, the identification of the chemicals of potential concern and then making a schematic of the sources of pollution present on site, how the pollution moves around, the exposure pathways and receptors affected. This scheme will enable the Assessor to identify the CHS present at the site (see the conceptual model in Figure 4-3).

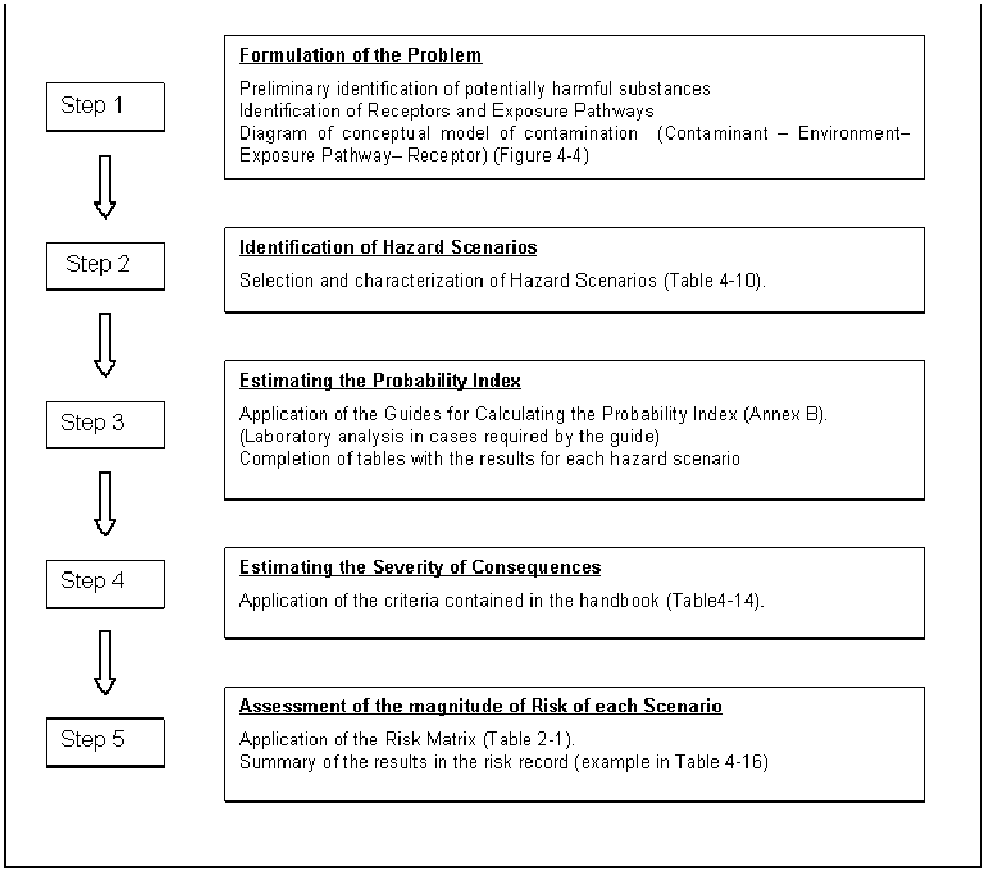
Step 2 – Identification of Hazard Scenarios present at the SD/AMS. In applying the concept of contamination risk, the assessment must recognize chemicals of potential concern, receptors and exposure pathways. Where these three elements are present (as specified in the conceptual model), then a CHS exists and can be described in an explanatory text.

Step 3 – Estimating the Probability Index (PI). This is done by applying the procedures contained in the 'Guides for Calculating the Probability Index for Chemical Contamination' (Annex B1). In some cases it will be necessary to conduct laboratory analyses on a limited number of parameters to enable the PI to be determined accurately.

Step 4 – Estimating the Severity of Consequences, based on information gathered in the Area of Study and from cartographic information available.

Step 5 – Assessing the magnitude of risk, by application of the Risk Matrix. This process concludes with a record of the risks assessed in the SRA as a whole for each environmental medium (air, water, soil, etc.) and each receptor (people, the environment, economic activities).

Figure 4-2: SRA process for chemical contamination



4.2.2.1 STEP 1: Formulation of the Problem

a. Procedure

Formulating the problem consists of identifying the elements in the Conceptual Contamination Model (Figure 4-3), namely:

- Chemical source that contains the contaminant (minerals present in the rock, tailings, waste, etc.).

- Mechanism that allows the chemicals of potential concern to be released (wind action, water action, leaching, etc.).
- Transport medium or residence medium that promotes the transfer of the contaminant from the source to the receptor (air, water, animals, man-made transport, etc.).
- Potential exposure pathway (inhalation, ingestion or skin contact).
- Potential receptor that could be affected (people, terrestrial fauna and flora, etc.).

The Assessor can represent this model in schematic form, as illustrated in Figure 4-3, with lines drawn between the blocks applicable in each case. New blocks can also be added if relevant.

> ***=>*** *The Assessor shall draw the lines representing the Contamination Model in the RARF (Form CHS Step 1)(Annex E) and provide an explanatory text. If the scheme is confusing due to the complex nature of the site, separate sheets may be used for each case of chemical contamination found.*

4.2.2.2 STEP 2: Identification of Hazard Scenarios

a. Procedure

Once the Contamination Model is formulated, the contamination hazard scenarios must be identified. Table 4-10 lists all HS related to chemical contamination that could be present in the installations, works and/or deposits of a SD/AMS, and that could pollute environmental media such as surface water, groundwater, soil and/or air. The Assessor should use Table 4-10 as a checklist. It should be noted that the same component may present one or more Hazard Scenarios.

Figure 4-3: Contamination Model Scheme

Source of contam-ination	Mechanisms for release	Transport or residence medium	Exposure pathways	Potential direct receptors	Indirect receptors
Minerals	Wind action	Air	Inhalation	People	People
Tailings	Water action	Surface water	Ingestion of food	Terrestrial fauna	Terrestrial fauna
Leaching waste	Leaching	Ground-water	Skin contact	Aquatic life	Game and livestock
Waste rock, low grade ore	Evaporation and gaseous release	Soil	Direct ingestion	Plants and fodder crops	
Small scale industrial and mining waste	Physical removal	Man-made transport	Uptake by plants	Food crops	
				Game and livestock	
				Aquaculture and fishing products	

Table 4-10: Contamination hazard scenarios

Component	Installations Deposits Works	Code	Contamination Hazard Scenario	Medium Susceptible to Contamination	PI Estimation Guide
MINE	Underground Workings	CHS 1	Presence of drainage that has in the past, or could in future contaminate **surface water**, affecting people, the environment and/or economic activities.	Surface water	GUIDE 1
		CHS 2	Infiltration of drainage that has in the past, or could in future contaminate **groundwater**, affecting people, the environment and/or economic activities.	Groundwater	GUIDE 2
		CHS 3	Presence of contaminated water in underground mine workings that could be used for drinking water or other uses (irrigation, bathing, livestock).	Not applicable	GUIDE 3
	Open Pit	CHS 1	Presence of drainage that has in the past, or could in future contaminate **surface water**, affecting people, the environment and/or economic activities.	Surface water	GUIDE 1
		CHS 2	Infiltration of drainage that has in the past, or could in future contaminate **groundwater**, affecting people, the environment and/or economic activities.	Groundwater	GUIDE 2
		CHS 3	Presence of contaminated water the open pit that could be used for drinking water or other uses (irrigation, bathing, livestock).	Not applicable	GUIDE 3
PLANTS	Processing Plants	CHS 3	Presence of contaminated water in the plant area that could be used for drinking water or other uses (irrigation, bathing, livestock).	Not applicable	GUIDE 3
		CHS 4	Movement of remnant hazardous waste from contaminated structures, machinery or soil that has in the past, or could in future pollute **surface water**, affecting people, the environment and/or economic activities.	Surface water	GUIDE 4

Component	Installations Deposits Works	Code	Contamination Hazard Scenario	Medium Susceptible to Contamination	PI Estimation Guide
PLANTS	Processing Plants	CHS 5	Movement of remnant hazardous waste from contaminated structures, machinery or soil that has in the past, or could in future pollute **groundwater**, affecting people, the environment and/or economic activities.	Groundwater	GUIDE 5
		CHS 6	Movement of remnant hazardous waste from contaminated structures, machinery or soil that has in the past, or could in future pollute the **soil** and affect people (by ingestion or skin contact), the environment and/or economic activities.	Soil	GUIDE 6
		CHS 8	Movement of particulate matter by wind action that has in the past, or could in future affect people (by inhalation), the environment and/or economic activities.	Air	GUIDE 8
		CHS 9	Ingestion, inhalation or dermal contact with hazardous waste.	Not applicable	GUIDE 9
LARGE SCALE MINING WASTE	Tailings Dams and Impoundments Heap Leach Waste Dumps for Waste Rock, Low Grade Ore	CHS 1	Presence of drainage that has in the past, or could in future contaminate **surface water**, affecting people, the environment and/or economic activities.	Surface water	GUIDE 1
		CHS 2	Infiltration of drainage that has in the past, or could in future contaminate **groundwater**, affecting people, the environment and/or economic activities.	Groundwater	GUIDE 2
		CHS 3	Presence of contaminated water in tailings ponds, slurry dams etc., that could be used for drinking water or other uses (irrigation, bathing, livestock).	Not applicable	GUIDE 3
		CHS 7	Activities carried out on the surface of tailings deposits or contaminated soil that could affect people (through inhalation, accidental ingestion or skin contact), the environment and/or economic activities.	Soil	GUIDE 7

Component	Installations Deposits Works	Code	Contamination Hazard Scenario	Medium Susceptible to Contamination	PI Estimation Guide
		CHS 8	Movement of particulate matter by wind action that has in the past, or could in future affect people (from inhalation), the environment and/or economic activities.	Air	GUIDE 8
SMALL SCALE MINING WASTE AND INDUSTRIAL WASTE SMALL SCALE MINING WASTE AND INDUSTRIAL WASTE	Small scale mining waste dumps and Industrial Waste Dumps	CHS 1	Presence of drainage that has in the past, or could in future contaminate **surface water**, affecting people, the environment and/or economic activities.	Surface water	GUIDE 1
		CHS 2	Seepage that has in the past, or could in future contaminate **groundwater**, affecting people, the environment and/or economic activities.	Groundwater	GUIDE 2
		CHS 3	Presence of contaminated water in mine works that could be used for drinking water or other uses (irrigation, bathing, livestock).	Not applicable	GUIDE 3
		CHS 4	Movement of remnant hazardous waste from contaminated structures, machinery or soil that has in the past, or could in future pollute **surface water**, affecting people, the environment and/or economic activities.	Surface water	GUIDE 4
		CHS 5	Movement of remnant hazardous waste from contaminated structures, machinery or soil that has in the past, or could in future pollute **groundwater**, affecting people, the environment and/or economic activities	Groundwater	GUIDE 5
		CHS 6	Movement of remnant hazardous waste from contaminated structures, machinery or soil that has in the past, or could in future pollute the **soil** and affect people (by ingestion or skin contact), the environment and/or economic activities.	Soil	GUIDE 6
		CHS 7	Activities carried out on the surface of waste dumps or contaminated soil that could affect people (through inhalation, accidental ingestion or skin contact), the environment and/or economic activities.	Soil	GUIDE 7

Component	Installations Deposits Works	Code	Contamination Hazard Scenario	Medium Susceptible to Contamination	PI Estimation Guide
		CHS 8	Movement of particulate matter by wind action that could affect people (from inhalation), the environment and/or economic activities.	Air	GUIDE 8
		CHS 9	Ingestion, inhalation or dermal contact with hazardous waste.	Not applicable	GUIDE 9
ASSOCIATED INFRA-STRUCTURE	Workshops and Storehouses Power Lines and Substations	CHS 3	Presence of water in water storage structures that may be polluted, which could be used for drinking water or other uses (irrigation, bathing, livestock).	Not applicable	GUIDE 3
		CHS 4	Movement of remnant hazardous waste from contaminated structures, machinery or soil that has in the past, or could in future pollute **surface water**, affecting people, the environment and/or economic activities.	Surface water	GUIDE 4
	Workshops and Storehouses Power Lines and Substations	CHS 5	Movement of remnant hazardous waste from contaminated structures, machinery or soil that has in the past, or could in future pollute **groundwater**, affecting people, the environment and/or economic activities	Groundwater	GUIDE 5
		CHS 6	Movement of remnant hazardous waste from contaminated structures, machinery or soil that has in the past, or could in future pollute the **soil** and affect people (by ingestion or skin contact), the environment and/or economic activities.	Soil	GUIDE 6
		CHS 9	Ingestion, inhalation or dermal contact with hazardous waste.	Not applicable	GUIDE 9

b. Description of Contamination Hazard Scenarios (CHS)

CHS 1: Presence of drainage that has in the past, or could in future, contaminate surface water, affecting people, the environment and/or economic activities.

This refers to drainage of water loaded with metals or other dissolved elements that has in the past, or could in future, drain off the site, contaminating surface watercourses. Such effects could come from underground mines, open pits, large scale mining deposits such as tailings, waste rock, and other mining waste deposits, and are directly related to the mineralogical characteristics and climatic conditions that affect the chemical composition of the drainage: most metals of potential concern go into solution under progressively acidic conditions; other elements of environmental concern – such as molybdenum, aluminium and zinc – are dissolved in basic environments (pH greater than 7).

Drainage from underground mines could seep to the surface via tunnels or mine entrances. In some cases this may produce outflows downstream from an underground mine, where water that was in contact with mine workings comes to the surface (see Annex B2).

For open pit mines, accumulated water in the bottom of the pit can seep through the subsoil and surface as springs downstream from the mine site. Such drainage can be acidic with a high content of dissolved metals, or can be basic with high concentrations of metals such as molybdenum or zinc, or highly saline with elevated concentrations of calcium, magnesium, sodium, chloride, for example.

Effluents from tailings deposits or return water dams can also contaminate surface watercourses and/or water bodies via spillways, where these are present, or by overflow where they are not. Discharge can be caused by higher than average rainfall that causes the overflow of water carrying solids, or by seepage from the pond or dam wall. Pollution can also be caused by direct surface runoff from the tailings dam walls, if not properly contained with toe drains and cut-off trenches.



Plate 4.9: Pollution of the river from tailings dam overflow and seepage at Otjihase Mine. Note reddish colour indicates iron precipitation due to acidic conditions. White salt crust indicates a high level of salinity

Waste rock dumps contain unmineralized material that was removed to access the ore body and low

grade ore stockpiles contain material that was uneconomic to process when the mine was in operation. Within this waste, low grade ore deposits are the ones most likely to generate drainage with contaminants due to the greater mineral content. Most of these dumps are located close to the mine or pit, and in some cases may cut across drainage lines thus directly affecting water quality.

Depending on its mineralogical nature, small amounts of mining waste and industrial waste (ash, smelter dust, etc.) can also generate acid drainage when the waste comes into contact with oxygen and water. An SD/AMS can also contain a myriad of other wastes which can cause contamination of surface water in the form of hydrocarbon pollution, salinity and alkalinity. Furthermore, general runoff from an old mine site will usually contain high loads of suspended solids, which could cause sedimentation problems downstream and other economic impacts.

CHS 2: Infiltration of drainage that has in the past, or could in future, contaminate groundwater, affecting people, the environment and/or economic activities.

Groundwater infiltrating through underground mine workings can result in contamination of the aquifer, thus affecting nearby boreholes used by farmers for drinking, irrigation and stock watering. The nature of the contamination depends on the geochemistry of the ore body and host rock. Water which accumulates at the base of the open pit is often in direct contact with the water table, and depending on the groundwater gradient, could migrate laterally causing a pollution plume down gradient of the mine – again affecting nearby groundwater users.

CHS 3: Presence of contaminated water in mine workings that could be used for drinking water or other uses (irrigation, bathing, livestock).

In some open pit mines once dewatering stops on mine closure, pools are formed at the bottom of the pit that may contain contaminated water. In some cases local residents use these pools for recreation, as drinking water for livestock and even for fishing. Depending on the water composition, such scenarios may represent a health risk to receptors – directly through consumption and contact and indirectly through bioaccumulation of contaminants in fish tissues. It should also be noted that even uncontaminated pools present a safety risk (see section 4.1).

In some cases local inhabitants may use the tailings ponds or return water dams for recreation, livestock drinking, irrigation or fishing. These water bodies may also be used by game species, which, if killed and eaten could result in the bioaccumulation of some metals up the food chain. All water in these water bodies should be tested to determine whether it meets water quality standards for human and/or animal consumption and to determine if there is any health risk to receptors.

A similar situation may be found in other places that water accumulates such as evaporation ponds, water tanks, etc.



Plate 4.10: There was evidence of fishing and animals at this pool at the base of the Brandberg West tin mine

CHS 4: Movement of remnant hazardous waste from contaminated structures, machinery or soil that has in the past, or could in future, pollute surface water, affecting people, the environment and/or economic activities.

Activities that normally take place in a mining operation generate both hazardous and non-hazardous industrial waste. Non-hazardous waste (scrap metal, wood, plastic, rubber, PVC pipes, cables, etc.) in general is not a cause for concern in the SRA for Chemical Contamination, although the Assessor may define a Hazard Scenario associated with this kind of waste and duly justify it.

Among the types of hazardous waste that could be present in abandoned mine sites are reagents from processing (cyanide, sulphuric acid, zinc, mercury), concentrate deposits produced in the process that are abandoned on site, waste containing oils and lubricants, tanks with remnants of fuel, asbestos, askarels (PCBs), arsenic waste, etc.

This Hazard Scenario is applicable in cases where there is a possibility that hazardous waste has been or will be released by precipitation or runoff and carried to surface watercourses or water bodies.



Plate 4.11: Drums of highly toxic tar and resin waste were found at Tsumeb causing pollution to the groundwater and soil

CHS 5: Movement of remnant hazardous waste from contaminated structures, machinery or soil that has in the past, or could in future, pollute groundwater, affecting people, the environment and/or economic activities.

This scenario is similar to the above but addresses potential contamination of groundwater by seepage.

CHS 6: Movement of remnant hazardous waste from contaminated structures, machinery or soil that has in the past, or could in future, pollute the soil and affect people (by ingestion or skin contact), the environment and/or economic activities.

This case addresses the possibility of hazardous waste from a site being transported by water (rain or runoff) or by wind, and deposited around the site, where the contaminants have in the past or could in future affect people and/or animals that enter into direct contact with them through ingestion, inhalation or skin contact. Windblown particulates can also accumulate on soil and on the leaves of palatable plants and thus enter the food chain via root crops, leafy vegetables and meat and milk products.



Plate 4.12: Species such as kudu are highly susceptible to ingesting pollutants deposited on the leaves of trees and shrubs

CHS 7: Activities carried out on the surface of tailings deposits or contaminated soil that could affect people (through inhalation, accidental ingestion or skin contact), the environment and/or economic activities.

These are cases where people engage in activities on the surface of abandoned tailings deposits, slag deposits or contaminated soil (for recreation, sports, and other activities), taking advantage of the flat, dry surface. Sometimes, dry tailings are used for building materials and slag may be used to surface roads (see Plate 3.4). For tailings dams, the direct exposure of people to the deposits and their fine particulate matter and potentially toxic substances, is a potential risk that should be assessed. This situation occurs especially when abandoned sites are near populated areas and access has not been closed off.

CHS 8: Movement of particulate matter by wind action that has in the past or could in future affect people (by inhalation), the environment and/or economic activities.

Abandoned tailings or other large scale deposits are a source of particulate matter release to the environment. The pollutants released will depend on the size of the particles, their specific gravity, wind patterns, the moisture content of the material and the level of revegetation of other means of stabilisaiton. The moisture level depends on the geographic location (level of precipitation or fog frequency) and time since the dam was decommissioned. In the southern and western arid parts of Namibia, these deposits are often dry and less well vegetated, while in the northern and central parts of the country they will be dry only half the year and are likely to be better vegetated so long as the substrate is not phytotoxic. Both the fine particulates and the contaminants present in the deposit represent a potential risk to people, the environment and/or economic activities.



Plate 4.13: Dust from the tailings dam at Oamites Mine causing risks to human health and fauna and flora

CHS 9: Ingestion, inhalation or dermal contact with hazardous waste.

Hazardous waste is commonly found in mine sites, particularly old mine sites. This waste is generally composed of process reagents (such as cyanide); process remnants (waste from mercury amalgamation processes or arsenic from roasting); deposits of concentrates, smelter dust and/or

other material; maintenance waste, etc. Hazardous chemical reagents that have not been stored or labelled properly, may also be found in abandoned mine sites where they could be handled by those who are unaware of their potentially harmful effects.

These kinds of hazardous industrial wastes can be found stored or lying around in different forms — drums, sacks, pools, dumps or deposits — and may be in such poor condition that their contents are exposed to the air and therefore represent a danger to those who come into contact with them.

A Hazard Scenario is deemed to occur when there is an immediate or very short term negative effect (poisoning, intoxication, burns) on humans when they are directly exposed to hazardous substances, or when there is a medium or long term effect such as fatal illness (such as cancer), or where health impacts are observed (nervous system impacts, loss of concentration, etc.).

When the characteristics of the material found on site are not known but they are suspected to be hazardous, a sample should be taken and analyzed in the laboratory to determine its toxicity (section 3.3.2).



Plate 4.14: Unlabelled drums of waste can pose a risk to health and safety. These drums at Abenab contained concentrations of arsenic, lead, zinc, copper and some mercury

c. Logging the results of Contamination Hazard Scenario identification.

Contamination Hazard Scenarios identified for a SD/AMS should be recorded by the Assessor in a table that is included in the RARF (Form CHS Step 2)(Annex E). This table should be filled out in a manner similar to the safety assessment (section 4.1.2.1d). In other words, the Assessor shall:

- Select from the list the CHSs identified for that site.
- Select the standard code representing each CHS.
- Select the standard definition that corresponds to each CHS.
- Combine the code for the installation, deposit or work with the standard CHS code.
- Describe the CHS making reference to the receptors that could be affected directly or indirectly, the exposure pathway (inhalation, ingestion, or skin contact) and the

environmental medium involved (surface water, soil, air, etc.), supported by the site schematic performed in Step 1.

=> *In the RARF (Form CHS Step 2)(Annex E) each of the Hazard Scenarios identified will be recorded and assigned its corresponding code; the receptor, exposure pathway and environmental medium of transport will be described briefly.*

The code of the CHS will be assigned using the same procedure as that indicated in Section 4.1.2.1 (for Safety Hazard Scenarios), i.e. combining the SD/AMS component code with the code 'CHS–n', where 'n' is the CHS referred to in Table 4-10.

For example, for an abandoned tailings dam the identification code would be 'LW1', and the hazard for drainage that could affect surface water could be assigned the code 'CHS1'. Thus, the final code for this scenario would be 'LW1-CHS1'. If three similar ponds exist on the same site and present the same potential chemical hazard, each of these would be assigned its own number, as follows: 'LW1-CHS1', 'LW2-CHS1' and 'LW3-CHS1', respectively.

By way of additional example, Table 4-11 provides an example of a record of contamination hazard scenarios for the Abenab abandoned mine site (see Annex E for completed works sheets).

While performing this step, the Assessor may identify a CHS that is not accounted for in Table 4-10, in which case he or she should add the scenario in the appropriate manner to the RARF. The description of any new hazard scenario added should:

(1) Indicate the *Negative effect* that could occur.

(2) Indicate the *Receptor*.

(3) Indicate the code with a consecutive number after 9 (for example: M1-CHS10).

Table 4-11: Sample record of Contamination Hazard Scenarios

Facility type	Name	Code	Standard CHS code	CHS description (according to the handbook)	CHS site code	CHS description
Open pit mine	Breccia pipe	OP1	CHS 2	Presence of drainage that could percolate and contaminate groundwater, affecting persons, environment or economic activity.	OP1-CHS2	Open pit pool is in direct contact with groundwater. Groundwater is being pumped for human and animal consumption
Tailings dumps (dry)	Tailings dump	LW2	CHS 7	Surface activity involving tailings, stockpiles or contaminated soils, which could affect persons, environment or economy activity through inhalation, accidental ingestion or skin contact.	LW2-CHS7	Livestock and game are eating the vegetation growing in tailings, which have a high metal content. The vegetation could be bio-accumulating some of these metals
Resin and / or hydrocarbons	Veld	SW5	CHS 6	Movement of hazardous wastes remaining in structures, equipment or contaminated soil, which could contaminate the soil, affecting persons (via ingestion or skin contact), environment or economic activity.	SW5-CHS6	Toxic resin deposited on the soil surface has prevented vegetation growth. Inhalation of fumes could be dangerous to people and livestock

4.2.2.3 STEP 3: Estimating the Probability Index

To estimate the **Probability Index (PI)** (Step 3) a series of guides are available to assist the Assessor in determining the category of each Contamination Hazard Scenario (Annex B-1). The Guide for each CHS is indicated in Table 4.10. Categories are assigned based on qualitative factors; the Probability Index scale ranges from: 'None' to 'Negligible', 'Low', 'Medium' and 'High'.

A Probability Index of 'Negligible' is for cases where the concentration of hazardous substances in components of an abandoned mine site is insignificant or where there is no possibility that the chemicals of potential concern can be released into the air, water or soil, or where these will not reach receptors in higher than trace concentrations.

A Probability Index of 'High' is reserved for cases where there is a presumed existence of high concentrations of chemicals of potential concern in the abandoned site, making it possible for these to be transported by air, soil or water to nearby receptors and where exposure is frequent.

In cases where drainage is coming from a site, assessing the Probability Index will require measurement of the pH and conductivity (eC) during the field visit, as this will provide evidence of potential contamination and toxicity status.

In general, acidic pH is associated with the presence of heavy metals dissolved in water, which could have toxic effects on aquatic and terrestrial life, including humans. Similarly, water with basic pH may also cause negative effects on exposed receptors, as elements like zinc, arsenic and molybdenum are soluble in higher pH. The chemical characteristics of any drainage from an abandoned mine site should be established and compared with current Namibian standards or internationally accepted guidelines such as WHO Guideline Values for Drinking Water, or the South African Receiving Water Quality Objectives for different water users e.g. irrigation, aquatic ecology etc. For the latest standards applicable in Namibia, the Assessor is encouraged to search the relevant websites to ensure that the latest standards are being used (see Annex C-1).

In some mines, salinity may be an indicator of pollution, rather than acidity. High salinity renders the water non-potable and can seriously affect the livelihoods of irrigation farmers and aquatic life.

The Assessor must always take a portable pH/eC meter to the field to test each potentially contaminated water body present on the old mine site. Full chemical analysis of discharge must be carried out when the pH is below 6.5 or above 7.5, or the eC is greater than 100mS/m or when there is evidence of other forms of contamination (e.g. algal blooms indicating eutrophication).

The 'Guides for Calculating the Probability Index' in Annex B1 enable the Assessor to establish the level of pH for each of the Hazard Scenarios identified.

To summarize, the following information should be recorded on the RARF:

- The number of the Guide used.
- The PI rating obtained by applying the procedure in the aforementioned Guide for the CHS.
- A brief rationale for the rating given.

    => *In the RARF (Form CHS Step 3)(Annex E) a rating for Probability will be recorded for each CHS identified at the site. This rating will be arrived at by following the procedure given in the corresponding Guide, found in Annex B-1.*

By way of example, Table 4-12 offers sample PI ratings for the Abenab mine site containing contamination hazard scenarios.

Table 4-12: Sample record of CHS Probability Indices

Name	CHS site code	CHS description	Applied guide	Probability index	Justification
Breccia pipe	OP1-CHS2	Open pit pool is in direct contact with groundwater. Groundwater is being pumped for human and animal consumption	**GUIDE 2**	**Low**	**No water quality data available. High buffering capacity (pH probably >7.5) and so solution of heavy metals unlikely. People drinking water without any apparent ill effects. NEEDS VALIDATING**
Tailings dump	LW2-CHS7	Livestock and game are eating the vegetation growing in tailings, which have a high metal content. The vegetation could be bioaccumulating some of these metals	**GUIDE 7**	**High**	**No data on soils or vegetation are available. Much evidence of livestock present on areas covered with windblown and eroded tailings. NEEDS VALIDATION**
Veld	SW5-CHS6	Toxic resin deposited on the soil surface has prevented vegetation growth. Inhalation of fumes could be dangerous to people and livestock	**GUIDE 6**	**High**	**Frequent access by livestock to the resin area. Resin crust being broken up by hoof action. Effects on soil, livestock, groundwater and humans unknown. NEEDS VALIDATION**

4.2.2.4 STEP 4: Estimating the Severity of Consequences

The Severity of Consequences is assessed by taking into account 8 types of potential receptors associated with people (public health), the environment and economic activities (Table 4-13):

Table 4-13: Receptors for risk assessment

People	The environment			Economic activities			
1	2	3	4	5	6	7	8
Public Health	Terrestrial Fauna and Flora	Aquatic Life	Protected or Env. Sensitive Areas	Agriculture (crop farming)	Game Farming & Livestock Activity	Aquaculture and Fishing	Tourism

For each Hazard Scenario the Severity of Consequences is determined by the number of receptors specified for each Scenario in the Area of Study. These receptors would have been identified when

the Area of Study was defined (Chapter 3), and when the Assessor identified the receptors (people, the environment and/or economic activities) that could be affected by contaminants transported from the SD/AMS installations along a given exposure pathway (ingestion, inhalation or skin contact).

The assessment therefore leads to a Severity of Consequences rating for each potential Receptor and Hazard Scenario. Like the PI values, ratings assigned here are also qualitative and are as follows: Negligible, Low, Moderate, High or Catastrophic.

A rating of 'Negligible' indicated for cases where there are no receptors identified for the Area of Study, or when the level of impact is low/minor and the extent of the impact is limited (e.g. an animal with dispersed distribution, an occasional visitor entering the Area of Study, an isolated crop, etc.). Hazard Scenarios that have more potentially severe consequences are rated on a scale of 'Low' to 'Catastrophic', depending on the number of people, environmental elements and/or economic activities that could be affected by contamination from that scenario.

It is important to bear in mind that a rating of 'Catastrophic' is reserved for human receptors (People), while the maximum rating for the environment or economic activities is 'High'.

The criteria applied to assign a Severity of Consequences rating to a CHS identified for a SD/AMS are presented in Table 4-14. For some receptors, there are several categories for measuring the severity of consequences, e.g. for terrestrial wildlife, the Assessor can assess the loss of habitat due to contamination (such as the impact of toxic dust on browse and forage plants); or the loss of biodiversity as evidenced by a lack of spoor and visual sightings; or whether the water sources available to wildlife have been polluted. The Assessor must choose the **highest** severity of consequences rating, if more than one of these categories are assessed. The same logic must be applied to the other receptors where there is more than one category: aquatic ecosystems, crop farming, game and livestock farming.

After the assessment of Severity of Consequences, a summary table is obtained that contains ratings for each of the 8 types of receptors considered.

> ***=>*** *In the RARF (Forms CHS Step 4-1, CHS Step 4-2, CHS Step 4-3)(AnnexE) a rating for Severity of the Consequences is recorded for each CHS identified and receptor potentially affected. This rating is obtained by applying the criteria indicated in Table 4-14.*

Table 4-14: Severity of Consequences in the SRA due to Chemical Contamination

		Severity of Consequences				
		Negligible	**Low**	**Moderate**	**High**	**Catastrophic**
PEOPLE	Public Health (nº of people that could come into contact with the contaminant)	None	1 - 9 people on a once-off basis	10 - 99 people on a once-off basis; OR 1-9 people on a regular basis	100 - 500 people on a once-off basis; OR 10 – 99 people on a regular basis	> 500 people on a once-off basis; OR 100 – 500 people on a regular basis
THE ENVIRONMENT	Aquatic Life (surface area or length of water body/course affected by contamination)	No habitat loss	< 5 ha for wetlands and dams; OR < 0.5 km for rivers/coast	5 - 10 ha for wetlands and dams; OR 0.5 - 2 km for rivers/coast	> 10 ha for wetlands and dams or >2 km for rivers/coast	Not applicable
	Aquatic Life (loss of biodiversity)	No biodiversity loss	Some loss of biodiversity. Ecosystem under low threat. Effects would be reversible	Biodiversity low. Species limited to a few tolerant individuals. Ecosystem under stress. Possible irreversible impacts.	No biodiversity. No living creatures evident. Ecosystem dead. Irreversible effects.	Not applicable
	Terrestrial Fauna & Flora (total area of habitat affected)	No habitat loss	< 10 ha	10 - 100 ha	> 100 ha	Not applicable
	Terrestrial Fauna & Flora (biodiversity loss)	No biodiversity loss	Some loss of biodiversity. Ecosystem under low threat. Effects would be reversible	Biodiversity low. Species limited to a few tolerant individuals. Ecosystem under stress. Possible irreversible impacts.	No biodiversity. No living creatures evident. Ecosystem dead. Irreversible effects.	Not applicable
	Terrestrial Fauna & Flora (drinking water resources affected)	None contaminated	Many other sources of uncontaminated water within 10km radius	One or two alternative uncontaminated water sources within a 10km radius	Only source of water within a 10km radius is contaminated	Not applicable

		Severity of Consequences				
		Negligible	**Low**	**Moderate**	**High**	**Catastrophic**
	Protected or Environmentally Sensitive Areas (area or sites affected by contamination)	None	< 1 ha	1 - 10 ha; OR cultural heritage sites of local importance	>10 ha; OR cultural heritage sites of regional/national importance	Not applicable
ECONOMIC ACTIVITIES	Crop Farming (crop production type)	No toxic effects	Only certain species susceptible to contamination or pollution are affected e.g. salt intolerant spp, root vegetables etc	Only a few very tolerant species can be grown	No crops can be grown because of high levels of soil and crop contamination	Not applicable
	Crop production - yield and income	No effects on yield and/or income	Loss of <20% of yield and/or income due to contamination. Limited effect on livelihoods	Loss of 21-50% of crop yield and/or income due to contamination. Moderate impact on livelihoods	Loss of >50% of crop yield and/or income. Lands have to be abandoned. Major impact on livelihoods	
	Game Farming & Livestock Activity – grazing areas	No loss of grazing area or grazing quality	Loss of <20% of grazing area due to contamination	Loss of 21-50% of grazing land due to contamination	Loss of >50% 0f grazing area due to contamination	Not applicable
	Game Farming & Livestock Activity - production rate and income	No loss of income	<20% drop in production. Limited impact on livelihoods	Loss of 21-50% in production and/or income due to contamination. Some products cannot be sold or consumed. Moderate impact on livelihoods	Loss of >50% in production and/or income. Lands have to be abandoned. Major impact on livelihoods	
	Aquaculture and Fishing	No loss of income	<20% drop in production. Limited impact on livelihoods	Loss of 21-50% in production and/or income due to contamination. Some products cannot be sold or consumed. Moderate impact on livelihoods	Loss of >50% in production and/or income. Business has to be abandoned. Major impact on livelihoods	Not applicable

		Severity of Consequences				
		Negligible	**Low**	**Moderate**	**High**	**Catastrophic**
	Tourism - impacts of contamination on tourist facilities	Absent	1 tour operator or 1 tourist site	2-5 tour operators or tourist sites	>5 tour operators or tourist sites	Not applicable

The table below offers an example of Severity of Consequences ratings for people in contamination hazard scenarios that could exist at the Abenab Mine site (Table 4-15).

Table 4-15: Severity of Consequences for People

Name	CHS site code	CHS description	Severity of consequences for people	Justification
Breccia pipe	OP1-CHS2	Open pit pool is in direct contact with groundwater. Groundwater is being pumped for human and animal consumption	**Negligible**	**No contact with pool in open pit**
Tailings dump	LW2-CHS7	Livestock and game are eating the vegetation growing in tailings, which have a high metal content. The vegetation could be bioaccumulating some of these metals	**Moderate**	**All the villagers (including children) consume livestock products**
Veld	SW5-CHS6	Toxic resin deposited on the soil surface has prevented vegetation growth. Inhalation of fumes could be dangerous to people and livestock	**Negligible**	**Area is far from residential area**

4.2.2.5 STEP 5: Assessing the Magnitude of Risk

To determine the Magnitude of Risk for each Hazard Scenario, two factors involved are combined in the Risk Matrix: Probability and Severity of Consequences. The results of this assessment are transposed onto the matrix, which was presented in Section 4.1.2.4 of this Handbook for risks associated with Safety Hazard Scenarios (Table 4-9).

To conduct the risk assessment the same method is used as in the aforementioned section (see Figure 4-2), namely:

(1) For a given Hazard Scenario, the Probability Index assigned will be verified and the corresponding line in the Risk Matrix located.

(2) For the same Hazard Scenario the Severity of Consequences assigned is verified for a receptor and then the corresponding column in the Risk Matrix is located.

(3) The row and column selected determine the magnitude of risk for the Hazard Scenario for this receptor, and the magnitude of risk should be recorded by writing the respective Hazard Scenario code along with the receptor code (for example, LW1-CHS1 -pe) in the cell selected.

(4) The risks associated with each CHS are evaluated after the assessment for each receptor identified has been located on the risk matrix.

(5) The operation is repeated for each of the CHS identified for the site being assessed.

The assignation of codes to contamination hazard scenarios for the purpose of incorporating them into the matrix follows the same criteria applied for safety hazards, namely using the standard code (i.e M1-CHS3) along with a suffix to identify the receptor that could be affected (people, the environment or economic activity).

The suffixes used are the same as those indicated for safety assessments (section 4.1.2.3), namely: '**pe'** where receptors are people; for the environment, **'tf', 'aq'** or '**pa',** for Terrestrial Fauna and Flora, Aquatic Life and Protected or Environmentally Sensitive Areas, respectively; and for economic activities, **'ag', 'ga', 'ac',** and **'to'** for Agriculture, Game Farming and Livestock Activities, Aquaculture/Fishing, and Tourism respectively.

4.2.3 Results of the Risk Assessment for Chemical Contamination

Once the risk assessment for each CHS identified is complete for a given SD/AMS, the Simplified Risk Assessment for chemical contamination finishes with the Contamination Risk Matrices of the SD/AMS being drawn up. In this table, each CHS is codified and situated in a corresponding cell based on the magnitude of its Probability and Severity of Consequences.

By way of example, the table below presents the contamination Risk Matrix for the Abenab Mine site where 3 contamination hazard scenarios have been described (Table 4-16). The table indicates effects on receptors, in this case people, using the suffix 'pe'. In this risk record, each of the risks identified occupies the position determined by the probability and severity ratings arrived at in the assessment.

The assessment shows that the highest potential contamination safety risk arises from the tailings which cover a large part of the mine site and are extensively grazed by livestock. It is unknown whether the grass has taken up any of the contaminants from the tailings, and whether these metals are subsequently found in the meat, organs and milk products of the livestock. This is a situation where the risk may have been overestimated and further work is required to confirm this finding.

Table 4-16: Sample Risk Matrix for Contamination Risk

	SEVERITY OF CONSEQUENCES				
PROBABILITY INDEX	Negligible	Low	Moderate	High	Catastrophic
High	SW5-CHS6pe		LW2-CHS7pe		
Medium					
Low	OP-CHS2pe				
Negligible					

4.3 Summary of Risk Assessment for SD/AMS

Once the Simplified Risk Assessments for Safety (Section 4.1) and Contamination (Section 4.2) have been completed, the respective Risk Matrices for the SD/AMS will be available (Tables 4-9 and 4-16). These tables can be integrated to produce a single matrix that contains all of the risks present in the SD/AMS under assessment – in this case Abenab (Table 4-17). Note this only covers a sample of the safety risks and contamination risks identified at this mine. The completed tables are provided in Annex E.

Table 4-17: Sample risk assessment for safety and contamination of Abenab Mine

	SEVERITY OF CONSEQUENCES				
PROBABILITY INDEX	Negligible	Low	Moderate	High	Catastrophic
High	P1-SHS12ga SW5-CHS6pe	P1-SHS13pe	LW2-CHS7pe	I1-SHS4pe	
Medium	LW2-SHS12pe LW2-SHS12ga	OP1-SHS12ga		OP1-SHS12pe	
Low	OP-CHS2pe				
Negligible		I1-SHS4ga			

This table illustrates clearly and concisely the types of risks present in a given SD/AMS, the magnitude of each, whether they are related to safety or chemical contamination, and the receptors that could be affected by each. It can be seen, for example, that most of the risks at Abenab (based on this worked example) are related to safety issues.

=> In the RARF (Form Matrix(Annex E), the Assessor will record on the same Risk Matrix the contamination and safety risks present at the mine site, in the cells corresponding to the Hazard Scenarios assessed. Thus, a single table will contain all risks associated with safety and contamination for one site.

4.4 Cumulative Risk Assessment

4.4.1 Need for a Cumulative Risk Assessment

Once the Risk Assessment has been performed for a SD/AMS, the Assessor should determine whether, due to the proximity of two or more sites, there are cumulative affects that could affect the risk assessment already performed for each site separately.

Where cumulative effects exist due to the proximity of mine sites, the overall risk could be greater than the individual risk identified for each site. In other words, two sites may each have insignificant risks; when combined however, one or more of the risks present could be significant, leading to these sites being classified as MELs. This is because the proximity of two or more sites can increase the Likelihood of Occurrence of a Hazard Scenario and ultimately could increase the number of receptors affected and the Severity of Consequences upon them.

Risks that should be reviewed for potential cumulative effects include only those Hazard Scenarios that could be affected by the proximity of two or more mine sites. For this reason, the Assessor should review all Hazard Scenarios identified for the SD/AMS being assessed for potential cumulative effects, both in relation to safety and for contamination.

To determine whether it is advisable to conduct a Risk Assessment for Cumulative Effects (CRA) the Assessor should:

- Identify whether the Area of Study of one SD/AMS under assessment overlaps with Areas of Study for other SD/AMS. If there is no overlap of Areas of Study, there is no need for a Cumulative Risk Assessment. If the areas do overlap, however, then a Cumulative Risk Assessment should be performed.
- Determine whether any of the Hazard Scenarios of the mine sites could be affected by the occurrence of Hazard Scenarios from any other site or sites.
- Revise the Area of Study to delimit, if applicable, a new Area of Study that takes into account the combination of Hazard Scenarios.
- Review the assessment conducted for each SD/AMS (Probability and Severity of Consequences), taking into account the way in which sites could affect each other.

For example, for safety risk assessments, if it is determined that two tailings ponds from two different SD/AMS could have a cumulative effect because they are located in the same river catchment and at a distance where the collapse of one could impact the other, then a CRA needs to be performed. To do so, the Assessor must revise the probability of failure of the latter, taking the former into account, determining whether the number of potentially affected receptors changes were both dams to fail, and increasing the Severity of Consequences where appropriate.

Once the assessments of Probability and Severity of Consequences have been reviewed, the risk recorded for each SD/AMS will be confirmed or modified, as applicable.

For Risk Assessments for Chemical Contamination, the Assessor shall assess whether the combination of Hazard Scenarios of different mine sites could affect the receptors present in overlapping areas. For example, where the wind blows particulate matter from two or more nearby sites, the risk components need to be reviewed and adjusted for cumulative effects where applicable.

To simplify the process, the CRA should only be performed once the sites have been assessed individually.

> ***=>*** *In the RARF (Forms CRA-1 to CRA-4)(Annex E) the Assessor shall record information related to the Cumulative Risk Assessment, as applicable.*

4.5 Need to Perform a Detailed Risk Assessment (DRA)

4.5.1 General Aspects

Once the Simplified Risk Assessment (SRA) has been concluded for all Hazard Scenarios associated with the SD/AMS, the Assessor shall determine whether it is necessary to perform a Detailed Risk Assessment (DRA), depending on the degree of certainty of the site's definition as a MEL or non-MEL.

A DRA should be conducted in the following cases:

- For a site with **no significant risks**, but where the Assessor believes that any of the major risks found could be *under-estimated*, and/or where the assessment performed was not conclusive. In this context of uncertainty, there is a risk that a SD/AMS will not be declared a MEL when it should be so declared. The DRA will allow a conclusive assessment to be made by providing correct risk magnitudes.
- For a site with **significant risks**, but where the Assessor believes that all significant risks found could be *over-estimated*, and/or where the assessment performed was not conclusive. This could lead to a SD/AMS being erroneously classified as a MEL, which may

imply future investments in remediation that are actually unnecessary – as for example the findings at Abenab relating to the toxicity or not of the tailings (see above). The DRA will allow a conclusive assessment to be made of the real magnitude of risks that were initially classified as significant.

The Assessor should make a concerted effort throughout the process to minimize uncertainty in the SRA of all Hazard Scenarios, which includes collecting the greatest amount of information available and collecting all field information required for the SRA. It is advisable that the Assessor request the assistance of MME/GSN experts for areas in which the Assessor is not entirely sure of the assessment. In some cases the uncertainty may relate to a lack of analytical data (e.g. on water quality, soil, forage plants etc), which can be obtained though a relatively inexpensive procedure (sampling and analysis) to confirm the toxicity or otherwise of the medium in question; this step would be the equivalent of a Tier 1 assessment referred to in section 6.5. In those cases the Assessor should procure professional services to produce this information in order to avoid the need for a DRA. On the basis of the new information received, the Assessor will then be able to revise the risk assessment finding.

4.5.2 Process to Determine the Need for a DRA

The process to determine whether a DRA is called for begins with the Risk Matrix of a SD/AMS, which gathers together the results of the SRA for safety and chemical contamination (Table 4-17). This matrix contains all Hazard Scenarios based on their risk magnitude. Each of the cells contains an alphanumeric code as per the coding system set out in Chapter 2 (Table 4-18).

Table 4-18: Identification codes for Risk Matrix cells

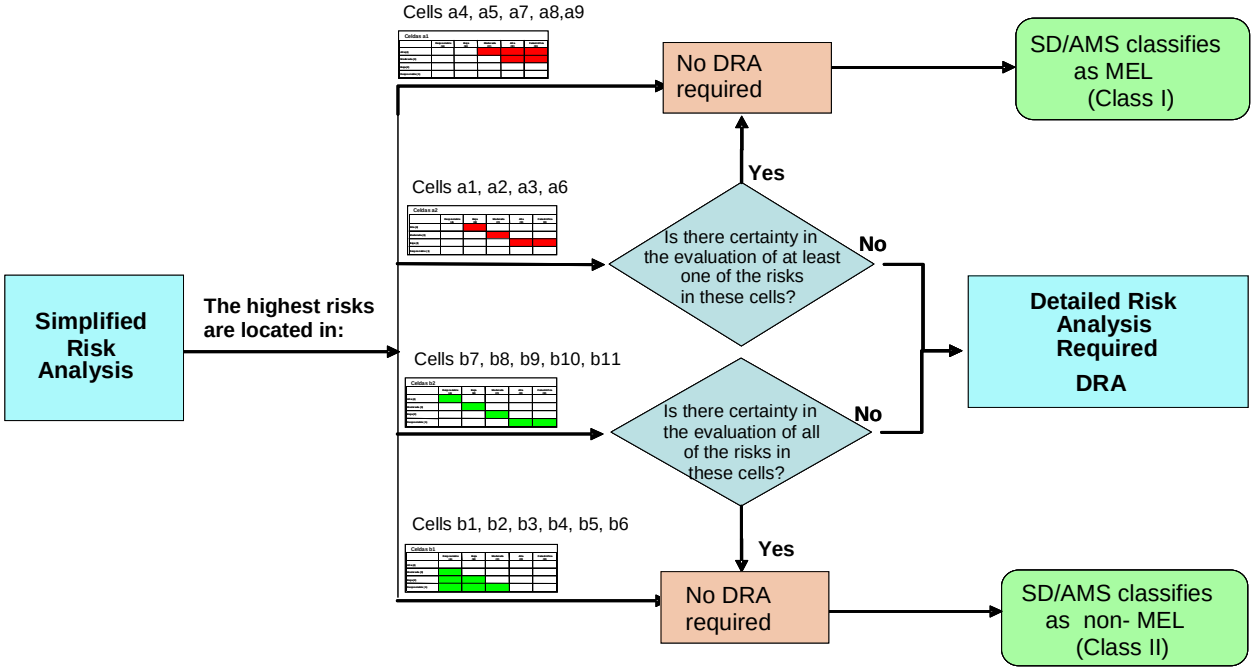
Significant risks correspond to those with greater magnitude and are shown in red in the matrix.

	SEVERITY OF CONSEQUENCES				
PROBABILITY	Negligible (A)	Low (B)	Moderate (C)	High (D)	Catastrophic (E)
High (4)	b7	a1	a4	a7	a9
Medium (3)	b4	b8	a2	a5	a8
Low (2)	b2	b5	b9	a3	a6
Negligible (1)	b1	b3	b6	b10	b11

Non-significant risks, on the other hand, are of lesser magnitude and are shown in green on the matrix (Table 4-18). At this stage of the process, the location of risks within the risk matrix is important, as the positions will determine whether there is a need to perform a Detailed Risk Assessment (DRA) or whether the SRA was sufficient to establish the status of a mine site as a MEL

or non-MEL. For this purpose, Figure 4-4 shows the steps that need to be taken to reach either conclusion. Specifically, the process consists of reviewing the Risk Matrix of the SD/AMS from highest to lowest magnitude risk, as shown below.

Figure 4-4: Classifying a SD/AMS based on Risk



- In the SD/AMS Risk Matrix, the Assessor should note when the risk with the greatest magnitude is located in cells **a4, a5, a7, a8 or a9** (significant risks). In this case the SD/AMS is classified as a MEL and therefore there is no need to perform a DRA.
- If however, the SD/AMS Risk Matrix displays a risk with the greatest magnitude located in **b1, b2, b3, b4, b5 or b6** (not significant), then the SD/AMS is classified as a non-MEL and therefore there is no need to perform a DRA.
- Where the risk with the highest magnitude is located in cells **a1, a2, a3 or a6,** however, the Assessor should determine whether the assessment is conclusive for at least one of the risks located in these cells.
    - If there is enough certainty in the assessment of at least one of these risks — if the Assessor is confident that one of these risks is truly significant, then the SD/AMS will be classified as a MEL and therefore the SRA concludes at this point and there is no need for a DRA.

- If however, all of the risks located in these cells are inconclusive, then it will be necessary to perform a DRA to assess these risks one by one (Chapters 5 or 6). The DRA is then performed for each risk occupying the corresponding position on the matrix, one by one. When any one of these is confirmed to be a significant risk, the uncertainty is resolved and the SD/AMS will be classified as a MEL, and the DRA will not have to be completed for risks not yet assessed.

- Finally, if the risks with the greatest magnitude on the SD/AMS Risk Matrix are located in cells **b7, b8, b9, b10 or b11**, this means that the site only has non-significant risks. However, in this case it is necessary to analyze the degree of certainty to ensure no error has been made. It is therefore necessary to analyze the conclusiveness of all risks situated in cells b7 to b11.
  - If in the Assessor's judgment, the assessment of all risks is conclusive, then the SD/AMS is classified as a non-MEL.
  - On the contrary, if any of the risks situated in cells b7 to b11 display any significant degree of uncertainty, then a DRA is called for (Chapters 5 or 6). The DRA will be applied to each risk, one by one. Where any of these risks is shown to be a significant risk (red on the matrix), then conclusive evidence exists that the SD/AMS is a MEL. If, however, after all risks are assessed, none of these is found to be significant, then the SD/AMS will be classified as a non-MEL.

To summarize, by performing this review (Figure 4-4), the Assessor can determine whether it is necessary or not to carry out a DRA (Chapters 5 or 6), or whether the final result of the risk assessment should be recorded for the mine site, classifying it as a MEL or non-MEL, for a global prioritization (Chapter 7).

=> *In the RARF (Form Classify)(Annex E) the Assessor will record the analysis performed to determine whether or not any of the risks assessed require more detailed assessment (Figure 4-5). In the respective cells, the Assessor can insert the corresponding rationale and underline the conclusion reached. If the result is positive, in other words, where a DRA needs to be performed, the RARF has an attached form (Form App 1_DRA)(Annex E) to identity which Hazard Scenarios merit a detailed assessment, along with the objectives and scope of this process.*

Modeling the resuspension of dust particles in mining districts of Namibia and Zambia

Bohdan Kříbek, Vladimír Majer and Ilja Knésl
Czech Geological Survey

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Imasiku Nyambe
Department of Geology, School of Mines, University of Zambia

Frederik Kamona and Benjamin Mapani
University of Namibia, Department of Geology

IUGS International Union of Geological Sciences

UNIVERSITY OF ZAMBIA

UNIVERSITY OF NAMIBIA

United Nations Educational, Scientific and Cultural Organization







OUTLINE

- Methods
- Modeling of total dust fallout from a tailings pond at Rosh Pinah, Namibia
- Modeling PM_{10} particles resuspension from cement and lime works at Ndola, Zambia
- Modeling of dust fall out around the Tsumeb Smelter, Namibia

METHODS

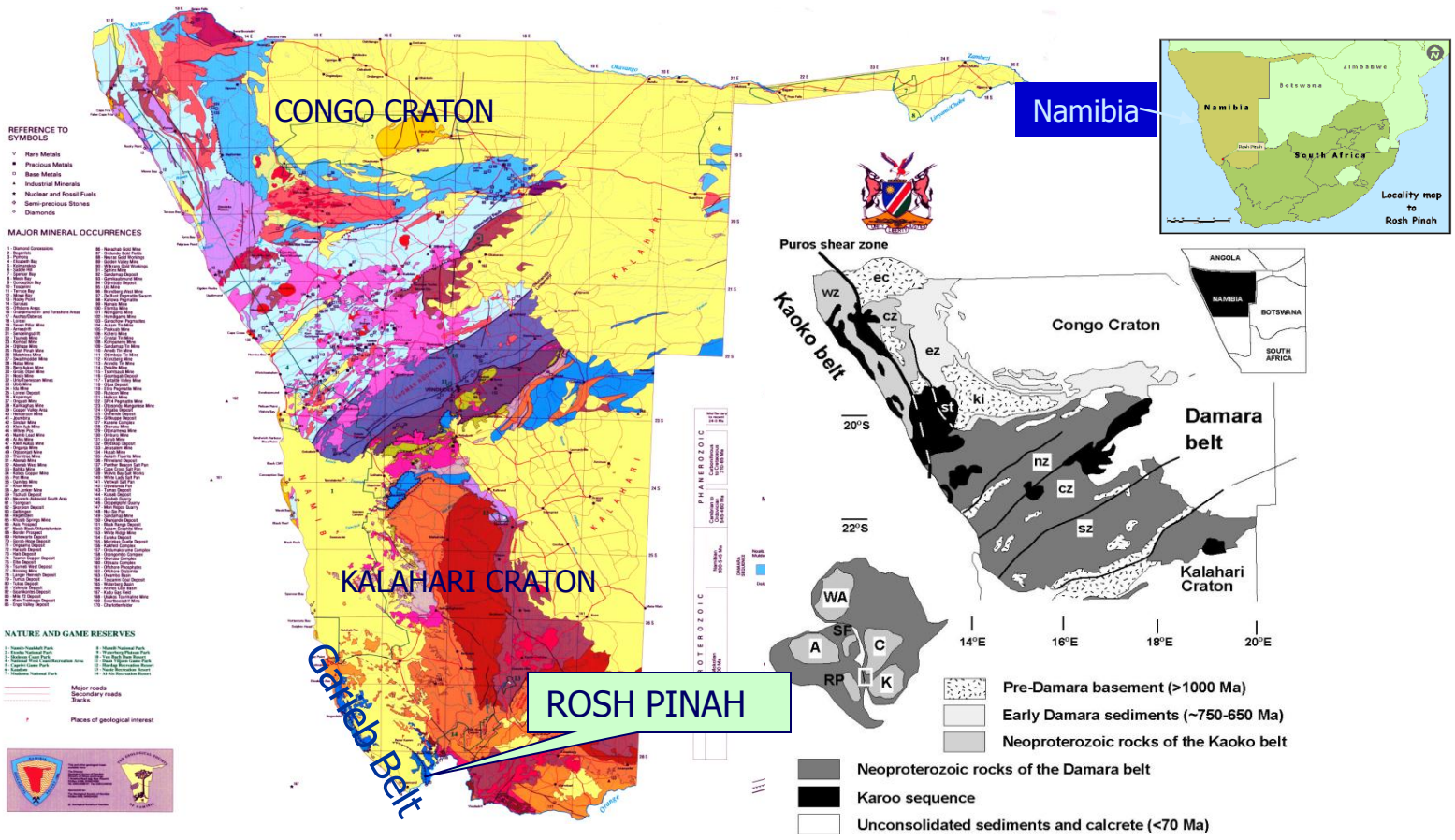
The gausian model based on the stationary solution of turbulent diffusion (SYSMOS´97; www.chmi.cz/uoco/prj/model/index.html) was used for modeling of concentration fields of resuspended dust particles from a tailing pond, smelter and cement works http://

Imput data for further calculations:

- Digital terrain model of the area studied
- Dust source coordinates and specification
- Size distribution and specific gravity of dust
- Weather data (wind direction, temperature, humidity, atmospheric stability)

Verification of the results of modeling: Dust particles sampling using portable equipment or soil sampling

MODELING OF DUST FALL OUT FROM TAILINGS DAM: ROSH PINAH EXAMPLE





Tailings dam complex at Rosh Pinah: Area of 60 hectars, heigh of tailings dam: 16-26 m



Results of multi-spectral imagery of the LANDSAT system in red spectral band
(courtesy by the Rosh Pinah Zinc Corporation (Pty) Ltd., and Kumba Resources)



METEOROLOGICAL MODELING OF DUST FALLOUT, ROSH PINAH

The objective of the modelling was to assess the efficiency of the tailing dam surface moistening and, to compare results of modeling with results of the environmental-geochemical survey of soil contamination.

Modeling of dust fallout from the tailings dam was carried out in two variants:

(1) for a dry surface of the tailing ponds (situation in the past),

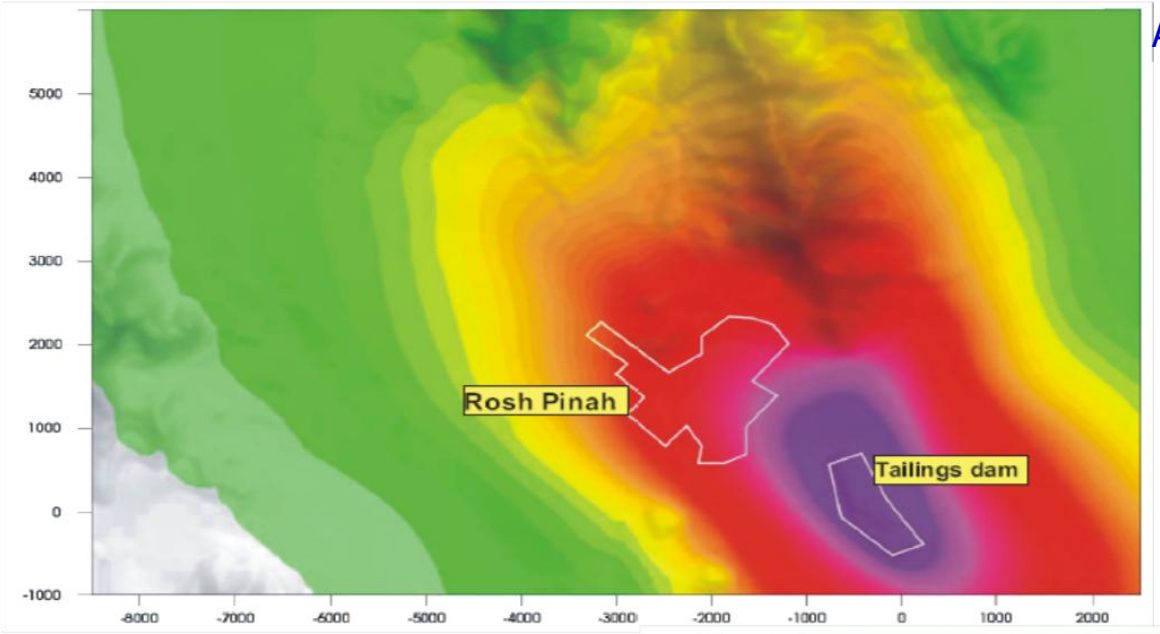
(2) for the present situation, where approximately two thirds of the tailings dam surface is moistened.





Moistening of the tailings dam surface

RESULTS OF METEOROLOGICAL MODELING: Fields of annual dust fallout data



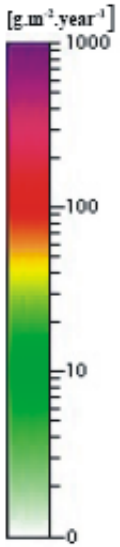
A. Without moistening of the tailings dam surface (situation in the past)

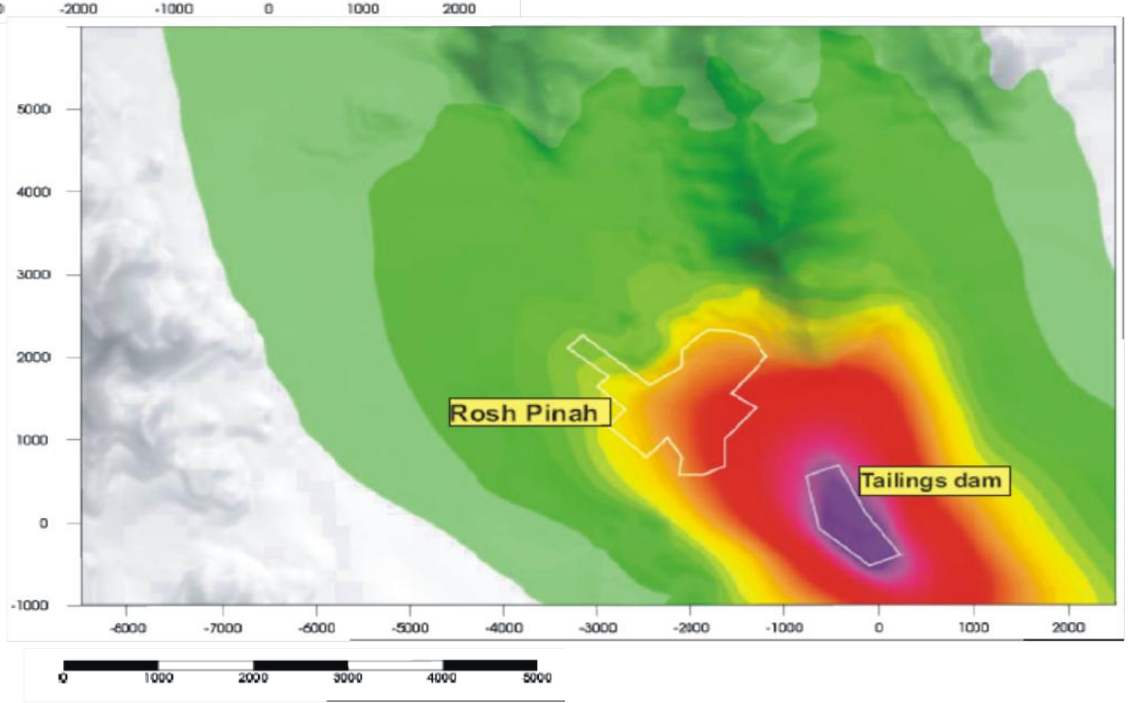
B. With moistening of the tailings dam surface (present situation)

Yearly Rosh Pinah dust fall out:

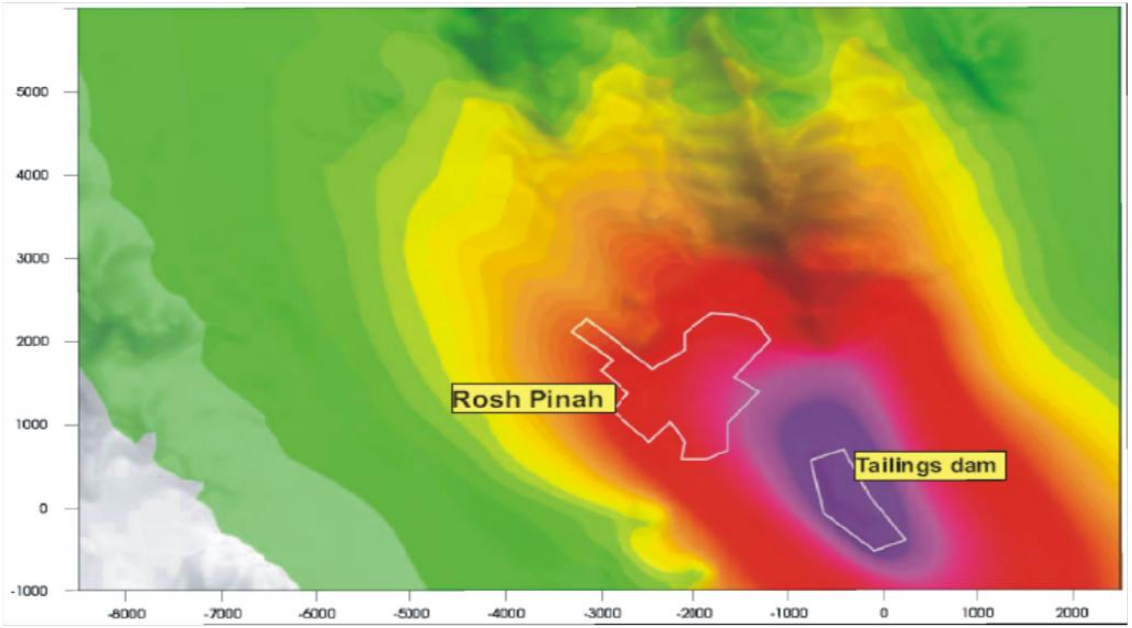
Without moistening:
80-400 $g.m^{-2}.year^{-1}$

With moistening:
20-100 $g.m^{-2}.year^{-1}$





RESULTS OF METEOROLOGICAL MODELLING: Fields of averrage dust particles concentration



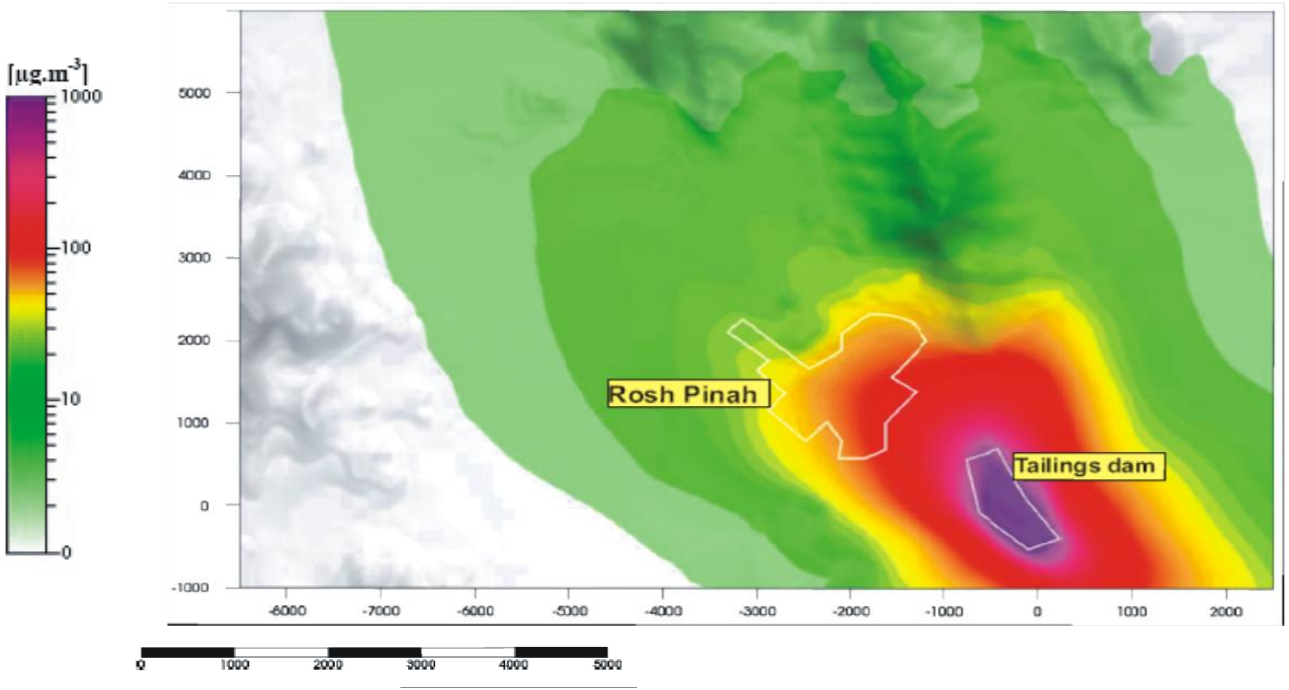
A. Without moistening of the tailings dam surface (situation in the past)

B. With moistening of the tailings dam surface (present situation)

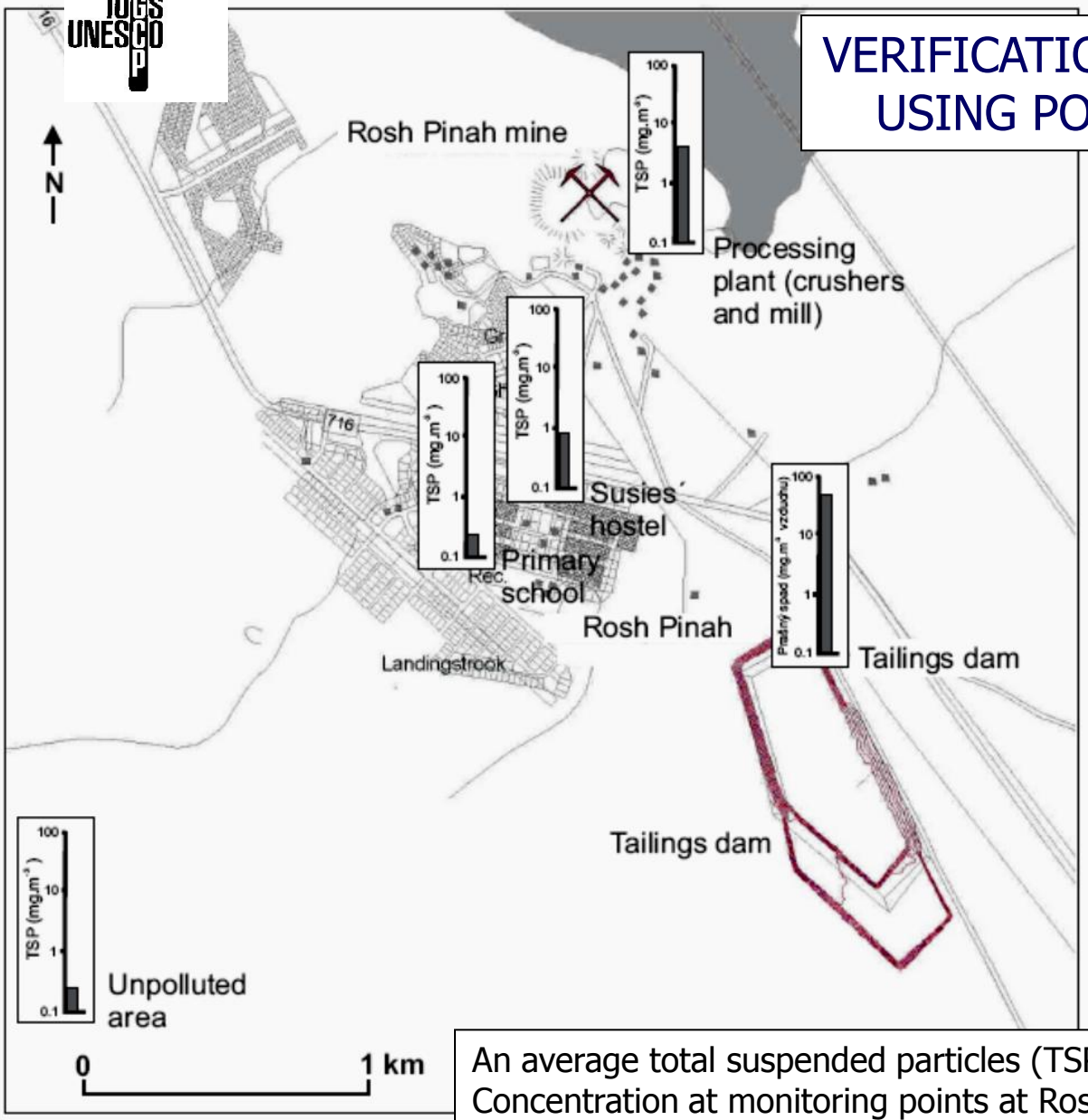
Average yearly concentration of dust in the Rosh Pinah town :

Without moistening: 0.35-2.43 $mg.m^{-3}$

With moistening: 0.25-0.95 $mg.m^{-3}$

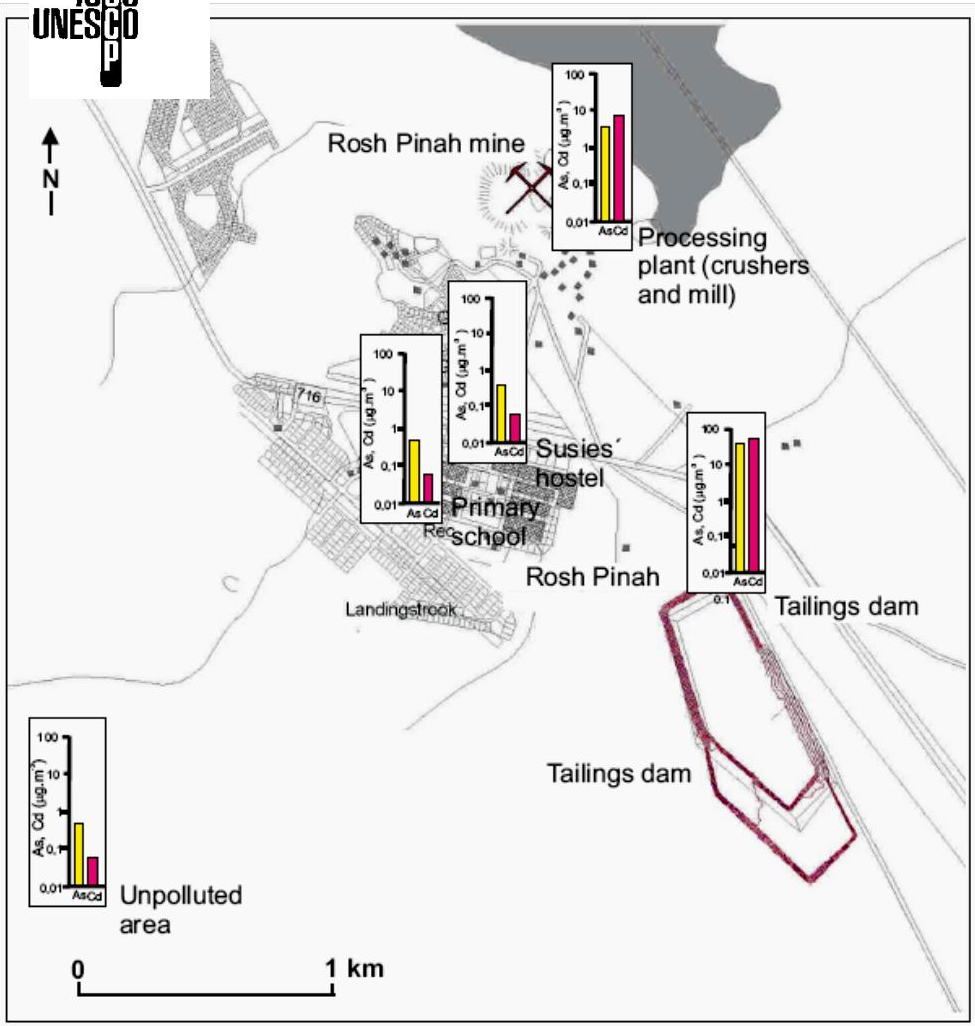


VERIFICATION OF MODELING RESULTS USING PORTABLE DUST SAMPLERS



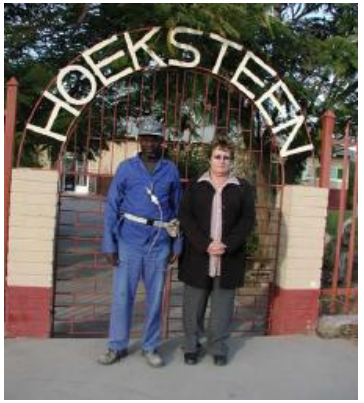


An average total suspended particles (TSP, in $mg.m^{-3}$ air) Concentration at monitoring points at Rosh Pinah.



WHO air guidelines for total suspended particles and TSP data from Rosh Pinah (24-hours average concentration)

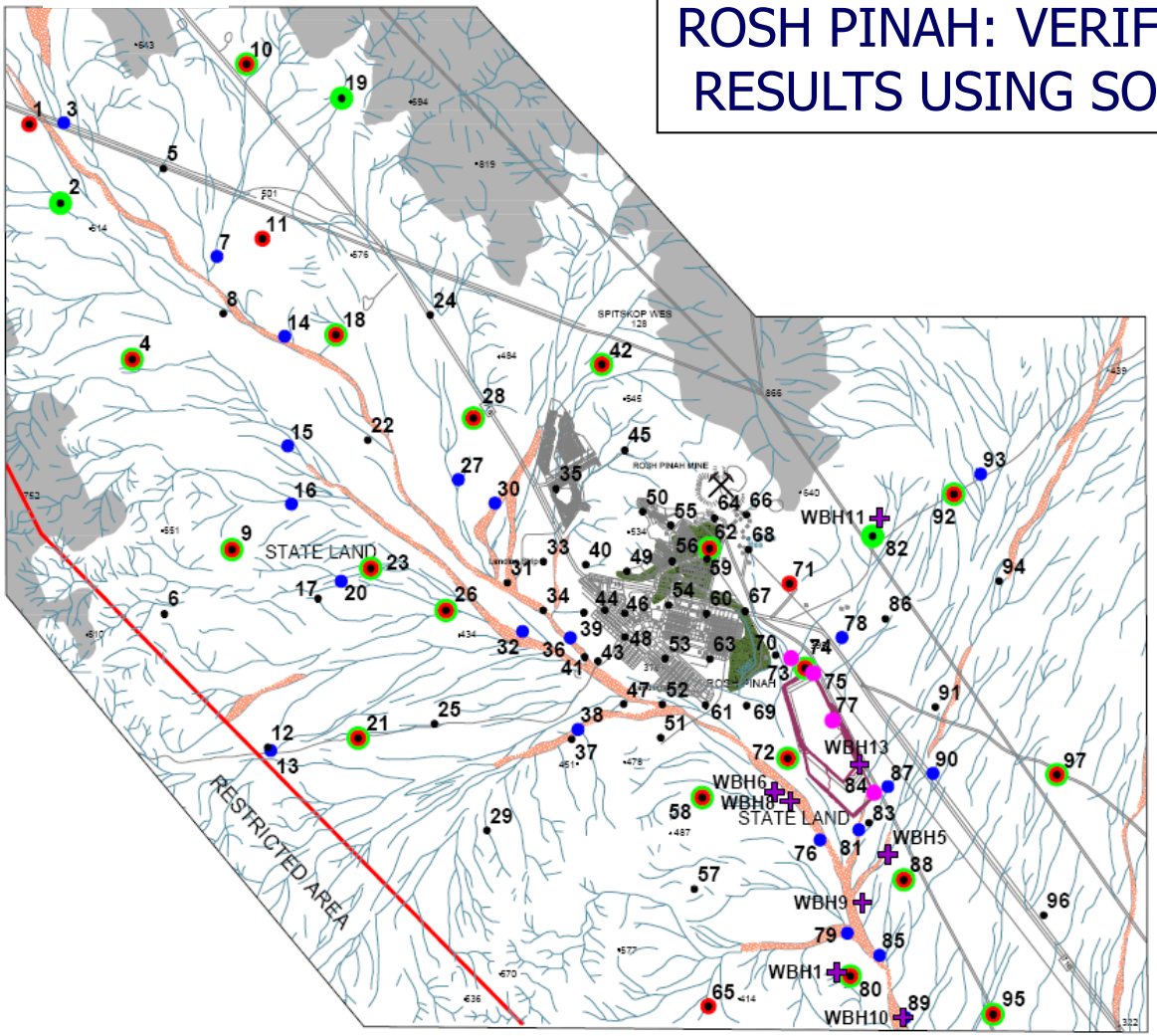
Rosh Pinah, Tailings area	46.65 $mg.m^{-3}$
Rosh Pinah, Processing plant	4.34 $mg.m^{-3}$
Rosh Pinah, Susies´Hotel	0.81 $mg.m^{-3}$
Rosh Pinah,Primary School	0.24 $mg.m^{-3}$
Rosh Pinah, Background	0.25 $mg.m^{-3}$
WHO guideline	0.30 $mg.m^{-3}$





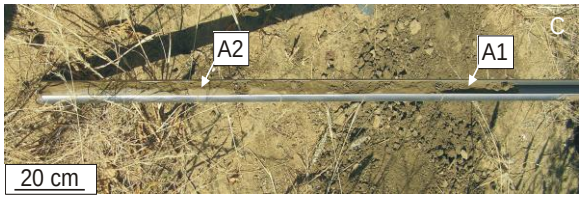
An average concentration of **arsenic and cadmium** in dust particles (in $\mu m.m^{-3}$) at monitoring points.

ROSH PINAH: VERIFICATION OF MODELING RESULTS USING SOIL SURVEY

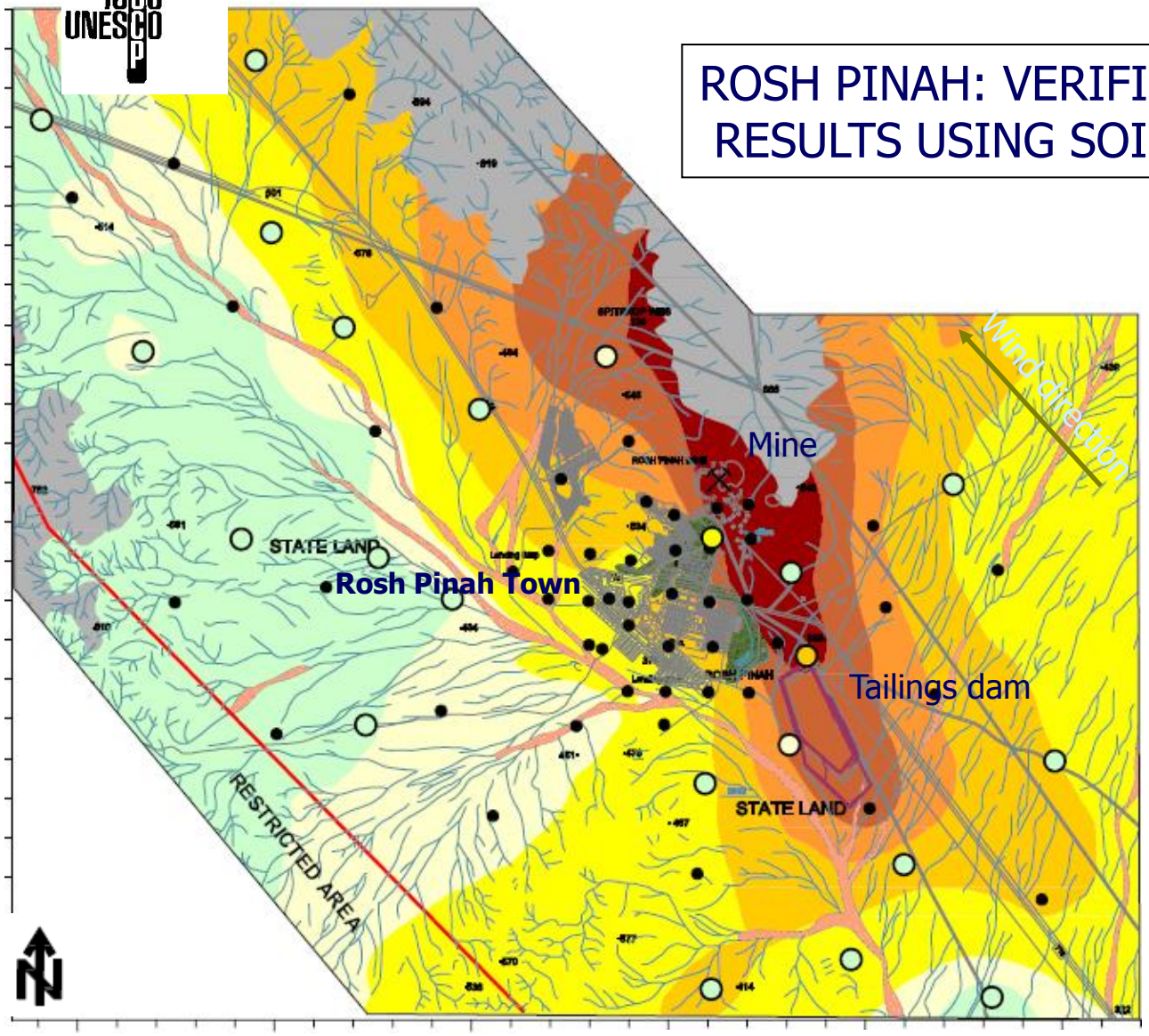


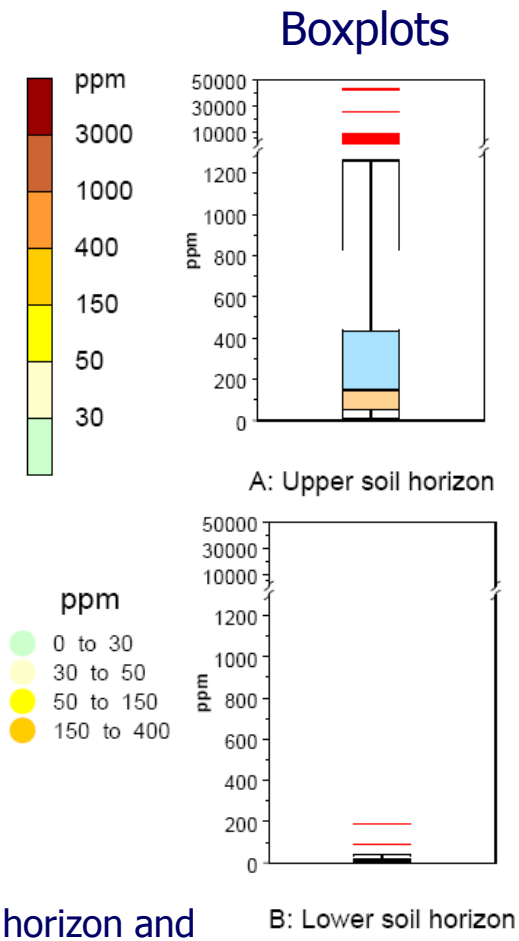
Location of sampling sites





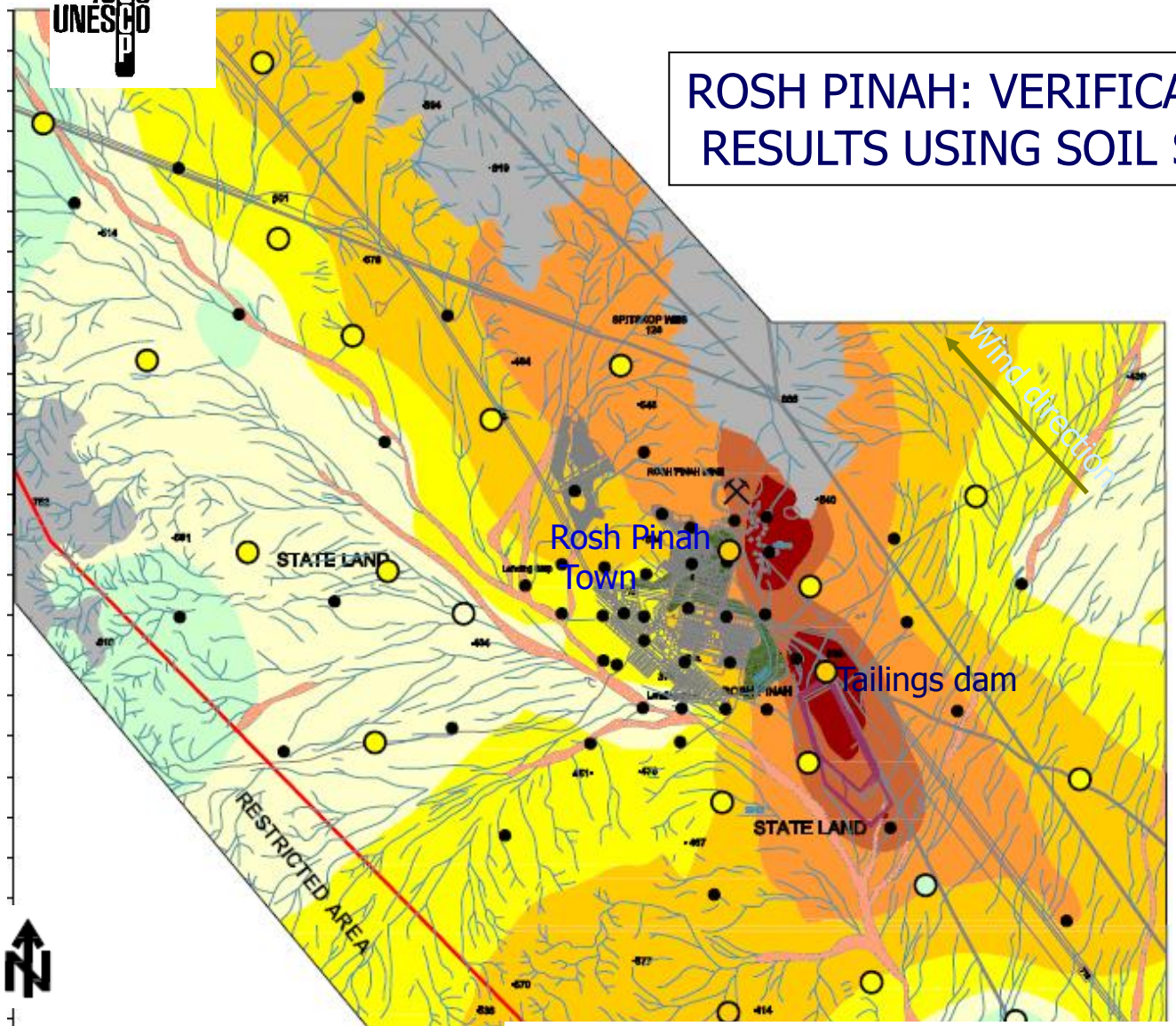
ROSH PINAH: VERIFICATION OF MODELING RESULTS USING SOIL SURVEY



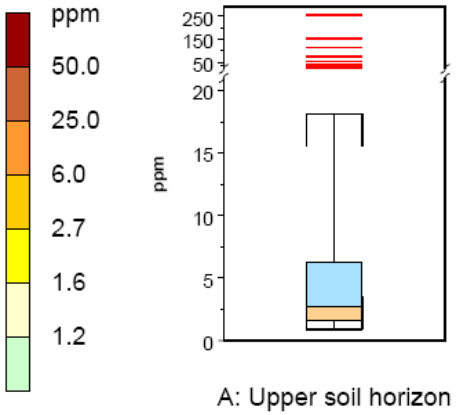


Contour map of Pb values in the upper soil horizon and classed point map of Pb values in the lower soil horizon

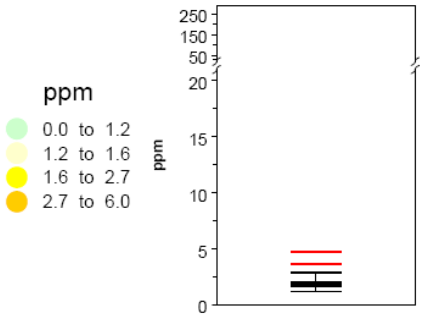
ROSH PINAH: VERIFICATION OF MODELING RESULTS USING SOIL SURVEY



Boxplots



A: Upper soil horizon



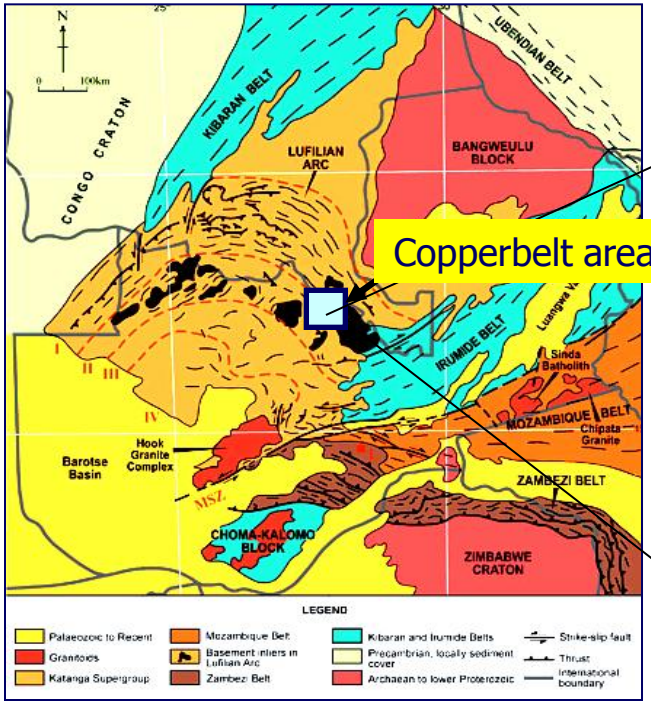
B: Lower soil horizon

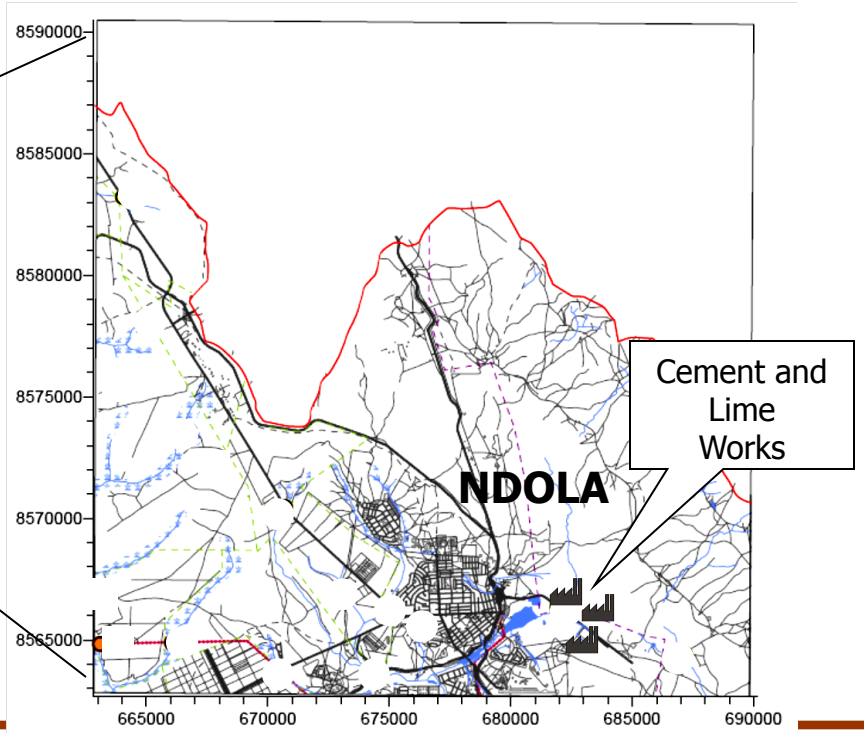
Contour map of As values in the upper soil horizon and classed point map of As values in the lower soil horizon

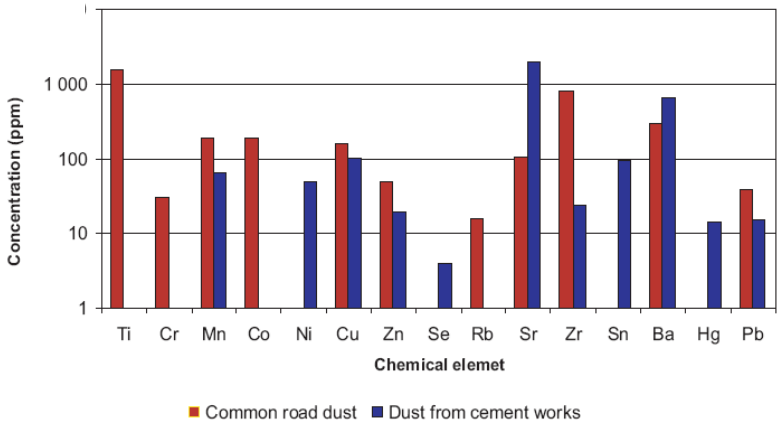
NDOLA AREA (ZAMBIA): FALLOUT FROM CEMENT AND LIME WORKS

Dust fallout from cement and lime works located at the eastern periphery of the city of Ndola represents significant source of dust contamination

GEOLOGICAL MAP OF ZAMBIA







Chemical composition of the common road dust at Ndola and chemical composition of dust collected on vegetation leaves close to the Lafarge Cement Works at Ndola, Zambia.

Chemical element (wt.%)	Road dust	Cement and lime dust
Potassium	0.29	<LOD
Calcium	1.87	**72.1**
Strontium	0.01	**0.19**
Titanium	0.15	<LOD
Iron	1.78	0.08
Nickel	<LOD	**0.005**
Selenium	<LOD	**0.004**
Lead	0.004	0.001
Mercury	<LOD	**0.002**

LOD: Limit of detection

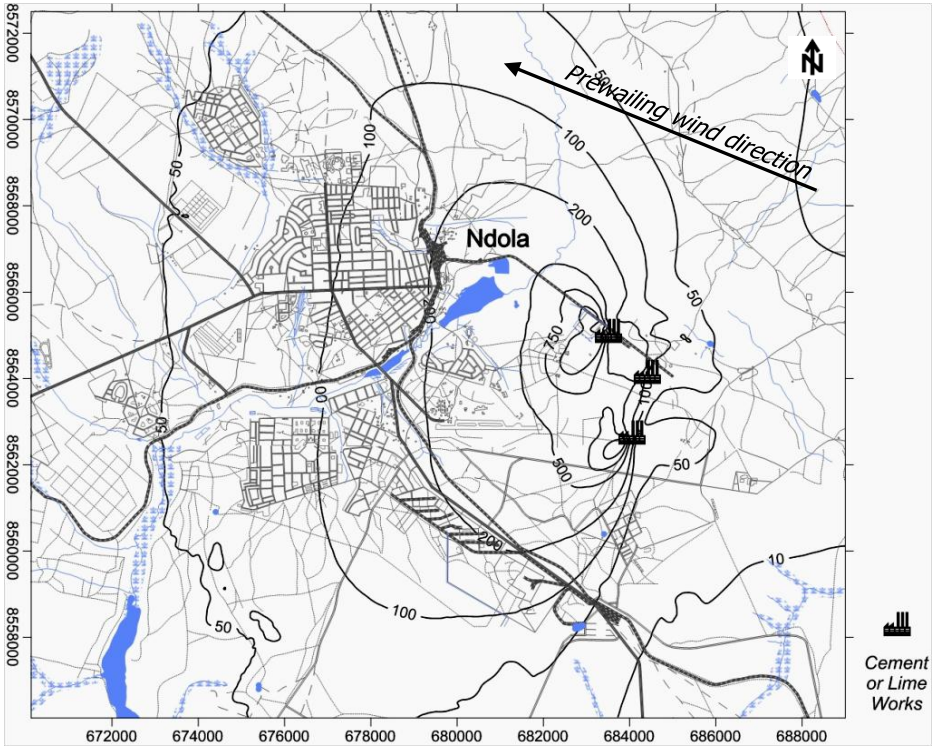


Dust fallout from the Ndola Lime Ltd. Lime works near the city of Ndola.

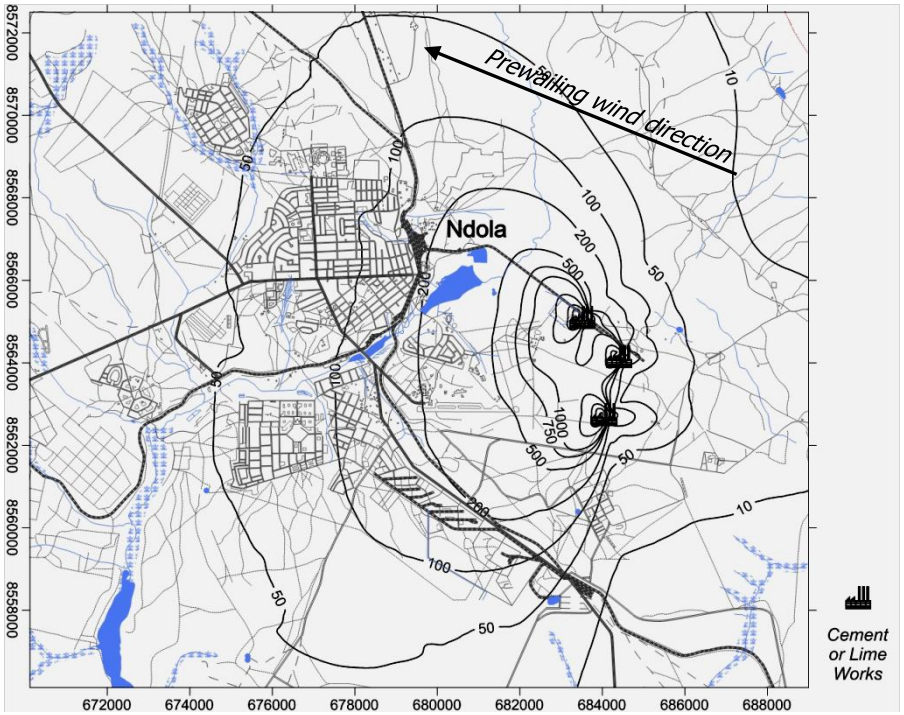


Vegetation in the neighbourhood of cement works of Lafarge Co., Ndola area.

MODELS OF DUST FALOUT AND RESUSPENDED PM_{10} PARTICLES CONCENTRATIONS FROM CEMENT AND LIME WORKS, NDOLA AREA, THE COPPEBELT PROVINCE, ZAMBIA



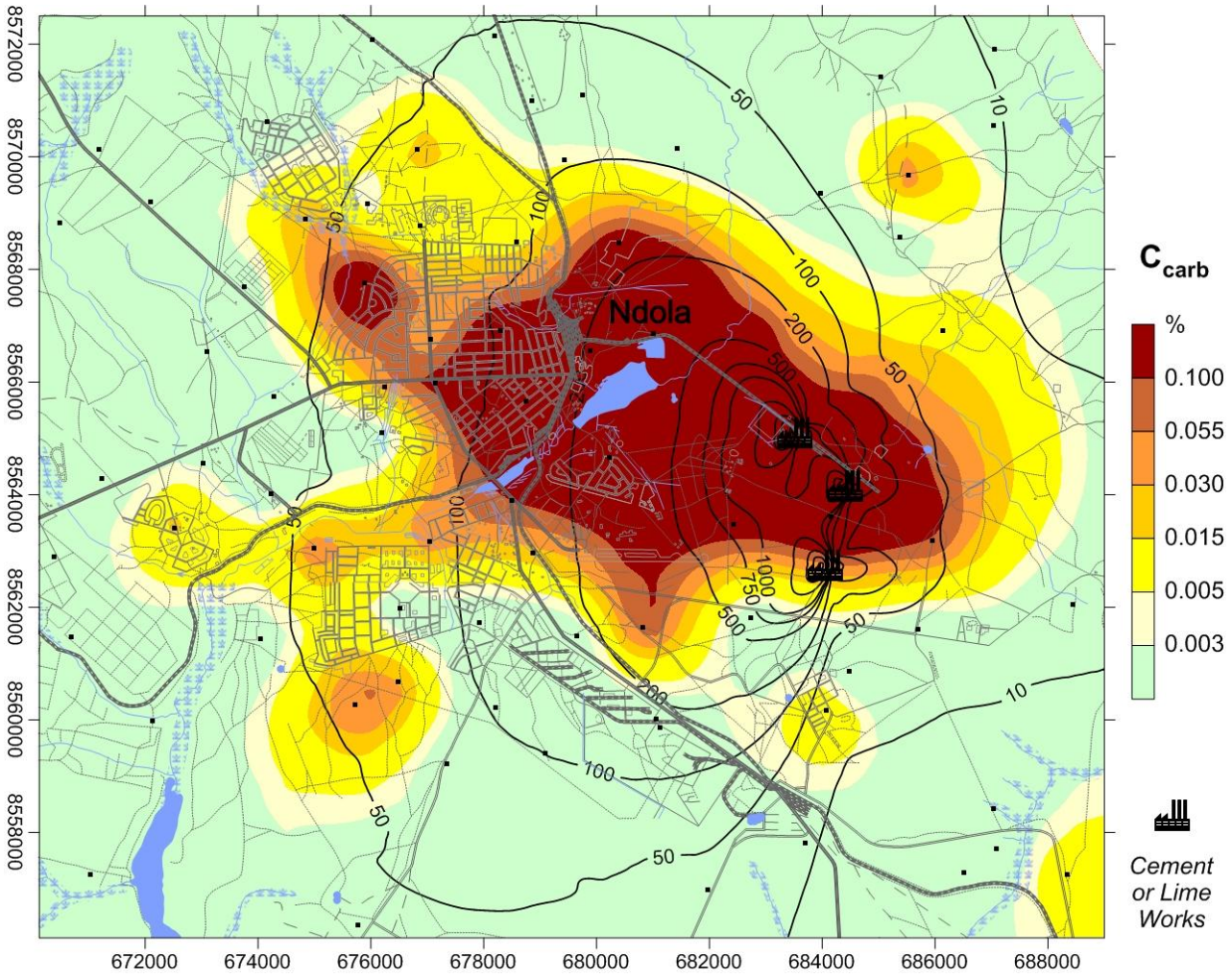
A model of annual dust fallout (in mg. m^{-2} soil)

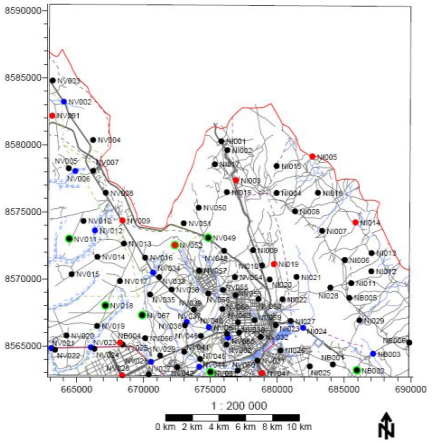


A model of concentration of MP_{10} (in $\mu g.m^{-3}$ air)

VERIFICATION OF MODELING RESULTS, NDOLA

Annual dust fallout (in mg. m^{-2} soil) *vs.* carbonate carbon content in surface soil

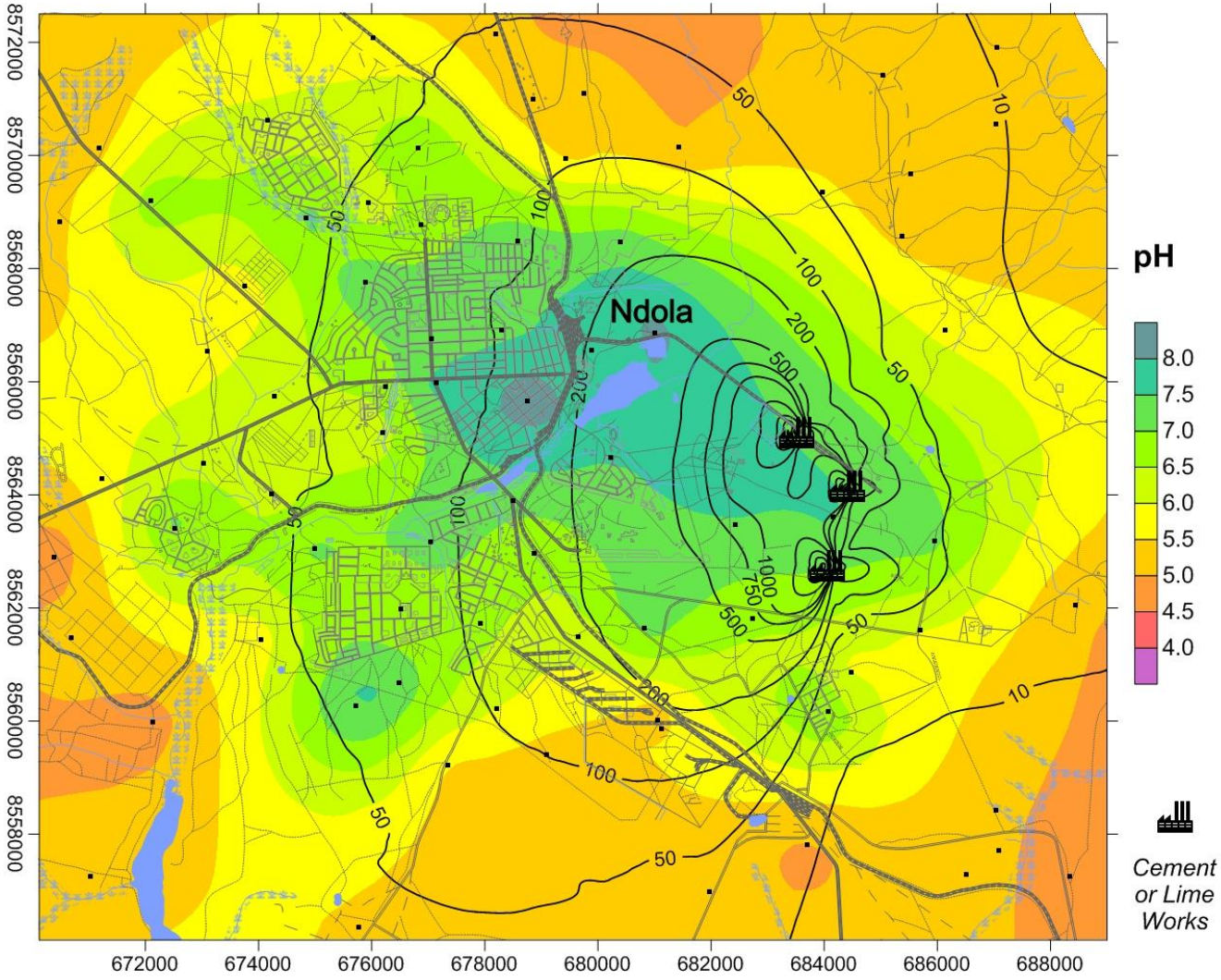


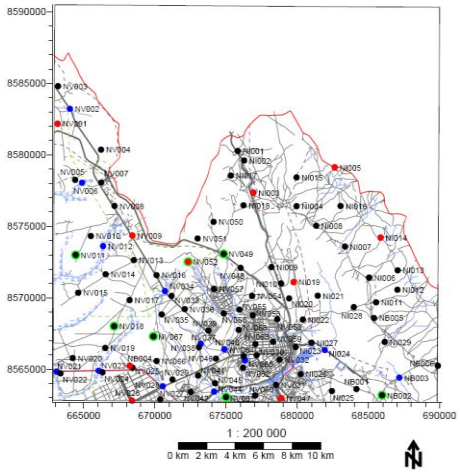


Sample location map

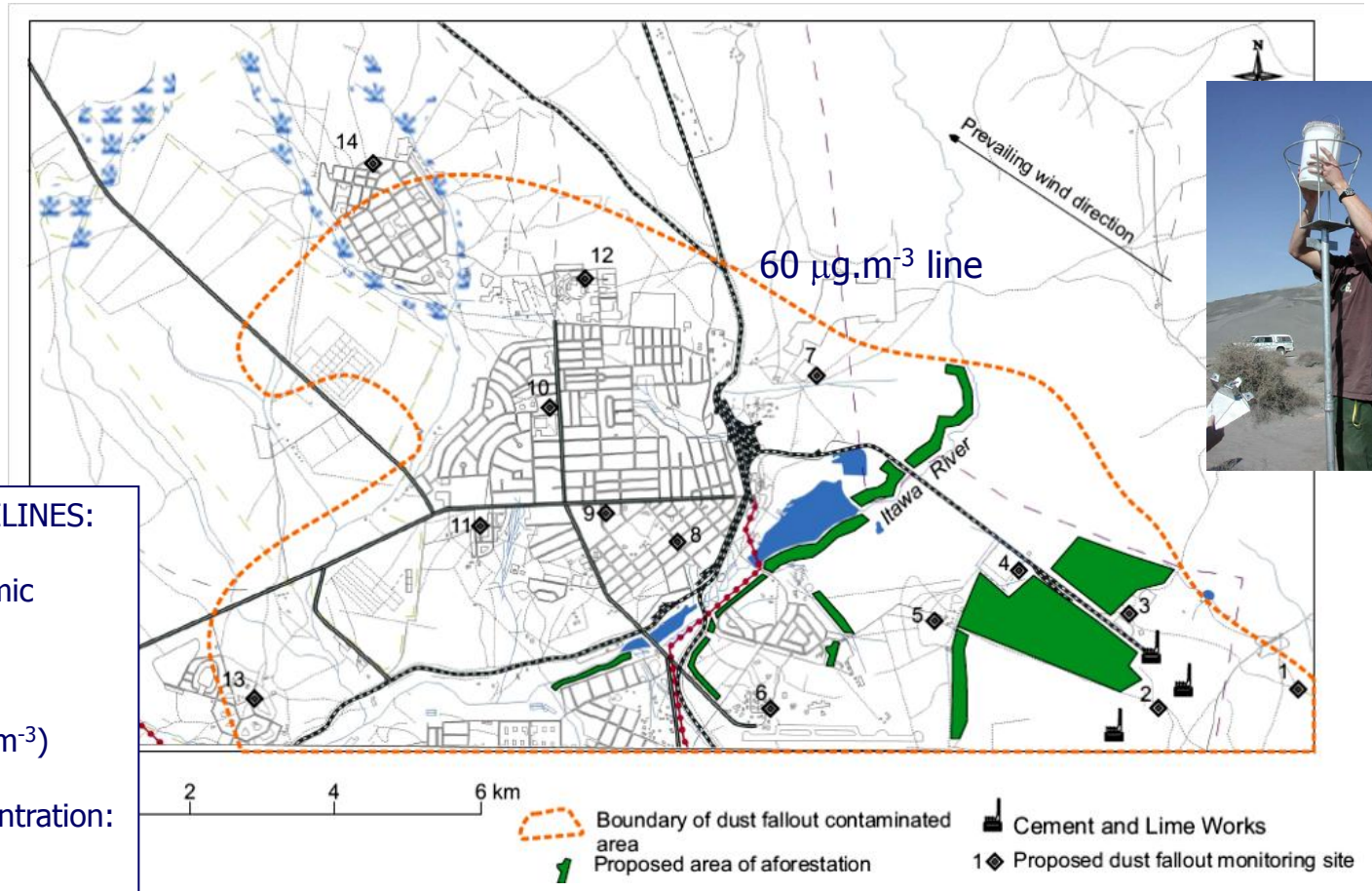
VERIFICATION OF MODELING RESULTS, NDOLA

Annual dust fall (in mg. m^{-2} soil) *vs.* pH values of the surface soil





Sample location map





WHO (1999) AIR GUIDELINES:

Particles with aerodynamic diamentes less than 10 μm (PM_{10})

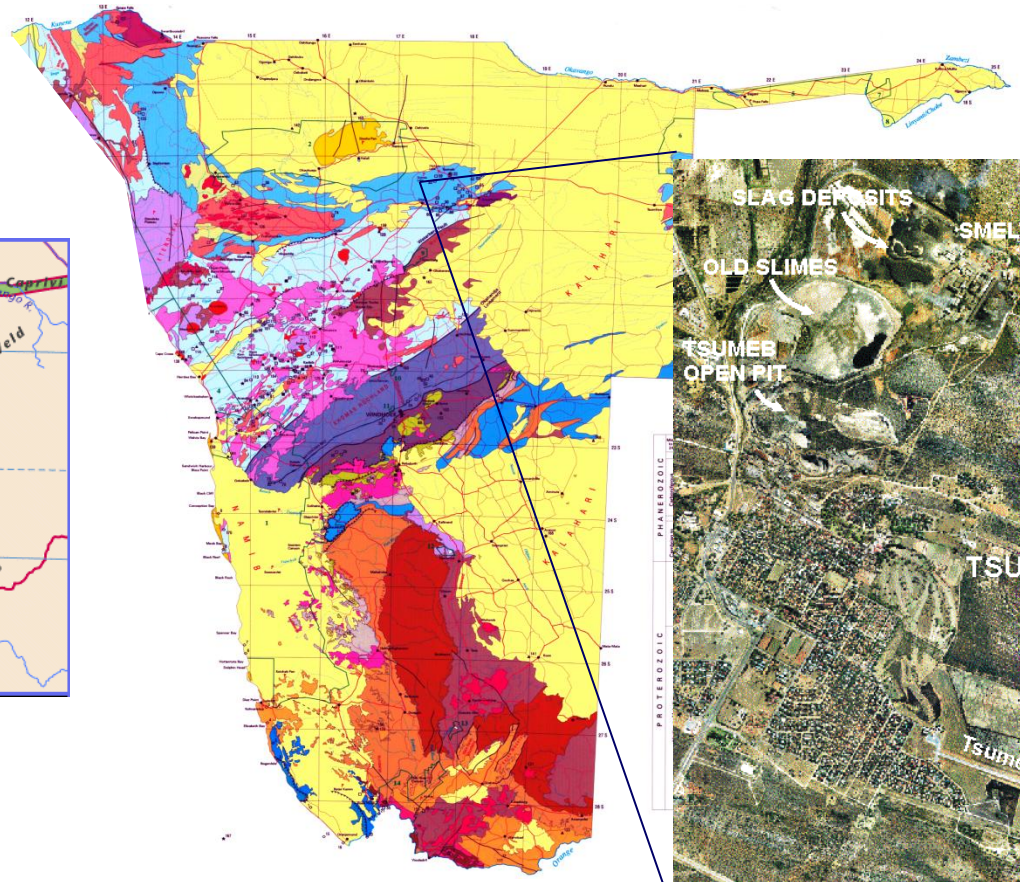
Annual Average: 60 $\mu g.m^{-3}$)

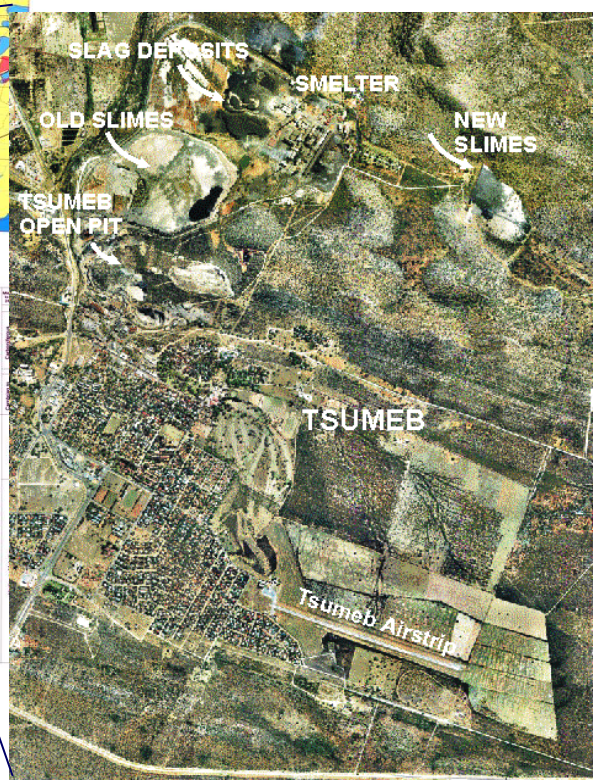
24-hours average concentration: 180 $\mu g.m^{-3}$

Proposal for the **dustiness control system** at Ndola and proposal for the **afforestation** of the eastern limits of the Ndola Town aimed at reducing the solid emissions from cement and lime works

TSUMEB AREA (NAMIBIA): MODELING DUST FALLOUT FROM SMELTER

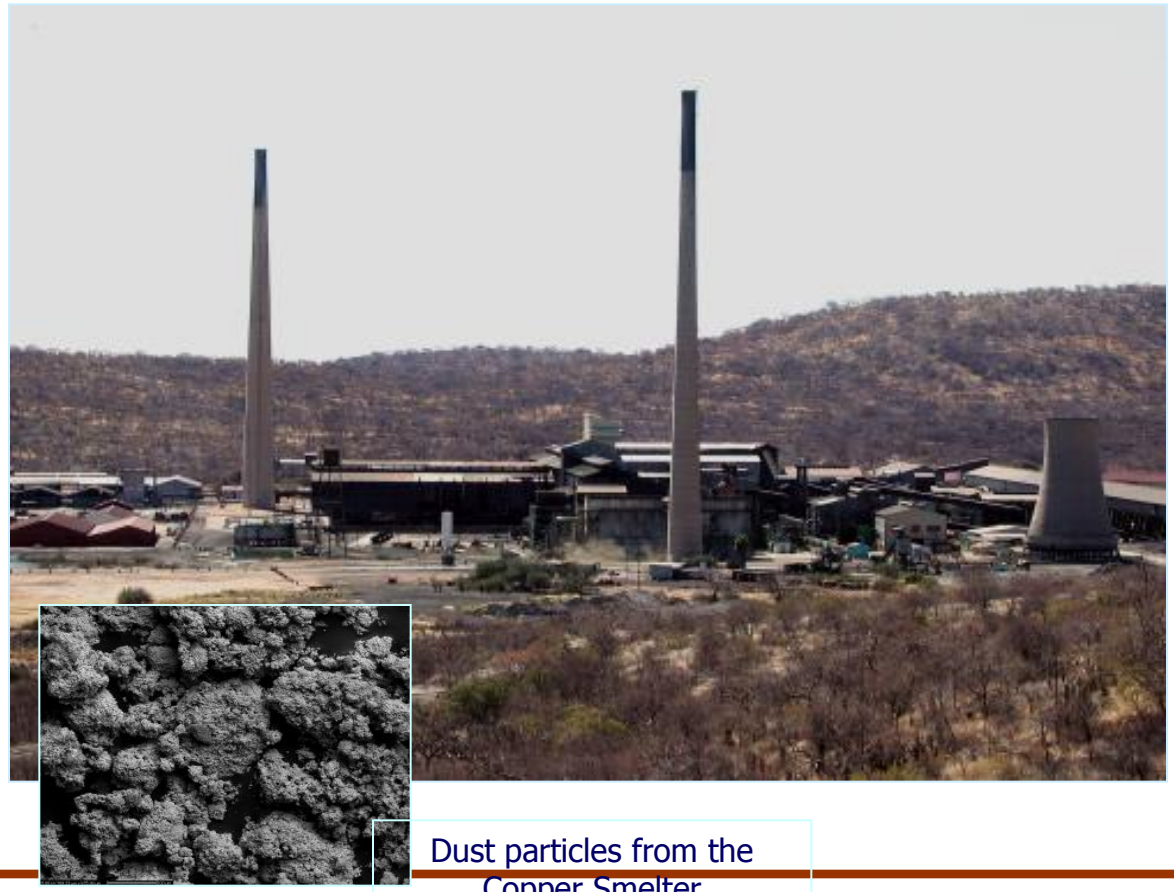






SOURCES OF ANTHROPOGENIC CONTAMINATION

Solid and Gasseous Emissions From the Copper and Lead Smelter



Dust particles from the Copper Smelter

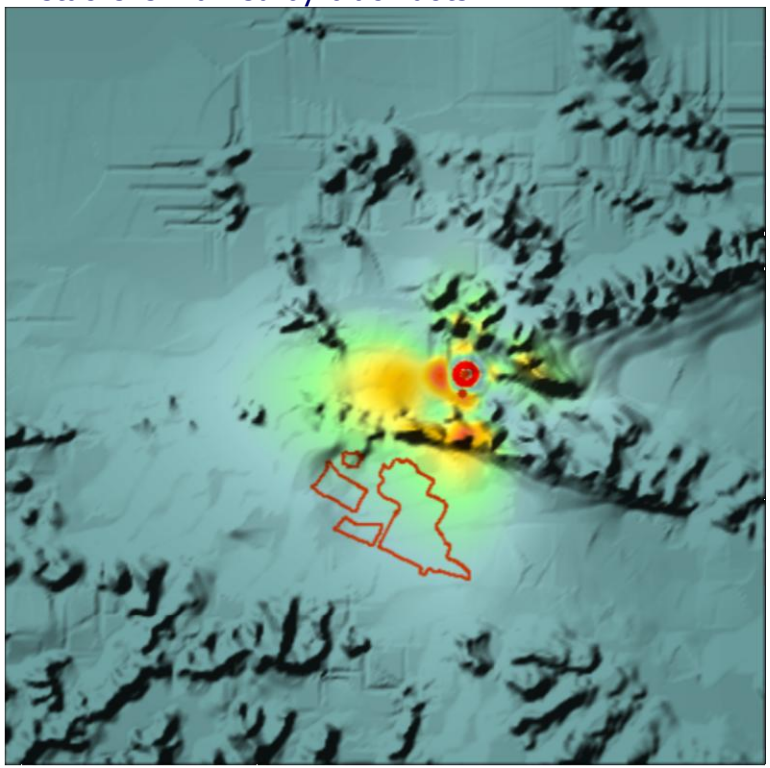
Estimated tonnage of pollutants:
250 tones/year
(150 tones of SO_2/year)

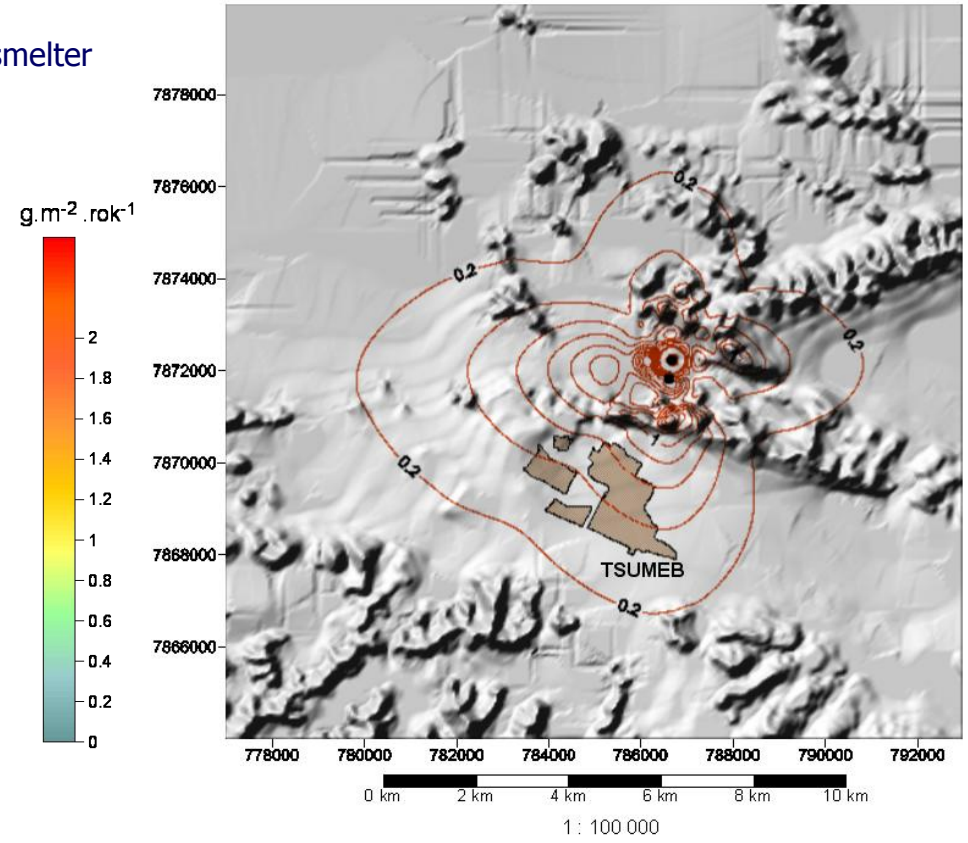
Particles of dustfall contain up to:

5.6 wt. % Cu
0.5 wt. % Pb
0.3 wt. % Pb
0.3 wt % Zn
5.6 ppm As
3800 ppm Cd
66.7 ppm Hg
69 ppm Mo
51.3 ppm Tl
8.5 ppm Ge

RESULTS OF MODELING: Annual dust fall from a smelter

Numerical model of the dust dispersion halo around the Tsumeb Smelter.Isolines represent annual average concentrations of dust fall (in g.m^{-2}). The position of smelter stacks is marked by black dots.

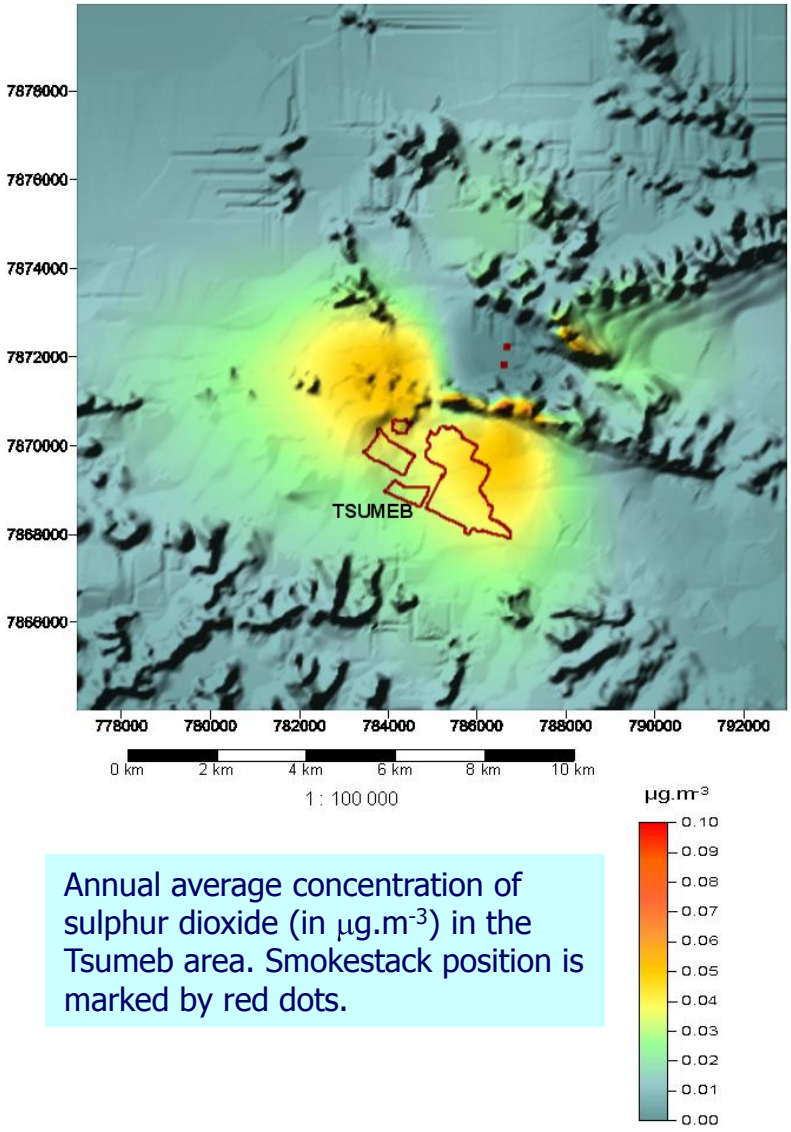




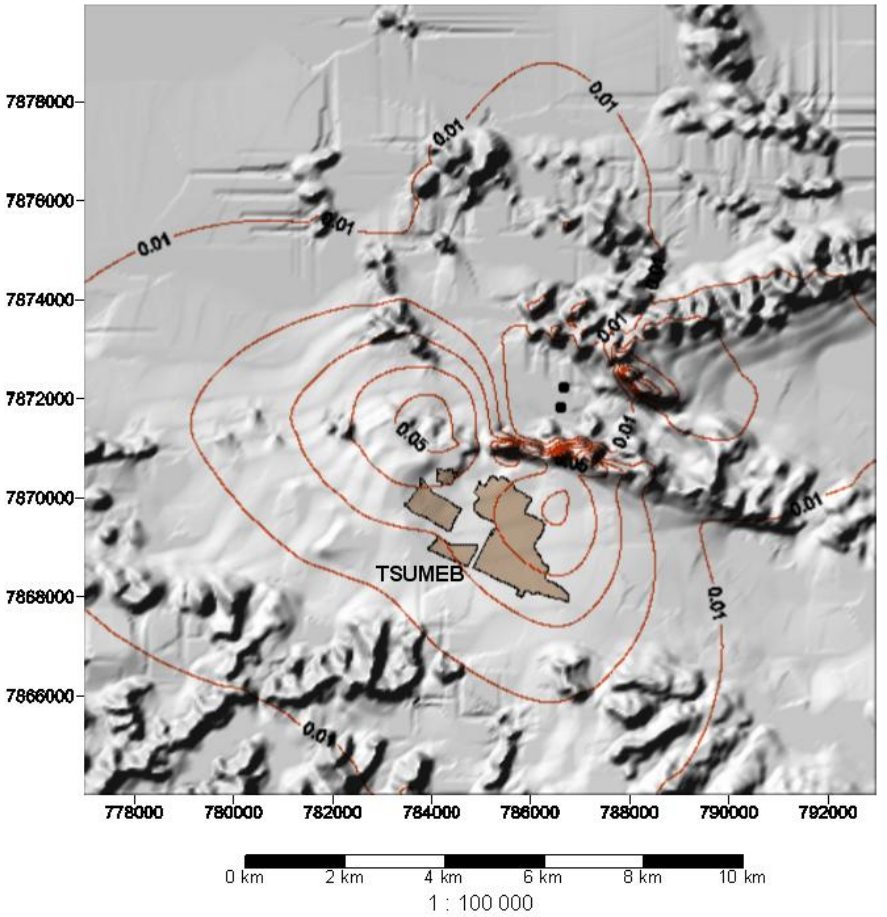
Annual dustfall (in g.m^{-2}) in the Tsumeb area. Smokestacks position is marked by red dots.

Isolines of annual dustfall (in g.m^{-2}) in the Tsumeb area. Smokestack position is marked by black dots.

RESULTS OF MODELING: Annual concentration of SO_2 in the air

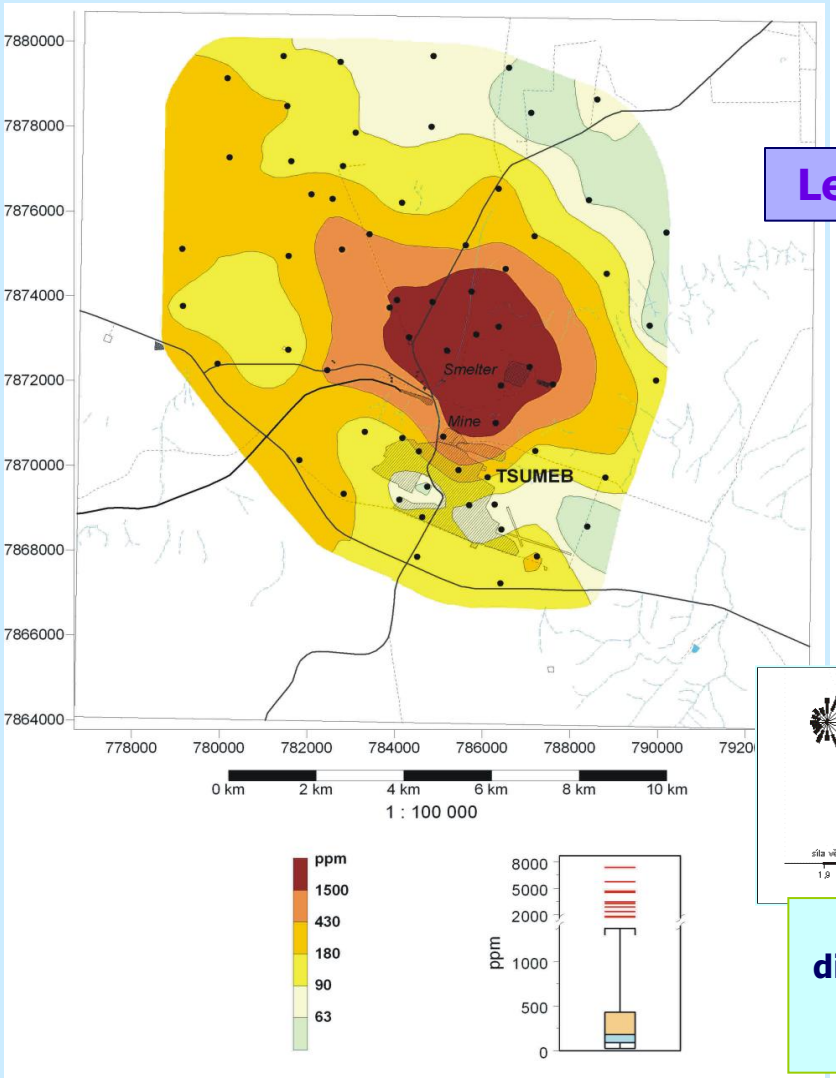


Annual average concentration of sulphur dioxide (in $\mu g.m^{-3}$) in the Tsumeb area. Smokestack position is marked by red dots.

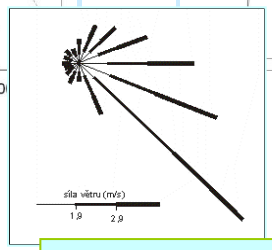


Isolines of the annual average concentration of sulphur dioxide (in $\mu g.m^{-3}$) in the Tsumeb area. Smokestack position is marked by black dots.

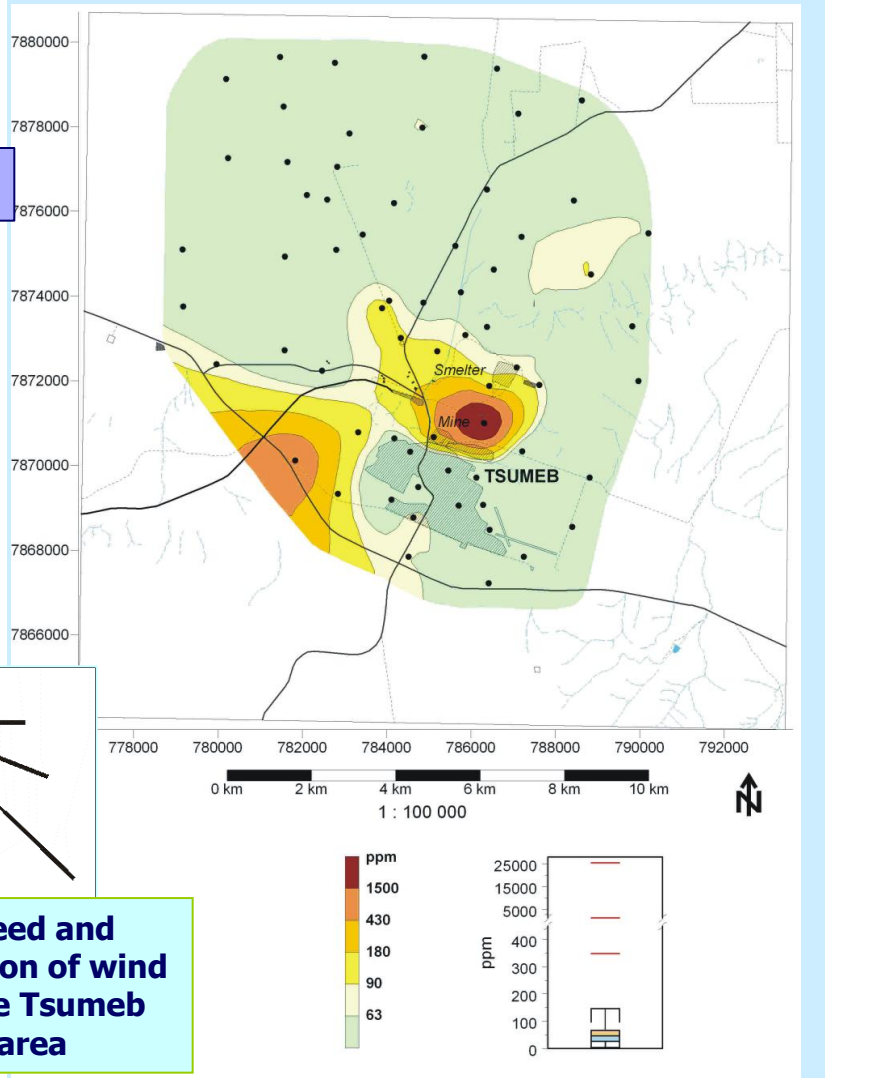
VERIFICATION OF MODELING: Soil geochemistry



Distribution of lead in surface soil layer

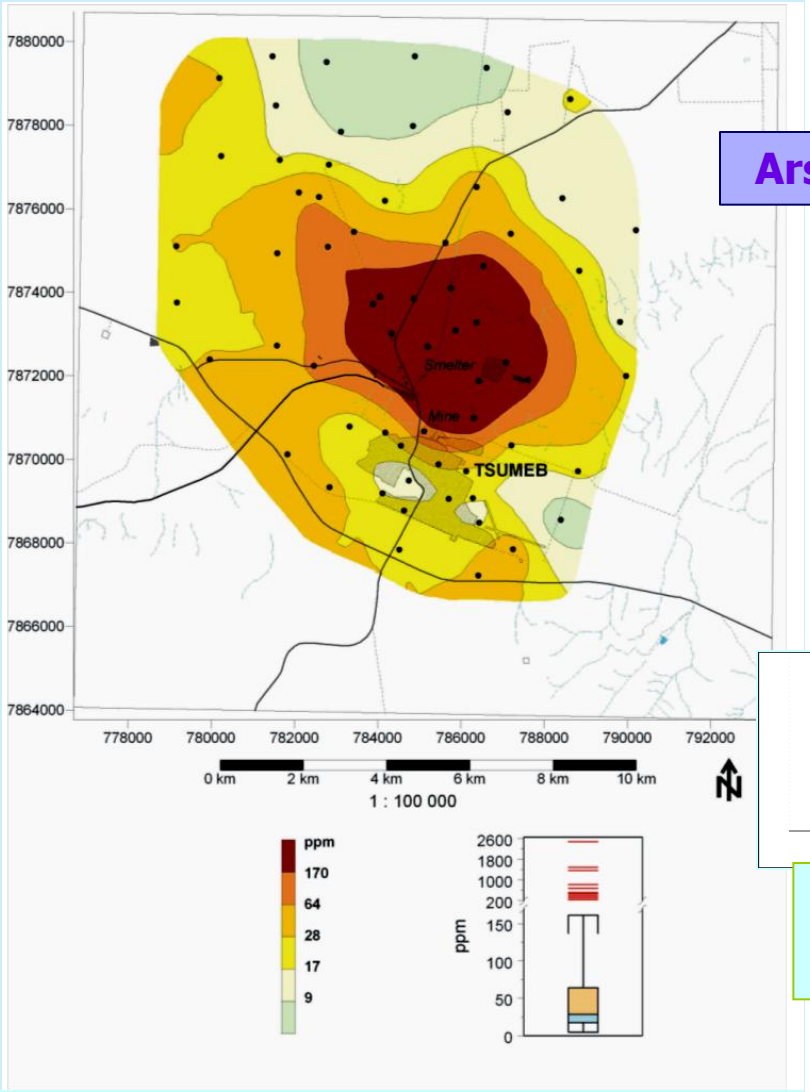


Speed and direction of wind in the Tsumeb area



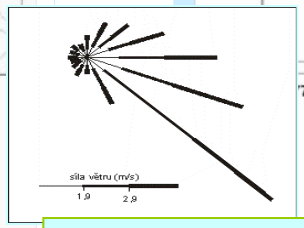
Distribution of lead in lower soil horizon

VERIFICATION OF MODELING: Soil geochemistry

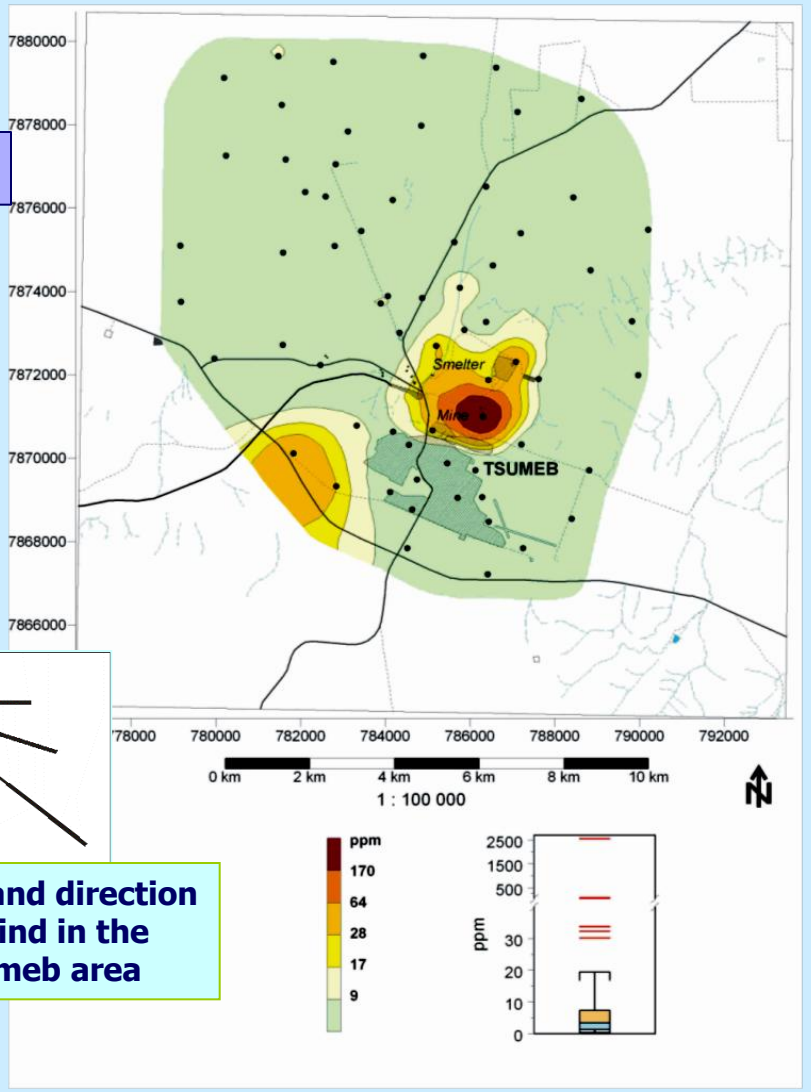


Distribution of arsenic in surface soil layer

Arsenic

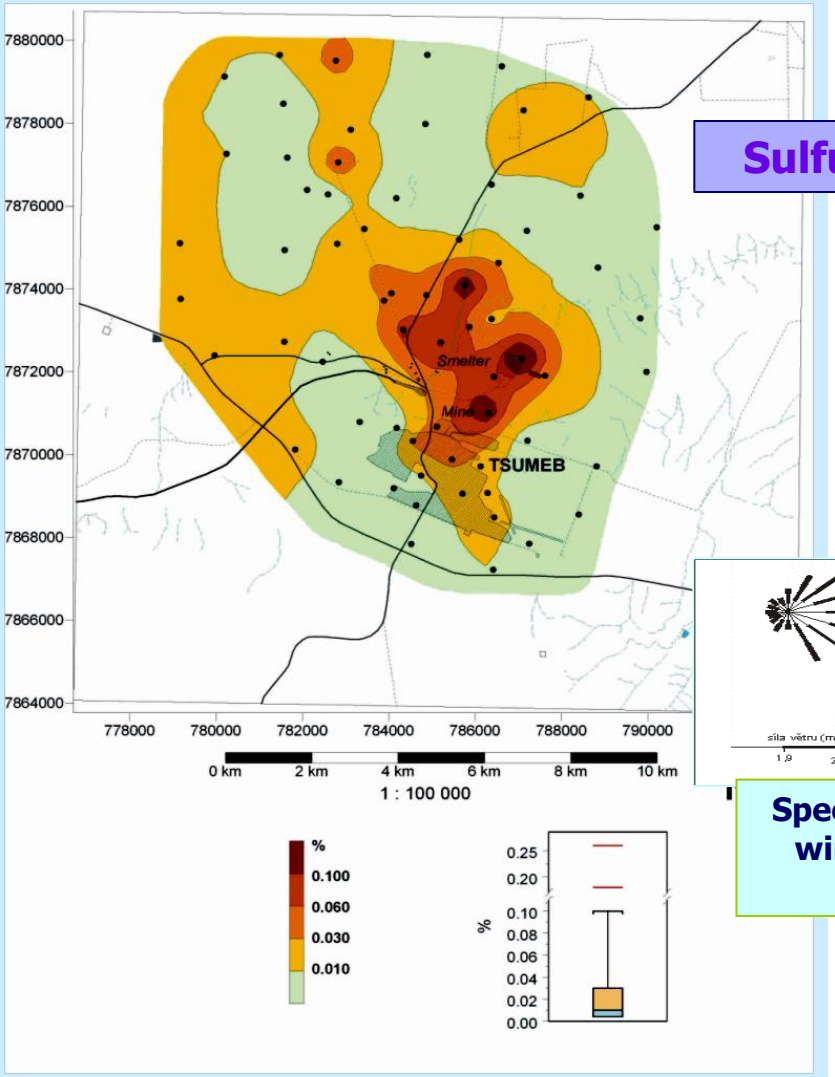


Speed and direction of wind in the Tsumeb area

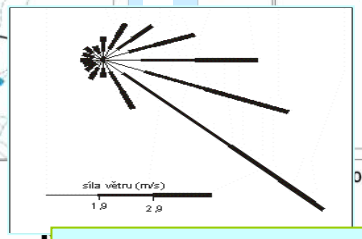


Distribution of arsenic in lower soil horizon

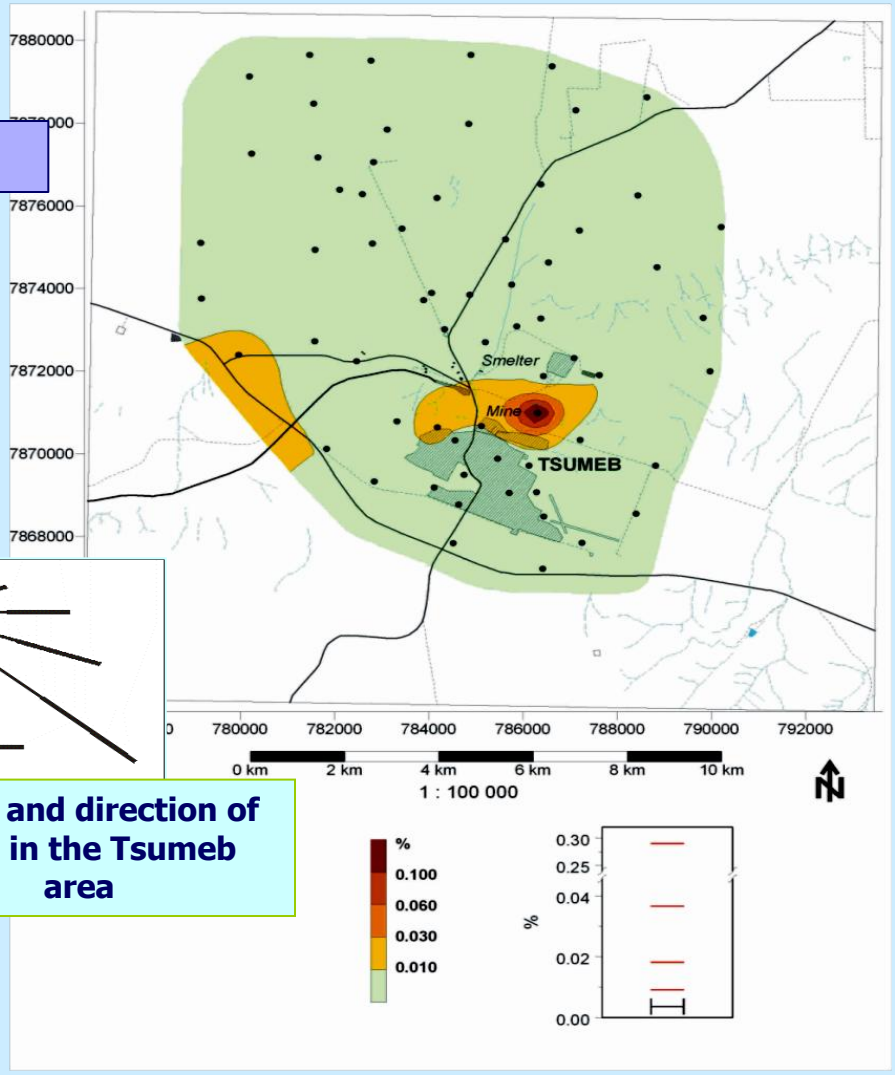
VERIFICATION OF MODELING: Soil geochemistry



Distribution of sulphur in surface soil layer



Speed and direction of wind in the Tsumeb area



Distribution of sulphur in lower soil horizon

CONCLUSIONS

Results of the study show that modelling resuspension of dust particles in areas affected by mining and mineral processing is a suitable tool enabling to assess the areal extent and shape of contaminated areas.

However, the results of modeling to large extent depend on the quality of available weather data, and therefore it is necessary to verify modeling results by monitoring of dust fallout and the amount of resuspended particles in the air and to carry out geochemical sampling of soil in areas of interest.


Thank you for your attention

5. DETAILED RISK ASSESSMENT FOR SAFETY

The Detailed Risk Assessment (DRA) is based on the present state of the art in terms of safety and is centred on determining, *inter alia*, the likelihood and consequences of a failure occurring in a Shut Down or Abandoned Mine Site (SD/AMS).

To assess the risks associated with the safety of installations, mines and works in greater detail, specific studies must be conducted by experts in relevant fields. The content of this section of the risk assessment seeks to assist the Geological Survey of Namibia in determining the nature of studies required with respect to specific incidences of risk in order to facilitate the effective review and approval of technical reports submitted by expert consultants.

It is important to bear in mind that it is not possible to perform a DRA for all potential safety risks associated with a SD/AMS. For example, accidents involving falling into an open mine shaft, or mine works, cannot be assessed much beyond what is carried out in a simplified risk assessment. Table 5-1 shows which risks can be assessed in depth and which cannot. In the former case the corresponding DRA section is listed.

A DRA may be undertaken with respect to the following specific geotechnical circumstances, namely:

- Subsidence (section 5.1);
- Slope stability (section 5.2);
- Tailings dams and impoundments (section 5.3);

The last of these may also include aspects of other technical issues.

Table 5-1 illustrates the potential scenarios for which a DRA is advisable. The DRA is sub-divided according to each mine site component and the corresponding Potential Safety Hazard.

Table 5-1: Safety Hazard Scenarios for which a DRA is indicated

Component	Mine Site Component	Code	Potential Safety Hazard	PI Estimation Guide
MINE	Underground Mine workings	SHS 1	Development of dolines or sinkholes on surface that may affect people or economic activities.	Yes – assessment of subsidence (5.1)
		SHS 3	The presence of toxic gasses in the mine.	No – SRA is sufficient
		SHS 12	The risk of falling down ore passes or travelling ways.	No – SRA is sufficient

Component	Mine Site Component	Code	Potential Safety Hazard	PI Estimation Guide
		SHS 13	The risk of rock falls.	No – SRA is sufficient
	Surface Mine (open pit)	SHS 2	The risk of slope failure that could affect people, the environment and/or economic activities	Yes – assessment of stability (5.2)
		SHS 2	Slope face approach and safety.	Yes – assessment of stability (5.2)
		SHS 4	Drowning in pool at bottom of pit	No – SRA is sufficient
		SHS 13	The risk of rock falls.	Yes – assessment of stability (5.2)
PLANTS	Processing Plants	SHS 12	The risk of falling from elevated structures.	No – SRA is sufficient
		SHS 13	Risk of falling rocks, remnant structures or other unsafe elements onto people.	No – SRA is sufficient
WASTE DUMPS	Tailings Dams	SHS 5	The release of tailings that could affect people, the environment and/or economic activities.	Yes – assessment of tailings pond or impoundment (5.3)
		SHS 12	The risk of falling on tailings dam	No – SRA is sufficient
	Tailings impoundments (dry)	SHS 6	Failure of slopes of dry stacked tailings from impoundments that could affect people, the environment and/or economic activities.	Yes – assessment of impoundment (5.3)
		SHS 12	The risk of falling on the tailings impoundment	No – SRA is sufficient
	Heap leach dumps	SHS 8	Failure of heap leach waste dump that could affect people, the environment and/or economic activities.	Yes – assessment of stability (5.2)
		SHS 12	The risk of falling from elevated structures.	No – SRA is sufficient
	Waste rock dumps or low grade ore stockpiles	SHS 9	Failure of waste dumps that could affect people, environment and/or economic activities.	Yes – assessment of stability (5.2)

Component	Mine Site Component	Code	Potential Safety Hazard	PI Estimation Guide
		SHS 12	The risk of falling from dumps.	No – SRA is sufficient
	Slag heap	SHS 12	The risk of falling from elevated structures.	No – SRA is sufficient
ASSOCIATED INFRA-STRUCTURE	Explosives magazines	SHS 10	Incorrect storage of explosives.	No – SRA is sufficient
	Offices and Camps	SHS 12	The risk of falling from elevated structures.	No – SRA is sufficient
	Workshops, Storehouses	SHS 12	The risk of falling from elevated structures.	No – SRA is sufficient
		SHS 14	Contact with waste elements and old machinery that could cause harm or injury.	No – SRA is sufficient
	Water pipes and tanks	SHS 12	The risk of falling from elevated structures.	No – SRA is sufficient
	Power lines and substations	SHS 12	The risk of falling from elevated structures.	No – SRA is sufficient
ASSOCIATED INFRA-STRUCTURE		SHS 14	Unauthorized entry into high voltage sub-stations, or contact with high voltage cables that could injury or death through electrocution.	No – SRA is sufficient
	Roads and bridges	SHS 11	Vehicle accidents on unsafe roads and structures (e.g. bridges).	No – SRA is sufficient
		SHS 12	The risk of falling from elevated structures.	No – SRA is sufficient

5.1 Subsidence study

Subsidence is movement in which there is no free side and the surface material is displaced vertically downwards with very little, or no, horizontal component. Typically, subsidence is associated with instability caused by near surface underground works. For the purposes of this Handbook, subsidence risks will be assessed only for sites that are abandoned and present an **'unwanted or unexpected'** subsidence of the surface. Mine sites with expected subsidence, i.e. where subsidence is considered an expected result of the normal mining process, are outside the scope of the detailed risk assessment.

The assessment of 'unwanted or unexpected' subsidence in abandoned mines is a complex issue that usually requires costly studies to determine their Likelihood of Occurrence due to mining activities or groundwater seepage.

Generally, the likelihood of collapse is related to the thickness of the rock overlying the underground works, the quality or strength of that rock and the quality and condition of supporting structures, if present.

In assessing the subsidence risk, the Assessor must include the effect on surface structures and/or infrastructure, in order to reduce the magnitude or risk without the need for extensive stabilization works. The recommended remedial action will be case dependant and a function of risk and the cost of implementing remediation measures.

5.1.1 Field Studies

The amount and extent of surface movement is variable and often difficult to predict as it is dependent on the thickness, depth and orientation of the mined-out ore body, the age of the stopes and the nature of the underground support. Nonetheless, it is important to carry out a field study of the affected area, which at the very least involves a description of the mine dimensions, the depth to surface and the nature and quality of the material between the underground workings and the surface.

Typically, field studies would comprise the following aspects:

- The identification of changes in the surface elevation below mined out, or dewatered underground areas, and the identification of radial surface cracks.
- Carry out an inspection of the near surface underground mines, if accessible, to gain an appreciation of the type and quality of supporting structures, evidence of support failure, stope collapse and groundwater seepage. Furthermore, the depth of the underground mine needs to be ascertained in order to evaluate the competency of the overlying rock (generally >3 times the height of the cavity) and the distance between pillars to determine the size of the mining spans.
- An estimation of the quality of the rock mass, using both the Norwegian Geotechnical Institute's Q-System (Barton *et al,* 1974*)* and Laubscher's (1990) Mining Rock Mass Rating Classification System.
- The construction of a geological cross-section with detail pertaining to the mine excavations and surface topography.
- A geotechnical assessment as to the stability of the excavations.

5.1.2 Laboratory Analysis

The amount of laboratory testing required will depend on the quality of the geotechnical data base for the site under assessment, particularly in relation to the material above and below the mine workings. These analyses would, typically, include an assessment of the soil-rock cohesion, friction and Intact Rock Strength (IRS) parameters.

5.1.3 Analysis and Modelling

Basic mine subsidence risk assessments are based on simple geometric rules that have been developed through empirical experience, such as those presented by Amuedo and Ivey in 1978. These rules are based on the observation that the area affected by subsidence is typically larger than the area excavated. When applied, these observations may be used to produce subsidence risk maps for specific areas. Such an assessment would require the mapping of all areas in which near surface mining works exist. For relatively flat stopes (less than 30°), the danger zone may be estimated by projecting a 35° angle from the lowest stoping level up to the surface. For safety reasons, an additional 60m wide buffer zone is typically added to the resultant area (see Figure 5-1). A similar procedure is applied to mine workings with steeper stopes.

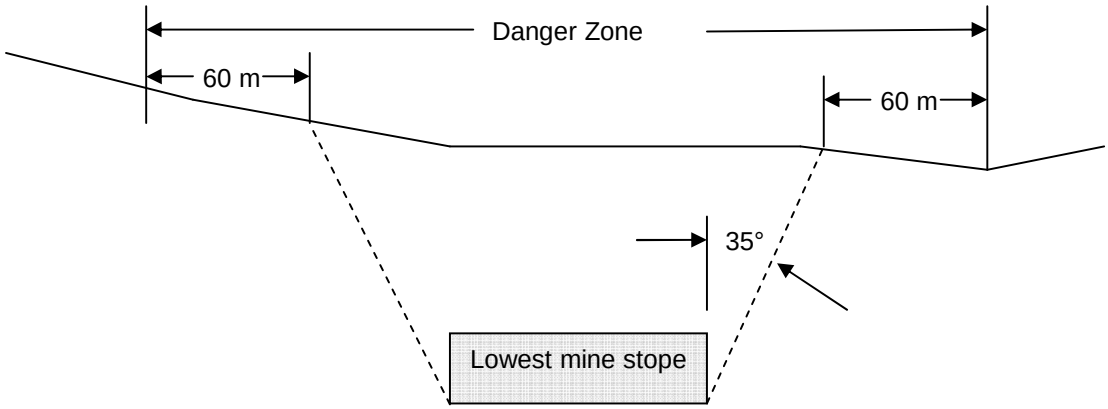


Figure 5-1: Defining subsidence risk in flat underground mine workings (less than 30°).

More sophisticated mine subsidence risk assessments are possible through the application of detailed geological and geotechnical data, i.e. direct evidence of surface cracking, rock mass quality data, the thickness of the overlying rock, the quality of installed support and the nature of the rock jointing.

Fault or fracture lines in the rock may create zones of weakness that result in subsidence. Depending on the orientation of these fracture zones, the boundary of the subsidence zone may be extended beyond the projected zone.

A crucial consideration when performing a subsidence DRA is the hydrological/hydrogeological regime developed in the area under investigation. Flowing and/or ponded water could weaken underground support structures, while flooding could help reduce the risk of subsidence by preventing mineral oxidation in the supporting pillars.

A detailed assessment of the likelihood of subsidence occurring would also take the mining method

into account. Although small-scale mining operations make use of methods that are not technically defined, medium and large-scale mining operations in Namibia employ high yield mining methods, which include: Panel Caving, Sub-level Caving, Sub-level Stoping, Room and Pillar and Cut and Fill mining.

5.1.4 Content of Subsidence Reports

Assessments of potential subsidence should include the estimated minimum and maximum limits of the affected zone, taking into account both the area and depth of possible subsidence. These assessments should also identify the mechanisms of subsidence. All data gathered during the field work and laboratory testing aspects of the study should be assimilated into the assessment.

Recommendations as to the remedial measures that may be implemented to control subsidence, as well as preventative measures that may be introduced to prevent future uncontrolled subsidence, are to be included as part of any risk subsidence assessment.

5.1.5 Bibliographic References

Whittaker B.N., Reddish D.J. (1989). Subsidence – Occurrence, Prediction and Control. Developments in Geotechnical Engineering 56.

5.2 Slope Stability Assessment

Slope stability may be assessed in terms of the following:

- Tailings deposits (either dry stacked or using another system that precludes a pond or dam);
- Heap leach waste dumps;
- Waste dumps;
- Open pit mines.

Open pit mines are closed once the ore reserves have been exhausted, or no more ore can be economically recovered; or they may just be abandoned (on an unplanned basis) for a variety of reasons. Active mine closure planning and implementation during mining operations has the effect of reducing the quantity of work required to be completed at the end of the mining operation. That being said, complete mine closure is a complex and involved process, and given that very few large-scale open pit mines have closed since the 1990's, there is little experience related to such closures. Nonetheless, risk assessments are an underlying approach to such closures and the risks associated with the facility and those remaining after closure must be understood. These risks are related to, *inter alia,* technical, safety and environmental; one such aspect being the long-term land use of a defunct mine. Once this has been established, it may be that the only economically viable solution to eliminate the safety risk to people is by preventing access to the site.

5.2.1 Slope Stability Study

The stability of a slope is a function of limiting equilibrium, i.e. the ratio of nominal capacity (resisting forces) and system demand (driving forces). Slope design requires specialized knowledge of the geology and material properties of the lithological units that will constitute the pit slopes. The aim of open pit design is to mine as steeply as possible while ensuring a safe and economical mining operation. In order to achieve this goal, the following is required:

- A dedicated geotechnical investigation, which includes the drilling of rotary cored boreholes and the geotechnical logging and representative sampling of the recovered cores.
- An assessment of the groundwater regime across the site.
- The implementation of a geomechanical laboratory testing programme.
- Kinematic analysis.
- Empirical slope stability analysis using empirical analysis techniques.
- Numerical slope stability analysis using limit equilibrium and finite element software packages.

The number and location of drill holes required per site is determined on a case by case basis. Guidelines in this regard are contained in. During the Life of Mine, the open pit should have been monitored in order to manage all aspects of slope stability on a day-today basis. Therefore the following information should be available to the Assessor of a SD/AMS:

- In-pit mapping, including joint surveys, of exposed pit faces along dedicated design section lines.
- The results of the slope monitoring programme.
- A Hazard Plan based on observations during regular inspections of the pit slopes and reported failures or rock falls. All hazards arising as a consequence of geological, geotechnical or hydrogeological conditions should have been identified and indicated on the hazard plan.
- A record of all slope failures in the open pit. All failures should have been inspected with respect to the local structural geology and an effort made to understand the failure mechanism involved.

Table 5-2: Recommended Borehole Positions

Application	Minimum data points and their location	Minimum depth
Embankments and reservoir walls	A minimum of one (1) borehole per 60m of embankment or slope as required. For regularly placed data points a minimum of one (1) borehole per 120m of embankment or slope is required. In critical zones, such as in weathered material, a minimum of three (3) boreholes are recommended in the transversal section to define sub-surface conditions.	The investigation depth should be at least twice the height of the embankment or slope, unless bedrock is encountered at a shallower depth. If weathered material occurs at a depth greater than double the height of the embankment or slope, the investigation depth should be sufficient to penetrate the weathered material until competent material is intersected (e.g. hard, cohesive material, non-cohesive compacted or dense material, rocky basement).
Cut slope	A minimum of one (1) borehole per 60m of slope as required. For regularly placed data points a minimum of one (1) borehole per 120m of slope is required. In critical zones such as in weathered material, a minimum of three (3) boreholes are recommended in the transversal section to define sub-surface conditions. For cuts in rock, geotechnical mapping should be performed along the length of the cut slope.	The investigation depth should be at least 10m below the maximum cut height, unless competent material is intersected at a shallower depth. The investigation depth should be sufficient to penetrate weathered material until competent material is intersected (e.g. hard, cohesive material, non-cohesive compacted or dense material, rocky basement). In places where the base of the cut is below groundwater level, the investigation depth should be increased to determine the depth of the saturated layer.

The most suitable techniques for determining slope stability are empirical and numerical slope stability analyses requiring the use of appropriate rock mass rating classification systems, published design charts, limit equilibrium and finite element analyses.

At SD/AMS, a walk-over inspection along access ramps and around the pit perimeter must be carried out by an engineering or mining geologist. It is essential that such inspections are carried out on foot to allow careful examination of the slope and to ensure that adequate time is spent on this activity. Furthermore, the development of small cracks, which may be indicative of the development of large-scale instability, may not be visible from a moving vehicle. In some cases where slope failure risks are rated as high, it may be necessary to conduct inspections on a regular (e.g. annual) basis.

In the case of dump stability, topographic techniques, specifically levelling, have been used successfully in monitoring the deformation of dump embankments. The main disadvantage of this technique is that failures could develop between levelling cycles. The development of a water table within a dump is another important aspect of stability. Monitoring of the water table within a dump is via the installation of piezometers, which facilitates the measurement of groundwater levels over time.

5.2.1.1 Laboratory Tests Related to Stability

Although laboratory testing programmes need to be tailored to suit the requirements of each site, there are specific testing procedures that form the basis of any testing programme. In terms of weathered material, i.e. soil, these would include, *inter alia*:

- Atterberg limits.
- Moisture Content.
- Triaxial shear strength testing.

In terms of rock geomechanical testing, specific laboratory tests would include, *inter alia*:

- Uniaxial Compressive Strength testing.
- Triaxial Strength testing.
- Shear strength (Base Friction Angle) testing on artificial saw-cuts.

Shear strength testing is required to derive the cohesion and friction angle parameters of either the rock mass or the developed discontinuities within a jointed rock mass, as these are the properties that determine the stability of the respective lithological units.

A soil's reaction to stress is a function of its permeability and porosity, with results of tests carried out on undrained and drained samples differing. Consequently, it is important that the correct test is selected when measuring soil stress, as the results are influenced by factors such as grain size distribution.

5.2.1.2 Data analysis and modelling

Traditionally, the performance of an open pit mine has been made on the basis of the allowable Factor of Safety (Fs), which is defined as the ratio of nominal capacity (resisting forces) and system demand (driving forces). Conceptually, limiting equilibrium is achieved when the Fs value = 1.0. Trial-and-error experience has resulted in the setting of recommended design Fs levels. In the case of open pit mine slopes, the recommended design Fs values vary between 1.2 (non-critical slopes) and 1.5 (slopes with critical infrastructure).

Various analytical models may be used in numerical slope stability analysis, namely:

a. Deterministic Methods

Deterministic modelling techniques are used when the slope parameters are known or are assumed. Values for specific geotechnical parameters, which define the behaviour of the materials, are selected as input into the model to define the allowable Factor of Safety value. Deterministic methods include limit equilibrium and stress-strain techniques.

Limit equilibrium techniques involve the selection of the limiting failure surface with a calculation of the resisting forces over the disturbing forces acting on the failure surface.

Use is commonly made of the SLIDE limit equilibrium software package to carry out limit equilibrium slope stability analysis. Typically, the SLIDE software package is selected for use as it is able to evaluate slope stability using both the Bishop's Simplified Method of Slices techniques and Monte Carlo simulation to calculate a Factor of Safety (Fs) and Probability of Failure (Pf) for pit slopes.

Stress-strain techniques take the stress-strain relationship of the materials into consideration during deformation. Materials deform under load and, depending on the resistance and deformational properties of the materials, different stress states are generated in different areas of the slope. Finite element analysis is used to analyze the pit slope model and generate the nature and magnitude of material displacements created. Typical finite element software packages available include FLAC 3D and Phase^2.

b. Probabilistic Methods

Probabilistic modelling techniques are used when the slope parameters are not known. Statistical distribution is assigned to the input parameters; this allows accounting for the degree of uncertainty in the value of the parameters. Many different values of factor of safety can be calculated on a given slip surface, resulting in a distribution of factor of safety from which a probability of failure for the slope can be calculated.

c. Analysis of Open Pits

Slope stability analysis for open pits typically comprises both empirical and numerical analysis techniques. Empirical techniques include the geotechnical logging of rotary-cored boreholes and the geotechnical mapping of accessible exposures. The assimilated data forms the basis for the classification of the quality of the rock mass using appropriate rock mass classification systems. Thereafter, use is made of published slope Design Charts, e.g. the Haines and Terbrugge (1991) Design Chart, to derive preliminary stack angles. As part of the empirical analysis, kinematic analyses are carried out to identify possible modes of failure, i.e. planar sliding, wedge and toppling failures, as well as the probability of occurrence of these types of failures. The results of the empirical

analyses form the basis for more vigorous numerical analysis which serves to verify and validate the recommended slope angles and the open pit geometry. Apart from SLIDE, other software packages used in numerical slope stability analysis include SWEDGE, which is used to identify large-scale wedge structures in pit slopes (Rocscience, 2002).

5.2.2 Considerations Related to the Water Table

Pit slopes are analysed under depressurized (dewatered) conditions. Nonetheless, it is very important in slope stability analysis to have an appreciation of the groundwater regime in the area being investigated. Apart from the pressure head imparted to the slope, the presence of water within a discontinuity reduces the shear strength of the material due to a reduction in the effective normal stress as a result of water pressure. The effect of water on the cohesive and frictional properties of a rock is dependent on the nature of the infill or cementing material in the discontinuity. The shear strength properties of the majority of hard rocks, as well as numerous sandy soils and gravels are not adversely affected by water, however, shale, mudstones and clays are, and these materials exhibit significant changes in their shear strength properties in the presence of water.

It is important, therefore, that any slope stability investigation includes a hydrogeological study in order to quantify the groundwater regime and facilitate the construction of a groundwater model of the site.

In addition to the above, it is important to ensure that adequate attention is paid to the control of surface and stormwater in and around the pit to prevent concentrated runoff from surrounding areas from entering the pit. In order to achieve this, appropriate drainage and intercept canals need to be installed around the pit crest to intercept any stormwater run-off, with the canals being directed away from the pit and discharged in such a manner that it will not re-enter the pit via the pit slopes. Furthermore, the ponding of stormwater on crest areas or ramps must not be allowed to occur and measures, such as the cambering of haul roads, need to be implemented to ensure that surface water is drained away from the pit. In-pit sumps of sufficient capacity should also be established and managed to effectively control in-pit water.

5.2.3 Mitigation of Risk

At shut down or abandoned mines where potential hazards have been identified, the Assessor should check whether the required remedial measures have been implemented. Typical remedial measures include:

- Dewatering of the slope using large-diameter wells and/or sub-horizontal drain holes installed into the pit slope.
- The implementation of a limit blasting programme.
- The addition of berms or buttresses at the base of the pit slope.

- Flattening the slope angle.

Such measures are valid for cases where the risk of slope failure is deemed to be significant.

5.2.4 References and Programmes Available for Slope Stability Analysis

The following are among the most common programmes available for analyzing slope stability using the limit equilibrium model, though the list is not exhaustive:

Slope/W (2004) Geo-Slope International Ltd. (http://www.geo-slope.com/)

Slide 5.0 (2005) Rocscience Inc. (http://www.rocscience.com/products/Slide.asp)

Xstable 5.0 (1994) Interactive Software Designs Ltd.
(http://www.xstabl.com/XSTABL/xstabl.htm)

Ansys (http://www.ansys.com)

Galena (http://www.slope-analysis.com/html/galena_details.html)

RocLab (http://www.rocscience.com/downloads/Downloads.asp)

Programmes that can be used in the application of stress-strain models include:

Slide 5.0 (2005) Rocscience Inc. (http://www.rocscience.com/products/Slide.asp)

Flac 5.0/ Flac3D 3.0 (2002) HCItasca Consulting Group Inc.
(http://www.itascacg.com/software/index.html)

Plaxis 8.2 (2006) Plaxis BV (http://www.plaxis.com/)

Phase2 (2005) Rocscience Inc. (http://www.rocscience.com/products/)

For open pit analyses, the following may be used:

SWEDGE (2002) Rocscience Inc. (http://www.rocscience.com/products/Swedge.asp)

Dips (http://www.rocscience.com/downloads/Downloads.asp).

5.3 Tailings Dams and Impoundments

The main aspects having a major impact on the overall stability of a tailings deposit are:

- Earthquakes, or earth tremors associated with an underground mine collapse;

- Rate of rise;
- Overtopping after a rainfall event or as a result of poor pool control;
- High phreatic surface within the facility;
- Penstock or decant failure.

To assess the stability of tailings deposits and especially retaining walls, numerical analyses are used to assess the stresses and deformation to which the deposit is subjected based on geometry and material parameters.

Given that stability studies are based on the same theoretical principles, the discussion in point 5.2 relating to slopes is also applicable to tailings storage facilities. The phreatic regime within the tailings storage facility is a critical factor in the stability of the facility, and therefore it is important to establish its location in order to assess the overall stability of the facility.

Another variable that has a significant impact on the overall stability of a tailings deposit is overtopping as a result of insufficient freeboard and poor pool control. The failure of a penstock or decant system also has a significant impact on the stability of a tailings storage facility. This could cause a sinkhole to form on top of the dam and significant volumes of slimes can be discharged to the environment via the failed system.

BOX 3
The Merriespruit Disaster

The Merriespruit tailings dam disaster occurred on the night of 22 February 1994 when a tailings dam failed and flooded the suburb of Merriespruit, Virginia, South Africa. Late afternoon on the day of the failure, a thunderstorm occurred and about 50 mm of rain fell in 30 minutes. When the dam failed, 600,000 m^3 of liquid flowed 4 km. The nearest houses were located 300 m downslope of the dam; when the wave of water and slime reached them it was 2.5 m high. Seventeen people were killed and there was widespread devastation and environmental damage. Eighty houses were destroyed.

The No 4 dam was in an unacceptable condition prior to failure. Contrary to legislative requirements, at the time of failure the dam did not have capacity to maintain a 0.5 m freeboard during a 1 in 100 year 24-hour storm event, as per legislative requirements.

The owner, operator and six of their employees were found guilty of negligence and heavy fines were imposed.

Source: Wikipedia

5.3.1 Field Investigations of Tailings Storage Facilities

The elements involved in field investigations of the tailings storage facilities depend on the size as well as the physical state of the facility. Aspects that are covered as part of a field investigation include but are not limited to: evidence of seepage, functionality of drainage systems, wall building technique employed, sloughing, instability of slopes and available freeboard.

5.3.1.1 Sloughing and Slope Stability

The slopes of an abandoned tailings storage facility with significant risks should be inspected on an annual basis to assess the condition of the slopes in terms of local sloughing, wet spots and instability concerns. These concerns should be reported to MME immediately so that remedial measures can be initiated.

5.3.1.2 Freeboard

High risk, abandoned tailings dams should be monitored on an annual basis by means of a tachometric/GPS freeboard survey. The purpose of the tachometric/GPS survey is to ascertain whether or not the tailings dam maintains the minimum freeboard of 800mm above the pool level in accordance with best practice.

Should problems be detected for whatever reason as a result of the freeboard survey, they must be reported to MME immediately and attended to as a matter of urgency if human life or economic activities are in danger. Any such concerns should be followed up by a confirmation tachometric survey. Should the check survey reveal that the freeboard is still inadequate, remedial measures should be put in place to rectify the freeboard concerns.

5.3.1.3 Rates of Rise

The rate of rise of the tailings dam should have been determined on an annual basis during the Life of Mine and this information should be available to the Assessor. This information is essential for understanding the stability constraints placed on the dam. If the rate of rise is found to have been in excess of the design requirement, the Assessor needs to field check other aspects of dam wall stability.

5.3.1.4 Seepage and Drains

Two forms of seepage that require monitoring are: seepage collected in the underdrains and discharged into the solution trench via the seepage drain outfall pipes and seepage emanating from the outer face of the tailings storage facility.

With respect to seepage water discharging into the solution trench via the drain outfall pipes, the seepage flow at high risk abandoned tailings dams must be monitored on an annual basis or at frequencies determined by MME. Flows are to be measured by determining the amount of water discharging from the drain outfall pipes in a specified time. Where flows are strong it is essential to capture the quantity of water over a period of at least 5 seconds. Where flows are weak it is essential to capture the quantity of water over a period of at least 60 seconds. It is essential that a good quality measuring cylinder and an accurate stopwatch be used where flows are strong (i.e. 5 second readings where two measurements should be taken) and be recorded. The results must be entered in the form of a histogram in order to monitor the trend in seepage. Any significant sudden increase or decrease shall be noted and investigated.

With respect to seepage water emanating from the outer face of the tailings storage facility, such seepage shall be reported to MME immediately for their attention. All seepage water emanating from the outer face of the facility shall be thoroughly investigated and appropriate action taken.

5.3.1.5 Phreatic Surface

At SD/AMS where there are valid concerns regarding the stability of a tailings dam, it is recommended that the phreatic surface and associated pore water pressures be monitored using installed standpipe piezometers. Piezometers must be installed at critical sections around the dam. There should be 3 piezometers on each line at 50m centres.

At annual intervals piezometer sections should be surveyed. Individual piezometers must be dipped on a quarterly basis with a dip meter and the associated phreatic surface plotted on the piezometer sections to monitor the effectiveness of the under-drainage system and current stability conditions at those locations.

The standpipes are to be protected from being damaged and where piezometer readings are in doubt, the dip meter should be checked and the piezometer re-dipped. Where readings are still in doubt, an 'upset test' should be conducted, where the standpipe is filled with clean water. The piezometer should then be re-dipped after 6, 12, 24 and 48 hours. If the piezometer is functioning the upset level will return to its original undisturbed level. If the total water column height within the piezometer has varied by more than 750mm from previous readings, it is recommended that a new piezometer be installed.

The results should be entered into the computer database and phreatic surface monitored on a quarterly basis.

5.3.1.6 Penstock Inlets

Where the tailings dam at a SD/AMs still contains a large pool of water, and/or it lies in the high rainfall zone of Namibia, the penstock inlets should be inspected at least quarterly, and the following recorded:

- Lean of penstock tower (can be measured with spirit level as a guide).
- State of penstock rings.
- Observations seen down the penstock towers (using mirrors to direct sunlight during observation).
- State of catwalk and penstock access platform.
- State of birdcage safety cage.

Should, for whatever reason, penstock intake(s) become blocked, MME is to be notified of the problem immediately and the necessary remedial steps taken.

5.3.1.7 Groundwater

In cases where seepage of poor quality water is occurring from the tailings dam, and where there are sensitive receptors nearby, it is recommended that a bi-annual programme of water sampling should be carried out in April and October, at the end of the wet and dry seasons respectively. Water samples should be analysed for pH, conductivity, total alkalinity, major cations and anions and relevant metals, depending on the geochemistry of the ore body of the mine (see section 6.4.2.1). The results should be collated in a suitable data base and reviewed for trends and any necessary action (see section 6.4.2.4).

5.3.1.8 Tailings Dam Inspections and Safety Observations

As noted above, in cases at SD/AMS where there are concerns about the stability of the tailings dam and where potential receptors may be affected, it is recommended that annual or even quarterly inspections and safety observations on the tailings dam should be conducted. These inspections should include:

- Local sloughing on the outer slopes and the presence of wet spots;
- Available freeboard (and associated tachometric survey if required);
- Seepage flow in the underdrains, solution trench and toes drains;
- Piezometer monitoring (of the phreatic surface); and
- Penstock inlets.

5.3.2 Bibliographic References Related to Tailings Dams and Impoundments

Given the catastrophic consequences of past tailings deposit failures, today there is an extensive bibliography available on the design and assessment of these works. Some of these documents are:

International Committee on Large Dams, ICOLD, has published the following documents specifically addressing aspects related to tailings (http://www.icold-cigb.net/listepublications.aspx):

Mine and Industrial Tailings Dams and Dumps (1982).

Mine and Industrial Tailings Dams and Dumps (1989).

Manual on Tailings Dams and Dumps (1982).

Tailings Dam Safety – Guidelines (1989).

Tailings Dams – Design of Drainage (1994).

Tailings Dams and Seismicity – Review and recommendations (1995).

Tailings Dams – Transport, Placement and Decantation (1995).

Tailings Dams and the Environment – Review and recommendations (1996).

Monitoring of Tailings Dams – Review and recommendations (1996).

A Guide to Tailings Dams and Impoundments – Design, construction, use and rehabilitation (1996).

Tailings Dams: Risk of dangerous occurrences – Lessons learnt from practical experience (2001).

6. DETAILED RISK ASSESSMENT FOR CONTAMINATION

6.1 Methodology Background

The Detailed Risk Assessment (DRA) for contamination requires complex methodologies that must be applied by experts in health risk assessment and specialists with knowledge of toxicology, epidemiology and environmental science. This Handbook thus offers only general notions of the methods used to assess risks to human receptors, the environment and economic activities (Figure 6-1).

The original paradigm for regulatory human health risk assessment (HHRA) in the USA was developed by the USA National Research Council[1]. This model has been adopted and refined by the US Environmental Protection Agency (USEPA)[2;3] and other agencies around the world[4], and is used widely for quantitative health risk assessments. The paradigm essentially divides human health risk assessment (HHRA) into a number of logical steps, as follows:

- Hazard identification (formulation of the problem);
- Dose-response assessment (toxicological assessment);
- Exposure assessment;
- Risk characterization;
- Uncertainty review.

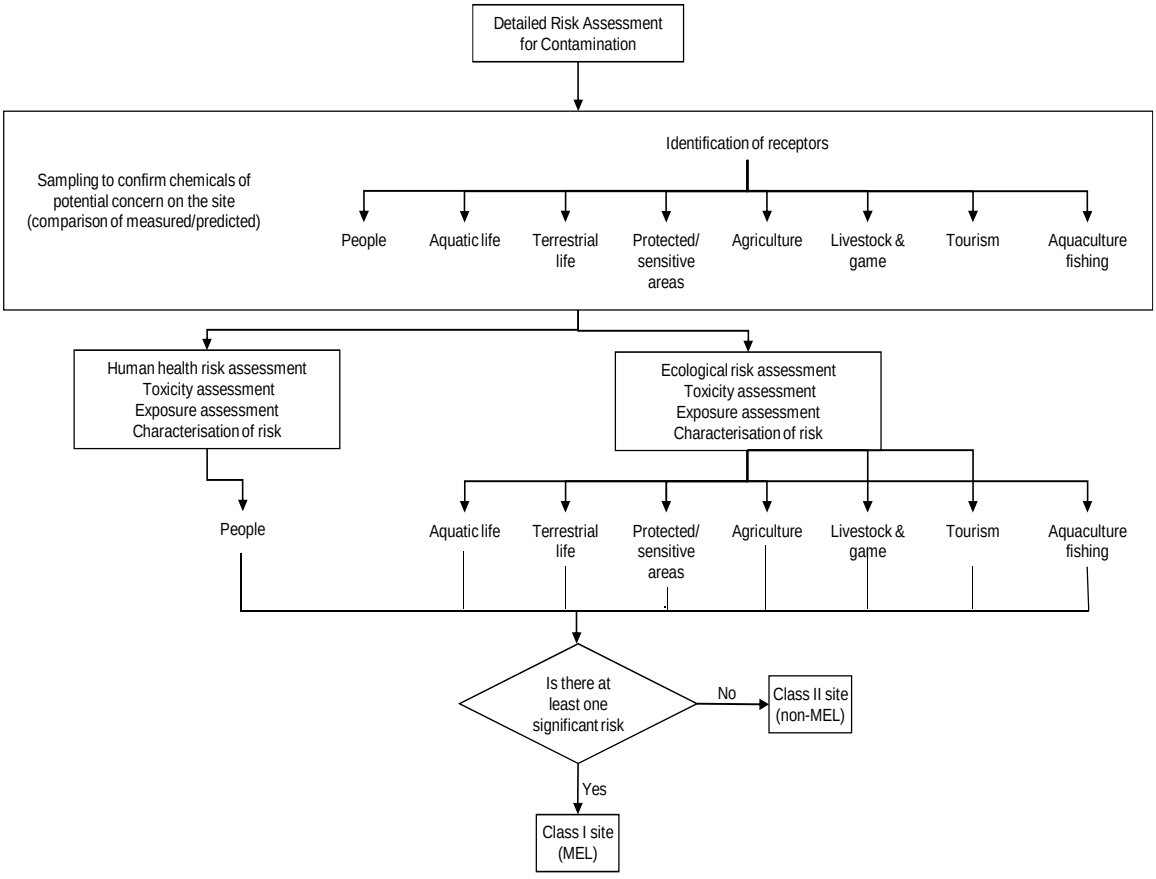
In its simplest form, ecological risk assessment (ERA) refers to the probability of an adverse effect occurring in an ecological system. In accordance with general risk assessment methodology, ecological risk assessment includes estimations of hazard and exposure due to an environmental stressor[5]. Compared to the framework for HHRA, the USEPA framework for ERA changes the first step from hazard identification to problem identification in a holistic context and the phrase 'dose-

[1] NRC, 1983. Risk Assessment in the Federal Government: Managing the Process. National Research Council, Committee on the Institutional Means for the Assessment of Risks to Public Health, National Academy Press, Washington, DC.
[2] USEPA, 1989. Risk Assessment Guidance for Superfund. Volume I. Human Health Evaluation Manual (Part A). Interim Final. EPA/540/1-89/002. US Environmental Protection Agency.
[3] USEPA, 1991. Risk Assessment Guidance for Superfund (RAGS), Volume I: Human Health Evaluation Manual (HHEM), Part B, Development of Risk-Based Preliminary Remediation Goals. US Environmental Protection Agency Office of Emergency and Remedial Response, Washington, DC. OERR 9285.7-01B. NTIS PB92-963333.
[4] IPCS, 1999. Environmental Health Criteria 210. Principles for the Assessment of Risks to Human Health from Exposure to Chemicals. World Health Organisation, Geneva.
[5] Landis W and Yu M-h, 1998. Introduction To Environmental Toxicology: Impacts Of Chemicals Upon Ecological Systems, Second Edition. CRC Press.

response' is replaced by 'stressor-response' to emphasize the possibility that physical changes (which are not measured in doses) as well as chemical contamination can stress ecosystems[6].

A DRA needs to be performed for all environmental media susceptible to chemical contamination (surface water, sediment, groundwater, soil, air) that could be present at a mine site. The DRA is likely to be different for each site and will depend on the results of the SRA.

Figure 6-1: Flowchart for Detailed Risk Assessment for Contamination



[6] US Environmental Protection Agency. 1998. Guidelines for Ecological Risk Assessment. USEPA EPA/630/R095/002F. U.S. Environmental Protection Agency, Risk Assessment Forum, Washington, DC, 175 pp.

6.2 DRA process for contamination

This section describes the steps to be taken for the Detailed Risk Assessment for Contamination, shown in Figure 6-2, namely:

Step 1 – Formulate the Problem (Hazard Identification): This requires identification of sources of contamination and compilation of a preliminary list of chemicals of potential concern, receptors and exposure pathways. These three elements are integrated into a conceptual model that illustrates contamination pathways from the source to the different environmental media (water, sediment, soil, air) and receptors of interest. It then defines the need for additional characterisation studies for the media susceptible to chemical contamination.

Step 2 – Collect Supplementary Information: This is based on a description of procedures for collecting supplementary information, which may include a site visit, sampling of different environmental media susceptible to chemical contamination and chemical analyses.

Step 3 – Confirm Chemicals of Potential Concern: Once the results of analyses have been obtained, chemicals of potential concern are assessed by comparing the analytical results with reference for different receptors (people, aquatic life, etc.). This comparison will yield one of the following situations:

- All results of the analyses are below reference concentrations, and therefore do not require additional assessment (proceed directly to Step 5).
- The results of the analyses present one or more values that exceed reference concentrations and therefore additional assessment is required (proceed to Step 4).

Step 4 – Risk Assessment: Assessment for Human Health and/or Ecological Factors (environment and economic activities) with regard to risk.

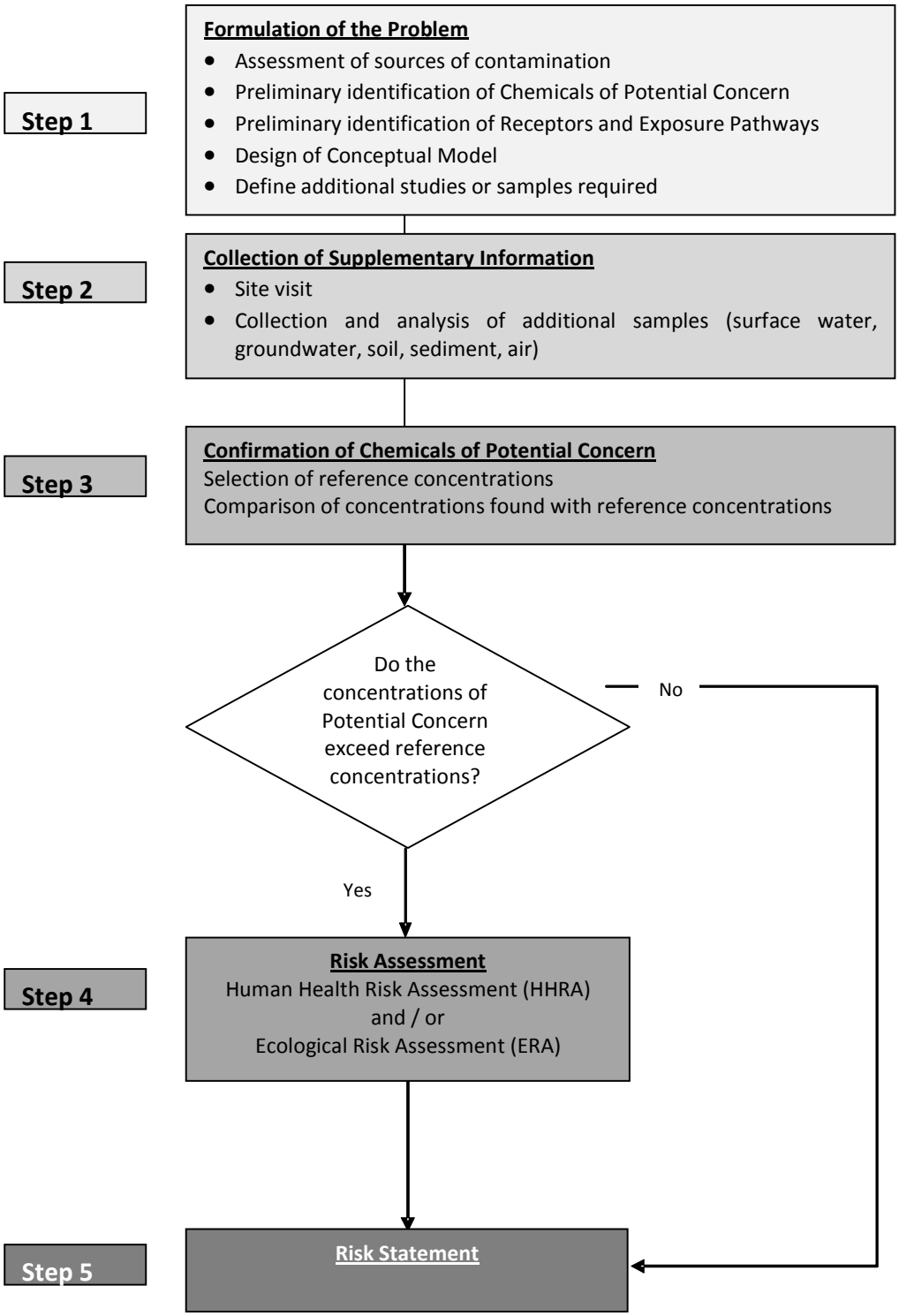
Step 5 – Risk Statement: Analysis of the quantified risk in terms of international perceptions of acceptable risk.

6.3 STEP 1- Formulate the Problem

6.3.1 Study Approach

The Detailed Risk Assessment (DRA) begins with the formulation of the problem, which is mainly qualitative and involves defining the nature of the problem and building preliminary hypotheses about how and why an effect has been observed or could potentially occur in future.

Figure 6-2: Steps in the Detailed Risk Assessment



Formulation of the problem should take into account:

- The source of contamination and preliminary identification of chemicals or pollutants of potential concern;
- Potential receptors that could be exposed to the contamination; and
- Pathways by which these receptors could come into contact with chemicals of potential concern.

These three elements are integrated into a conceptual model (Figure 4-3 in Chapter 4), which illustrates the contamination pathways from the source to the environmental media (water, sediment, soil, air) and receptors of interest.

It is important to note that the analysis must consider past, present and potential future use of the land, and relevant associated exposure pathways. For example, the likelihood of the land use changing in future (e.g., from agricultural to industrial) shall be assessed based on:

- Current or programmed planning instruments[7];
- The land use pattern in the zone where the site is located; and
- Information from government stakeholders such as MRLGH, MME, MET, Ministry of Youth Namibian Defence Force, Namibia Planning Advisory Board, National Planning Commission, etc.

Where land use is dynamic i.e. changing through time, past, current and future use shall be included in the risk assessment.

The process of formulating and understanding the problem will determine the need for additional characterization of the media susceptible to contamination. In formulating the problem, it is important to take into account results of the SRA in order to identify receptors and sources of pollution to be considered in the DRA. It is imperative that human health and ecological risk assessors coordinate their activities and communicate throughout the whole process so that all relevant data are accessible to all parties concerned.

The sections below describe the steps involved in formulating the problem.

6.3.2 Assessment of Sources of Contamination

A source of contamination corresponds to the area in which a hazardous substance may have been deposited, stored or disposed of, and the point of release of substances that could represent a risk to potential receptors. For SD/AMS, sources of contamination are those associated with

[7] Regional Development Plans, Municipal Zoning Plans, Sectional Plans, definition of City Limits, Strategic Environmental Assessments etc., as may be available and applicable.

installations, deposits and/or works of the mine site identified in the SRA. Table 6-1 presents a list of potential sources of contamination associated with installations and media susceptible to contamination. The list is provided as guidance and may not be completely representative of all mine sites.

Table 6-1: Potential Sources of Contamination and Media Susceptible to Contamination

Activity	Form of Contamination	Medium Susceptible to Contamination
Underground workings	Mine drainage	Surface water /sediment Groundwater
Open pits	Pit drainage or seepage Dust	Surface water /sediment Groundwater
Processing plants	Drainage or seepage due to runoff of hazardous waste Suspension of hazardous waste from wind action Processing stack emissions (past)	Surface water /sediment Groundwater Soil Air
Tailings dams, impoundments and deposits	Drainage or seepage from the deposit Tailings transported by rainwater or suspended by wind	Surface water /sediment Groundwater Soil Air
Heap leach residue dump	Drainage or seepage from the residue dump	Surface water /sediment Groundwater Soil
Waste rock Low grade ore	Drainage or seepage from deposit Dust	Surface water /sediment Groundwater Soil Air
Small scale process waste (smelter dust, discarded solutions, etc.), industrial waste	Drainage or seepage from the deposit Transport or suspension of hazardous waste due to rain or wind	Surface water /sediment Groundwater Soil Air
Associated infrastructure	Drainage or seepage due to the presence of hazardous waste (PCBs, oils, reagents, etc.) Transport or suspension of hazardous waste (asbestos, other)	Surface water /sediment Groundwater Soil Air

6.3.3 Preliminary Identification of Chemicals of Potential Concern

Chemicals of potential concern will vary with the type of mining and processes carried out on the site under assessment. Table 6-2 provides a guide to some of the elements of potential concern, but these will vary with the specific geology of the mine and the method used in ore processing. Therefore, sampling and analytical surveys must follow advice of specialists familiar with all activities at the site. Selection of target substances for analysis must be guided by an understanding of potential impacts on human health and the environment and must satisfy the requirements of the study that intends to address the issues under investigation.

Table 6-2: Types of Mineral and Chemicals of Potential Concern

Type of Mineral Found in SD/AMS in Namibia	Elements of Potential Concern*
Polymetallics (Cu, Pb, Zn, Cd, As)	Cu, Pb, Zn, As, Cd, Be, Ag, Mo, Sb, Ge, Co, Ni
Gold	SO_4, Fe, (Hg), (CN) (depending on the process used)
Uranium	U, Rn, Ra, V, B, Mn. Full radionuclide analysis
Tin	Sn
Fluorspar	F
Pyrite	SO_4, Fe, acid generation potential
Rare Earths and Rare Metals (Lithium, Niobium, Tantalum, Wolframite)	Thorium
Phosphate	PO_4
Graphite	SO_4, Fe
Manganese	Mn
Vanadium	V, Zn, Cd, As, Hg, Pb, Cu
Coal	SO_4, Fe, Se, B, Mn

*Full cation and anion analysis recommended. Also note that organic contamination (oils and grease) from underground fuel storage tanks may be present.

6.3.4 Preliminary Identification of Receptors and Exposure Pathways

Receptors can be humans (people), animals, or ecosystems that could be at risk as a result of exposure to contaminants. The aim of the preliminary identification of receptors is to determine which human or ecological receptors are most likely to be exposed to contamination and/or are more susceptible to contaminants of potential concern (see Chapter 3).

In the DRA, experts must define the receptors in accordance with the results of the SRA, using the receptor classification scheme that was applied in the SRA, namely:

- People
- Environment

  - Aquatic Life
  - Terrestrial Life (fauna and flora)
  - Protected or Environmentally Sensitive Areas
- Economic activities
  - Agriculture (crop farming)
  - Game Farming and Livestock Activities
  - Aquaculture and Fishing
  - Tourism.

It is important to take into account that the DRA must be performed only for the types of receptors indicated in the SRA. In other words, if the SRA results for a given mine site were to indicate that there are no risks associated with the receptors 'environment' and 'economic activities' and there is no uncertainty on those assessment results, then there would be no need to conduct a DRA for those receptors. However, if there is any uncertainty about the site's SRA for human receptors, then it should be necessary to conduct a DRA for that receptor.

Exposure pathways represent the environmental media through which receptors could come into contact with chemicals of potential concern. Routes of exposure are the mechanisms of intake of contaminants into the human body, for example ingestion, inhalation and dermal contact. For humans, pathways and routes of exposure may include ingestion of contaminated water or foodstuffs, skin contact with contaminated soil or water, and/or inhalation of vapour or dust. During the formulation of the problem, the exposure pathways associated with human and ecological receptors shall be assessed in preliminary form in order to ensure that the collection of samples which may be required, will provide the information necessary to corroborate or refute the importance of any potential exposure pathways.

6.3.5 Designing a Conceptual Model

Based on the information obtained from the site, the expert shall design a conceptual model to plan the risk assessment, including supplementary sample collection activities. The conceptual model shall illustrate the relationship between chemicals of potential concern and potential receptors. This model must also highlight important features of the site to allow subsequent steps in the assessment to focus on the most significant environmental issues. This model shall be reviewed regularly as more detailed information about the site is obtained. The conceptual model consists of a schematic diagram that shall cover no less than the following aspects:

- Identification of primary sources of contamination on site (e.g., release of acid drainage from an underground mine).
- Indication of how the chemicals can move from a source into the environment (e.g., a chemical released from a tailings deposit can seep into soil and penetrate the water table, or the tailings themselves can be transported by wind).

- Identification of potential exposure pathways and routes of exposure (e.g., ingestion of contaminated water, skin contact, inhalation of particulate matter).
- Identification of direct receptors (e.g., local residents, visitors, ecosystems, crops, etc.) that could come into contact with the contaminated medium.
- Identification of indirect receptors, e.g. people who may consume agricultural products (crops, livestock) which have been contaminated.

6.3.6 Requirements for Additional Studies and Sampling

After the problem has been formulated and is clear in detail, the need for specific additional studies and sampling of media susceptible to contamination must be defined in order to complete the characterization of the SD/AMS. For example, it may be necessary to collect samples, where applicable, of fish and/or other human and animal food sources.

The following section presents more detail on sampling and supporting methodologies.

6.4 STEP 2 - Collect Supplementary Information

6.4.1 Visit to the SD/AMS

Experts involved in the studies shall visit the SD/AMS to collect information on receptors, exposure pathways and media susceptible to contamination. This information will be useful in defining the Sampling Plan that would characterize the area under assessment. The visit shall cover no less than the following areas:

- Areas with confirmed contamination.
- Areas between the source of contamination and areas that could be affected.
- Areas located along known or potential animal migration routes that could spread the contamination to other locations.
- Suitable areas of reference.

An area of reference is an area that has similar hydrological, geological, meteorological and ecosystem characteristics to the area under investigation, but which is not affected by the site's contaminants, such as an area up gradient or up wind from the mine site.

Field information shall be collected through direct observation, supported by interviews with inhabitants in the Area of Study and its surroundings, with local authorities and with organizations having interests or involved in activities in the area.

For receptors denominated 'people', information to be gathered during the initial visit shall focus on the following aspects:

- Locating nearby and other populations potentially exposed to contaminants from the site under assessment.
- Identifying groundwater wells, surface water intake works and major water supply infrastructure.
- Determining the distance between sources of drinking water supply and contaminated areas.
- Identifying the existence of farming activities in the Area of Study that provide food to the population. This addresses the possibility that residents may consume food commodities grown in contaminated soil or irrigated with contaminated water.
- Determining the existence of livestock activity in the Area of Study. In this case, the assessment shall consider the possibility that animals are consuming fodder crops contaminated by dust, and/or irrigated with contaminated water and/or drinking contaminated water.
- Determining the existence of commercial game farming in the Area of Study. In this case the focus shall be primarily on the assessment of reproductive effects of contaminants on wildlife.
- Determining the existence of fishing and aquaculture activities as a source of food for the population. This refers to the possibility that the population is consuming aquatic life forms (fish, shellfish, etc.) from contaminated water.
- Assessing the possibility that contaminants or contaminated foods are transported to other populations beyond the Area of Study that could be affected in future.
- Identifying rivers, dams and/or other water bodies that are used for recreation.

With regard to ecological receptors, the site visit shall be planned to directly assess characteristics and conditions in the area, and therefore the field team shall include a biologist or ecologist familiar with local flora and fauna, preferably someone also experienced in ecological risk assessment. Prior to the field visit, the following information must be available, at minimum:

- Present and historical use of the site and neighbouring properties.
- Past, present and possible future water use.
- Presence of sensitive ecosystems on site and adjoining land.
- Presence of endemic and endangered species.
- Local and/or regional maps indicating vegetation, sampling points (where applicable), land use, conservation areas, surface water, etc.

The ecologist/biologist with specialist knowledge needs to identify and describe flora and fauna species of ecological importance and their populations (protected species and other species that

sustain them, endemic species, etc.), revise current or potential impact indicators and locate a suitable reference habitat. This information must be collected and mapped.

Some impact indicators (for example, changes in community structure or species diversity) may not be evident during a relatively short field visit. However, the absence of certain ecosystem features may be noted during these visits, as well as evidence of potential impacts. For example, the absence of certain piscivorous birds typically found close to river banks can point to potential ecological impacts (i.e. no fish).

The date of the field visit needs to be selected with special care, as the presence or abundance of certain plants and animals is closely related to seasonal factors. It is also important to bear in mind different species' activity patterns (diurnal/nocturnal, early morning/late afternoon, etc.).

The visit to each of the areas involved shall include observation walks around the entire area occupied by the installations, works and deposits of the SD/AMS, in areas down gradient where contaminants could accumulate, at any surface water courses, etc. During these visits the occurrence of major habitat types should be logged and mapped.

6.4.2 Collection and Analysis of Supplementary Samples

Once the problem under investigation has been formulated and the site visit conducted, the team can start collecting and analyzing supplementary samples (surface water, groundwater, sediment, soil, air) to build a physical-chemical characterization of potentially contaminated media at the SD/AMS. A detailed Sampling Plan shall be prepared for each sector to be assessed, which shall include, but not be limited to, the following:

- Statement of data quality objectives;
- Sampling design, determination of the appropriate number of samples and selection of sampling points;
- Sampling methodology;
- Laboratory analyses required;
- Statistical analysis of results;
- Quality assurance and quality control of sampling (QA/QC).



Plate 6.1: Taking radiation measurements on an abandoned tailings dam

6.4.2.1 Selection of Sampling Points and Sample Size

a. Sampling points

Table 6-3 presents a conceptual Sampling Plan for media susceptible to contamination: surface water, sediment, groundwater, soil and air, for the works and installations of the SD/AMS. An expert has to be consulted to identify the process nodes and areas where samples have to be collected for analysis and to advise on the parameters that have to be determined.

Background samples must be taken to determine the background concentration of chemicals to be assessed, i.e., their naturally occurring levels in surface water, groundwater and soil. These samples should be taken in the areas of reference that are free from the influence of site contamination, but which are similar in terms of geology, topography, meteorology and other physical characteristics.

b. Sample Size

Generally, the sample size (number of samples that must be taken) and location of sampling points must be determined at the same time. To determine a suitable number of samples for the detailed risk assessment of each site, the following aspects shall be considered:

- Number of areas of concern (areas with contaminants present).
- Methods that will be used to interpret the results.
- Practical considerations related to logistics and cost.

The final number of samples and sampling points should be determined by an expert in statistical sampling design, taking into account the purpose and sensitivity of the investigation.

c. Criteria for sampling points and size

This section offers general guidance for selecting sampling points and deciding on the number of samples that have to be collected. These recommendations are for guidance only; the expert directing the study shall determine the exact criteria in each case. Generally, for sampling of liquids and solids it is advisable to collect as many samples as practically possible and to combine these into a smaller number of composite samples for analysis. Typically, ten individual samples can be combined into one composite sample. Samples collected in this manner are more representative than single point samples. Composite samples are prepared by combining equal volumes or masses of individual samples to form a single sample for analysis.

Table 6-3: Conceptual Sampling Plan for Media Susceptible to Contamination

Activity	Surface Water	Sediment	Groundwater	Soil	Air
Underground mine workings	Sample of drainage from the mine Sample of water from receiving body (river/dam) Sample from water course upstream of mine	Sample of bottom sediment in receiving water body and upstream	Sample of water from boreholes in the Area of Study Installation of new monitoring wells when water table level is less than 20 meters	Not required	Not required
Open pit workings	Sample of water accumulated in the pit	Not required	Sample of water from boreholes in the Area of Study	Not required	Not required
Processing plants	Sample of receiving water body (river/dam) Sample from water course upstream of mine	Sample of bottom sediment in receiving water body and upstream	Sample of water from boreholes in the Area of Study Installation of new monitoring wells when water table level is less than 20 meters	Sample of shallow soil (<250mm depth)	Not applicable
Tailings dams	Sample of receiving water body (river/dam) Sample from water course upstream of mine	Sample of bottom sediment in receiving water body and upstream	Sample of water from boreholes in the Area of Study Installation of new monitoring wells when water table level is less than 20 meters	Sample of shallow soil (<250mm depth) in tailings deposit	Sample of airborne contaminants at locations in the area of receptors, taking predominant wind direction into account
Heap leach residues	Sample of receiving water body (river/dam) Sample from water course upstream of mine	Sample of bottom sediment in receiving water body and upstream	Sample of water from boreholes in the Area of Study Installation of new monitoring wells when water table level is less than 20 meters	Sample of heap leach residues	Not required

Activity	Surface Water	Sediment	Groundwater	Soil	Air
Waste rock / sterile rock/ low grade ore deposits	Sample of receiving water body (river/dam) Sample from water course upstream of mine	Sample of bottom sediment in receiving water body and upstream	Sample of water from boreholes in the Area of Study. Installation of new monitoring wells when water table level is less than 20 meters.	Sample of material deposited	Not required
Industrial waste (hazardous, non-hazardous)	Sample of receiving water body (river/dam) Sample from water course upstream of mine	Sample of bottom sediment in receiving water body and upstream	Sample of water from boreholes in the Area of Study Installation of new monitoring wells when water table level is less than 20 meters	Sample of shallow soil (<250mm depth) in waste deposition area.	Sample of airborne contaminants at locations in the area of receptors, taking predominant wind direction into account
Small scale process waste (smelter dust, discarded solutions, etc)	Sample of receiving water body (river/dam) Sample from water course upstream of mine	Sample of bottom sediment in receiving water body and upstream	Sample of water from boreholes in the Area of Study. Installation of new monitoring wells when water table level is less than 20 meters.	Sample of shallow soil (<250mm depth)	Sample of airborne contaminants at locations in the area of receptors, taking predominant wind direction into account

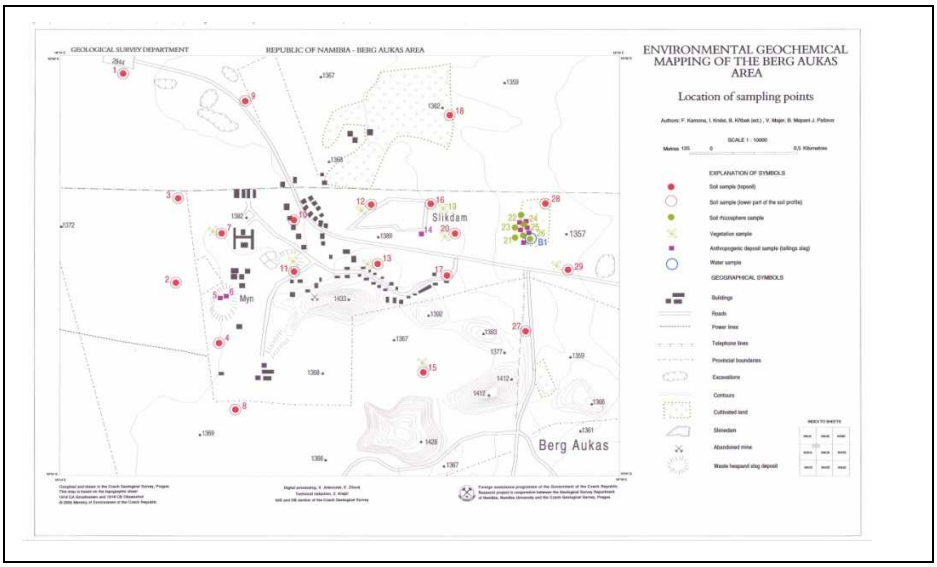


Plate 6.2: Location of soil, water and vegetation sampling points at Berg Aukas

c.1 Surface water

The following guidelines serve as a broad framework, which may be amended under certain site conditions:

- Collect samples of drainage from the mine site (underground mine, open pit, processing plant, heap leach residues, deposits of waste rock, low grade ore and waste deposits).
- Collect samples from the water body/ies upstream from each of the sources (to determine background levels). There may be more than one water course involved.
- Collect samples from the receiving water body/ies immediately downstream from the drainage discharge point. There may be more than one water course affected.
- Collect samples from the receiving water body every 500 m or in places where the water may be used within the Area of Study (consumption, irrigation, etc.), up to a distance to be determined by the expert.
- Collect a composite sample for every 500 m^2 of surface area for dams and ponds.
- Collect a composite sample for every 500 m^2 of water accumulated in a pit.

For sampling of surface water bodies, both perennial and seasonal receiving water bodies shall be taken into account, so long as there is water in the latter. If there is no flowing water in a water course, take a composite sample of the sediment (see below).

c.2 Sediment

Composite sediment samples shall be collected from the same locations where surface water sampling is conducted or from dry river beds, if there is currently no flow.



Plate 6.3: Collecting water samples from contaminated river at Otjihase Mine

c.3 Groundwater

Sampling points for groundwater comprise existing boreholes within the Area of Study. At least one sample shall be taken from each existing well.

Where groundwater is found less than 20 meters from the surface, monitoring wells may need to be installed for sampling, depending on the specific risks present in the SD/AMS. The number of wells and their location shall be determined by an environmental specialist and hydrogeologist.

c.4 Soil

For tailings deposits, heap leach residues, low grade ore, and dumps containing any other kinds of waste, a sampling grid shall be established according to the size of the deposit. The grid may be square, rectangular, triangular or hexagonal, depending on the form of the area to be sampled. The following shall be taken into account in this regard:

- At least 5 to 10 composite samples from different points around the deposit shall be collected.
- Samples shall be taken at a depth of 250mm, unless there is evidence of deep-soil contamination. Surface soil is understood to represent soil to a depth of no more than 250mm.

Soil samples in the processing plant area shall be collected as required in the field. At a minimum, one composite sample of surface soil shall be taken at points where evidence of contamination is observed.



Plate 6.4: Collecting and recording tailings samples at Oamites Mine

c.5 Air

Air monitoring programmes require that data be collected over a period of at least a year, to cover seasonal variations in meteorological conditions. Short-term monitoring programmes may be implemented for special investigations, but careful correlation with meteorological conditions must be established, with recording of wind directions, wind speeds, temperature and rain events as a minimum requirement. The location of a monitoring station shall be determined by the location of sources of air contamination and potential receptors, with due consideration to meteorological conditions. An air dispersion modelling specialist must be consulted for selecting the most appropriate location for the monitoring station(s). It is recommended that PM10s are monitored for the purposes of the HHRA and Total Suspended Particulates for the ERA. Sampling for other contaminants shall be determined by the expected source profile characteristic of the mining and processing activities.





Plates 6.5a and 6.5b: Different air quality monitoring instruments. Plate 6.5a shows a dust bucket to measure particulates; Plate 6.5b is a PM10 pump sampler.

d. Assessment of Background Levels

Background concentration is defined as the concentration of a substance in the environment in a defined geographic area, which derives from no anthropogenic sources. Obviously, around mine sites the concentrations of chemicals, and especially metals, may be naturally high, as this is the reason for the mine being there in the first place. Because of this fact, it is important to consider background data to determine whether the concentrations detected in the environment are a natural feature of the area or derive from anthropogenic activities.

In analyzing risk, it is important to determine the specific background concentrations of the mine site under assessment, as the concentration of naturally occurring metals in the environment can vary widely from one site to another and from one medium to another (water, soil and sediment). The following criteria need to be taken into account when deciding the location for background sampling:

- The sampling location must be inside the local geographic area.
- It must have the same rock deposits and surface geography found in the Area of Study.
- It must be representative of the concentration of elements attributable to natural sources.
- It must not include point source concentrations.

The number of samples required to determine background concentrations will depend on the characteristics of a particular site. In principle, background samples should be collected in 1 to 3 representative sectors for each medium (soil, water, air, etc.). However, the factors listed below may increase the number of sectors or samples that would be required to characterize background:

- Contamination of more than one medium.
- Heterogeneous geological material.
- Extensiveness of the area of interest, with variable terrain.
- Variation in concentrations of chemicals of potential concern is high compared to background.
- In cases where contamination is suspected on site, but the difference between on-site concentrations and background concentration is small.

6.4.2.2 Sampling Methodology

Instead of providing a list of sampling and analytical methods for assessing contamination in environmental media, this section provides references and links to website sources where comprehensive lists of methodologies are available online. Methodologies are being continually updated and it is prudent to consult the latest standard international documents. The most prominent sources are presented below.

- British Columbia Environmental Laboratory Manual for the Analysis of Water, Wastewater, Sediment, Biological Materials and Discrete Ambient Air Samples. 2007 Edition. http://freedownloadbooks.net/Environmental-sampling-and-analysis-lab-manual-rapidshare-pdf.html.
- FACT SHEET #29: Voluntary Remediation Program (VRP). http://deq.state.wy.us/volremedi/index.asp
- Sampling and Analysis Plans, 2007. http://deq.state.wy.us/volremedi/downloads/Current%20Fact%20Sheets/FS_29.pdf
- ASTM International (ASTM) http://www.astm.org/Standards/D5013.htm

  Searchable website providing comprehensive references to ASTM documents. The documents have to be ordered from ASTM.
- ASTM Standards on Environmental Sampling, 3rd Edition 2006

  This 3rd Edition provides access to 118 of the latest ASTM Standards on Environmental Sampling. The standards cover: Planning for sampling, screening samples in the field to indicate the need for additional sampling, interpreting data based on a specific sampling plan, various sampling techniques for a variety of environmental media, valuable information on different types of sampling equipment, sample holding times, preservation techniques, and QA/QC specifications. http://www.constructionbook.com/astm-standards-on-environmental-sampling-3rd-edition
- J Russell Boulding and Jon S Ginn, 2003. Practical Handbook of Soil, Vadose Zone, and Ground-Water Contamination. http://books.google.co.za/books

  This book serves as a comprehensive guide for conducting complex site investigations and identifying methods for effective soil and ground water cleanup. A list of applicable ASTM methods is provided.
- US Environmental Protection Agency (USEPA) Test Methods

  Test methods are approved procedures for measuring the presence and concentration of chemical pollutants and physical parameters.

  The Test Methods Collections page provides links to numerous sources of methods and guidelines. http://www.epa.gov/osa/fem/methcollectns.htm

  The Index to EPA Test Methods provides information on locating and obtaining test methods and provides both chemical names and numeric indices. The Index to EPA Test Methods can be accessed from: http://www.epa.gov/ne/info/testmethods/

Some methods are published as a part of official EPA publications. In these cases, the Test Method Index will list the EPA publication number. Many, but not all, of these publications are available in the National Service Center for Environmental Publications (NSCEP) catalogue Web site: http://www.epa.gov/nscep/

A web search can be conducted using the method number using on the search page at: http://www.epa.gov/epahome/search.html

Many test methods are published in Title 40 of the Code of Federal Regulations. This resource is available online at: http://www.gpoaccess.gov/ecfr/

- Environment, Health And Safety Online

  This is a free website that lists links to all USEPA Test Methods. Go to: http://www.ehso.com/testmethods.php

- International Standards Organization (ISO)

  Section 13: Environment Health Protection Safety provides access to ISO Methods for characterisation of contamination in air, soil and water.
  http://www.iso.org/iso/iso_catalogue/catalogue_ics/catalogue_ics_browse.htm?ICS1=13

6.4.2.3 Laboratory analysis

The parameters to be analyzed in environmental media will depend on the type of mining and metallurgical process at the investigation site, and the nature of the contamination. Generally, the assessment is divided into the classes of inorganic cations and anions, semi-volatile organic compounds and volatile organic compounds. Analytical methods are available from the standard database sources listed under Sampling Methodology above. Analytical laboratories often adapt methods for convenience to become 'in-house' procedures. This is acceptable as long as the laboratory has documented the procedure and recorded deviations from the original method. Methods must go through a validation process.

Chemicals that pose a greater ecological risk rather than a human health risk may need to be analysed in more detail than would otherwise be required. In addition, minimum required detection limits may be lower for ecological concerns than for human health concerns in some cases. Certain water quality parameters, such as pH, hardness, salinity and oxygen levels, are also more important for ecological assessments.

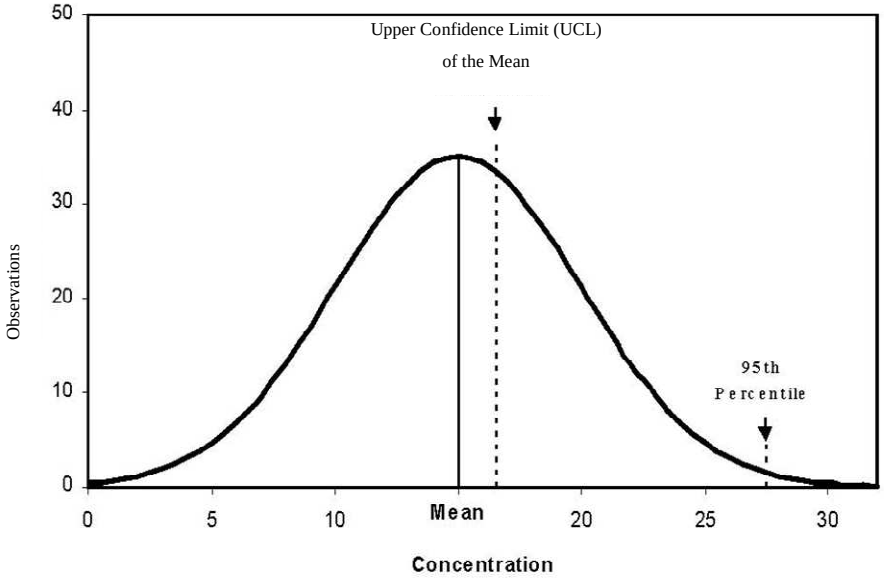
Special attention needs to be paid to the competence of the laboratory and methods of analysis to ensure that the detection limits of the analytical method are lower than the guideline concentrations for contaminants in the media under assessment.

Note that the laboratory facilities in Namibia are limited and may not be able to undertake all of the desired analyses or to the detection level required. Samples therefore may have to be sent to South Africa or overseas.

6.4.2.4 Statistical Analysis of the Results

A variety of factors come into play when assessing contamination risks, many of which have no definite natural distribution. A good example of this is the variation in concentrations of substances in a medium such as soil or water. The more samples that are analyzed, the better the information that will be generated of the range of potential results and typical concentrations (in statistics, this is known as the central limit theorem; see Figure 6-3).

Figure 6-3: Statistical Analysis of Laboratory Results. Comparison of UCL and 95th Percentile[8]



As the number of samples increases, the upper confidence limit (UCL) of the mean approaches the true mean, while the 95%-ile (95 percentile) of the distribution stays in the upper extreme of the distribution. The concentrations of contaminants at a site are usually characterized with statistical values such as:

- Range;
- Mean;
- Mean with 95% level of confidence (95% Upper Confidence Limit of the Mean (UCLM));
- 90th percentile;
- Percentage of samples that exceed the standard.

[8] Figure taken from the document "Supplemental Guidance to RAGS: Calculating the Concentration Term," US EPA, 1992

Risk assessors commonly use the mean with a confidence level of 95% as well as the 90th percentile, as it is preferable to overestimate rather than underestimate risks.

While it is possible to calculate these statistical parameters with a limited set of data, it does not always make sense to do so when the number of samples is insufficient (e.g., when the subset of contaminated locations is too small). For example, calculating the 90th percentile with less than 20 samples available generally does not yield a good estimation of the parameter. On the other hand, it is preferable to have 10-15 replicas for calculating the mean with a level of confidence of 95%. If less than 10 samples are available, it is possible to calculate this value and that of the mean; however, given the uncertainty of the statistical distribution, it will be more prudent to use the maximum value, with its associated risk, as an estimation of the level of contamination.

Good professional judgment is required in these cases; for example, if the bulk of the area presents a relatively low level of contamination but there are specific areas that are highly contaminated due to a particular activity (e.g., a loading area where concentrate was transferred to trucks and spills occurred), then the loading area shall be defined as 'Area of Environmental Concern (AEC) No. 1' and the next as 'AEC No. 2', as these are two different distribution 'populations' for the contaminants. Thus, separate risks will be calculated for each AEC. Furthermore, remediation decisions may be different for each AEC; for example, it may be decided to clean AEC No. 1, but to take a different approach to AEC No. 2.

The expert shall use his/her judgment in selecting the source of information to obtain values which best represent the different variables. For example, the consumption frequency of fish from a contaminated body of water is best based on information obtained through interviews with local inhabitants rather than through statistical data taken from a generic report on regional fish consumption patterns.

6.4.2.5 Quality Assurance and Quality Control of Sampling (QA/QC)

For quality assurance and quality control of sampling activities, the investigator shall take into account sampling protocols, sampling equipment and materials, quality control samples, sample containers and sample preservation procedures.

a. Sampling Protocol

The sampling protocol for risk analysis needs to include the following:

- Objectives of the study;
- Sample numbering system;
- Procedures for collecting, preserving, handling and transporting samples;
- Analytical strategies that will be used.

b. Sampling Equipment and Materials

The equipment and materials used for the collection, storage, preservation and transport of samples must not alter the samples. For example, some material used to build monitoring wells for taking groundwater samples may absorb certain chemical compounds, preventing them from appearing in the collected sample.

c. Quality Control Simples

Samples must be taken for quality control (trip blank, field blank, equipment blank, replicate sample, split sample). These samples shall be stored, transported and analyzed in exactly the same way as samples taken to characterize the site.

It is recommended that all of these quality control samples be identified in the same way as the samples taken to characterize the site, so that the laboratory is not aware of which samples are quality control ones.

Field Blank. This sample is taken to confirm that no contaminant has inadvertently been introduced from the site into the samples during the sampling and transport process. Field blanks may be containers of de-ionized water or background soil that are taken from the laboratory to the site in closed containers and then transferred to other clean containers at the sampling location. This action has to reflect as closely as possible the sample handling procedures during sampling.

Trip blank. This consists of containers of de-ionized water or background soil samples prepared in the lab. The trip blanks are kept closed in the same cooler as the other samples at each stage of the process, from the time the containers are sent to the field until they are accepted by the lab. During the entire process, the samples shall remain closed to avoid contamination during sample transport or during storage in the lab. At least one trip blank is required for each batch of samples sent to the analytical laboratory. Trip blanks are analysed only in cases where field blanks show unexpected contamination or high concentrations of the substances under investigation.

Equipment Blank. An equipment blank is a sample of analyte-free media which has been used to rinse the sampling equipment. It is collected after completion of decontamination and prior to sampling. This blank is useful in documenting adequate decontamination of sampling equipment.

Replicate (Duplicate) Sample. These are independent samples that are collected as close as possible to the same point in space and time. They are two separate samples taken from the same source, stored in separate containers, and analyzed independently. These duplicates are useful in documenting the precision of the sampling process. It must be understood that duplicate sampling does not add statistical significance to the analytical results, because a larger number of samples is required for calculation of mean values and confidence intervals.

Split Sample. Aliquots of sample taken from the same container and analyzed independently. In cases where aliquots of samples are impossible to obtain, field duplicate samples shall be taken for the matrix duplicate analysis. These are usually taken after mixing or compositing and are used to document intra- or inter-laboratory precision.

d. Sample containers

Sample containers must be selected according to the sampling and analytical objectives. For water, soil and sediment samples, containers may be of glass or amber glass bottles of different sizes, glass jars, plastic bottles or plastic bags (for soils and sediments). For certain applications the lids of glass bottles must be Teflon-lined. Teflon-lined septa are used on bottles for sampling of volatile substances. Care must be taken in the selection of plastic sampling bottles, because certain plastics may contaminate samples. Volatile substances could also be lost as a result of diffusion through plastics.



Plate 6.6: Labelling and recording soil samples

Air samples for volatile organics may be collected in Tedlar® bags or Summa canisters. These techniques are specialized and their limitations must be recognized. In many cases air sampling requires techniques other than collection in bags or canisters.

The choice of sample containers is critical for maintaining sample integrity and to avoid contamination. An expert must be consulted for advice on appropriate sample containers.

e. Preservation of Samples

Suitable procedures need to be established to preserve the samples from collection to analysis in the laboratory, so as not to alter the chemical concentrations present in the medium from which they were extracted. Advice on preservation is given by ASTM[9] and SquiRT Tables[10].

[9] ASTM Standards on Environmental Sampling, 3rd Edition 2006
This 3rd Edition provides access to 118 of the latest ASTM Standards on Environmental Sampling.
http://www.constructionbook.com/astm-standards-on-environmental-sampling-3rd.

The following are some common sample preservation techniques used for different matrices:

- Generally, water, soil and sediment samples must be transported and stored under cold conditions (4°C).
- Preservation of water samples may be done under acidic or alkaline conditions. Depending on the analytes of interest, acidic preservation uses sulphuric acid or nitric acid to pH < 2. Alkaline preservation uses sodium hydroxide to pH > 12. If the interest is in dissolved species (not suspended matter), samples must be filtered prior to preservation.
- Soil and sediment samples are not preserved by addition of acid or alkaline solutions.
- Biological samples must be kept cold (<4°C) and analyzed within 24 hours of collection, **OR** they must be kept frozen until they are analyzed.
- Holding times of samples depend on the sample matrix and analytes of interest. The appropriate holding time must be clarified with the analytical laboratory and must be documented in the sampling and analytical procedures. Advice on holding times is provided in ASTM Standards on Environmental Sampling, 3rd Edition 2006 and in the SquiRT Tables referred to above.

f. *Chain of Custody*

The possession and handling of samples from the time they are collected until they are analyzed in the laboratory shall be managed under chain of custody with sample details recorded on a chain of custody form.

The purpose of the chain of custody form is to control and document the transfer of samples from the point of collection to the analytical laboratory. The form is signed each time when a sample or batch of samples is relinquished by one person and accepted by another. Dates and times are recorded and important observations noted, for example, leaking of bottles or when samples are not cold. Each person in the chain of custody keeps a copy of the signed chain of custody form for quality assurance records.

It is common practice to combine the chain of custody form with an analytical request form. The laboratory then receives not only the sample detail on the chain of custody form, but also a clear instruction for the analyses that are required.

[10] Guidelines for preserving samples and for analytical technique options are available in the Screening Quick Reference Tables (SQuiRTs) present screening concentrations for inorganic and organic contaminants in various environmental media Buchman MF 2008. NOAA Screening Quick Reference Tables, NOAA OR&R Report 08-1, Seattle WA, Office of Response and Restoration Division, National Oceanic and Atmospheric Administration, 34 pages.
http://response.restoration.noaa.gov/.

6.5 STEP 3 – Assessment of Chemicals of Potential Concern

The 'tiered approach' in contaminated site investigations was introduced to simplify the assessment process where multiple chemicals are present in environmental media. The tiered approach does not affect the actual level of risk to humans and ecological receptors in any way; the higher Tiers in the assessment involve more extensive investigations to reduce uncertainties in the risk assessment process, thereby removing 'non-issues' from the study list, thus reducing the data sets to a more manageable size and focusing the study on those toxicants that are of critical concern.

Chemicals of Potential Concern are assessed in Tier-1 by comparison with selected reference concentrations for contaminants in environmental media. These reference values are usually conservative and do not take into account site-specific conditions. The assessment assumes that exposure may occur and pathways and receptors are not considered in detail in Tier-1. Chemicals that are present in the environmental medium (air, soil, sediment of water) at concentrations below their respective reference concentrations are not of concern and are removed from the study list. The assessment then continues only for those substances that are present at concentrations above the screening guidelines.

Screening guidelines are not remediation goals or remediation target levels, but serve to identify potential concerns and the need for further investigation of site contamination. The cleanup level for contaminants in environmental media is a site-specific criterion that a remedial action has to satisfy in order to keep exposure to potential receptors at or below a risk-based 'action level'.

Where concentrations of chemicals are equal to or less than background concentrations, these should not be included in the human health and/or ecological risk analysis, even when they are higher than the guideline concentrations. This is because it is impractical to attempt to reduce risk through remediation when contaminant concentrations are found to be lower than background levels.

The process of evaluating ecological risks of environmental contaminants comprises two Tiers. Tier-1 is a screening assessment where concentrations of contaminants in the environment are compared to no-observed-adverse-effects-level (NOAEL)-based toxicological benchmarks that represent concentrations of chemicals in environmental media (water, sediment, soil, food, etc.). These concentrations are presumed to be non-hazardous to the surrounding biota. The second tier (Tier-2) is a baseline ecological risk assessment, where toxicological benchmarks are one of several lines of evidence used to support or refute the presence of ecological effects.

Annexure C1 presents a summary of sources of guideline concentrations.

6.6 STEP 4 – Risk Assessment

6.6.1 Quantitative human health risk assessment

6.6.1.1 Introduction

A site-specific risk assessment is undertaken when concentrations of compounds are higher than the guideline concentrations.

The original paradigm for regulatory human health risk assessment in the USA was developed by the USA National Research Council[11]. This model has been adopted and refined by the US Environmental Protection Agency (USEPA)[12; 13] and other agencies around the world[14], and is widely used for quantitative health risk assessments. The paradigm essentially divides human health risk assessment into a number of logical steps, as is outlined below:

- ***Hazard assessment*** is the identification of chemical and biological contaminants suspected to pose hazards and a description of the types of toxicity that they may evoke. This has been dealt with in Steps 1 to 3 (sections 6.3 – 6.5) above.
- ***Dose-response assessment*** (toxicological assessment) addresses the relationship between levels of biological exposure and the manifestation of adverse health effects in humans, and/or how humans can be expected to respond to different doses or concentrations of contaminants. This is a quantitative assessment that distinguishes between carcinogens and non-carcinogens. Risk quantification for carcinogens uses a cancer slope factor (CSF) for each substance, whereas non-carcinogens are characterised by reference doses (RfDs) and tolerable daily intake (TDI) values, as defined below:
- ***Exposure assessment*** includes a description of the environmental pathways and distribution of hazardous substances, identification of potentially exposed individuals or communities, the routes of direct and indirect exposure, and an estimate of concentrations and duration of the exposure. Determination of the intake of a substance (i.e., dose), expressed in mg per kg body weight per day (mg/kg-day), is the critical outcome of an exposure assessment.
- ***Risk characterization*** involves the integration of each component described above, with the purpose of determining whether specific exposures to an individual or a community might lead to adverse health effects. Risks are indicated by numbers such as a hazard quotient of larger or smaller than one, or a cancer risk of one in a hundred thousand or one in a million.
- ***Uncertainty review*** identifies the nature and, when possible, the magnitude of the uncertainty and variability inherent in the characterisation of risks. The results of any risk

[11] NRC. 1983. Risk Assessment in the Federal Government: Managing the Process. National Research Council, Committee on the Institutional Means for the Assessment of Risks to Public Health, National Academy Press, Washington, DC.
[12] USEPA. 1989. Risk Assessment Guidance for Superfund. Volume I. Human Health Evaluation Manual (Part A). Interim Final. EPA/540/1-89/002. US Environmental Protection Agency.
[13] USEPA. 1991. Risk Assessment Guidance for Superfund (RAGS), Volume I: Human Health Evaluation Manual (HHEM), Part B, Development of Risk-Based Preliminary Remediation Goals. US Environmental Protection Agency Office of Emergency and Remedial Response, Washington, DC. OERR 9285.7-01B. NTIS PB92-963333.
[14] IPCS. 1999. Environmental Health Criteria 210. Principles for the Assessment of Risks to Human Health from Exposure to Chemicals. World Health Organisation, Geneva.

assessment reflect scientific uncertainty associated with limitations in available data and assumptions that are made in the absence of such data, and the variability in exposure and toxicological response expected, given the diversity within the human population. Uncertainty review demonstrates the level of confidence in the outcome of the risk assessment and indicates whether additional data might be required, or whether elements of the precautionary principle have to be applied.

The approach to derive cleanup or remediation target levels is essentially a 'backwards' health risk assessment, working from levels of acceptable health risk for specific land-use options, through the exposure scenario and toxicological information, to contaminant concentrations in the environmental media relating to the acceptable risk levels.

The land use determines potential exposure pathways and routes of exposure to site contaminants, and defines the human and ecological receptors. These parameters, together with the toxicity profiles of contaminants, determine the maximum levels of exposure to which humans and ecological receptors may be subjected before health effects could potentially develop. To define the receptors, exposure pathways, and the frequency and duration of exposure, the assessor must take into account past, current and future land use patterns by consulting zoning plans, conducting interviews or consulting historical documents for each area under assessment.

6.6.1.2 Dose-Response Assessment (Toxicological Assessment for Humans)

Toxicological information is available from various databases and literature sources. The most prominent are the USEPA Integrated Risk Information System (IRIS)[15], the Agency for Toxic Substances and Disease Registry (ATSDR)[16], International Agency for Research on Cancer (IARC)[17], International Toxicity Estimates for Risk (ITER)[18], California Office of Environmental Health Hazard Assessment (OEHHA)[19], Health Canada[20], Baars *et al., 2001*[21], and World Health Organization (WHO)[22].

[15] Integrated Risk Information System (IRIS), http://www.epa.gov/ncea/iris/index.html.
[16] Agency for Toxic Substances and Disease Registry (ATSDR), http://www.atsdr.cdc.gov/.
[17] International Agency for Research on Cancer (IARC), http://www.iarc.fr/.
[18] International Toxicity Estimates for Risk, http://toxnet.nlm.nih.gov/cgi-bin/sis/htmlgen?iter.
[19] California Office of Environmental Health Hazard Assessment (OEHHA), http://oehha.ca.gov/about.html.
[20] Health Canada, Environment & Workplace Health, Reports & Publications. http://www.hc-sc.gc.ca/ewh-semt/pubs/.
[21] Baars AJ, Theelen RMC, Janssen PJCM, Hesse JM, Van Apeldoorn ME, Meijerink MCM, Verdam L & Zeilmaker MJ. 2001. Re-evaluation of human-toxicological maximum permissible risk levels. Bilthoven, The Netherlands: National Institute of Public Health and the Environment, March 2001, p 47-57. RIVM report no. 711701025. http://www.rivm.nl/bibliotheek/rapporten/711701025.pdf or at http://www.rivm.nl/en/.
[22] International Programme on Chemical Safety, Environmental Health Criteria. Geneva: World Health Organization.

The cancer slope factor per USEPA definition[23] *is "an upper bound, approximating a 95 per cent confidence limit, on the increased cancer risk from a lifetime exposure to an agent. This estimate, usually expressed in units of proportion (of a population) affected per mg/kg-day, is generally reserved for use in the low-dose region of the dose-response relationship, that is, for exposures corresponding to risks less than 1 in 100".* Dose is expressed as intake in milligrams of a substance per kilogram body weight per day. The slope factor therefore has the units $(mg/kg\text{-}day)^{-1}$.

USEPA[24] has identified several carcinogens that act via a mutagenic mode of action, and to account for their early-life exposures, default age-dependent adjustment factors (ADAFs) of 10 for ages 0-to-2 and 3 for ages 2-to-16 years have been introduced by USEPA in the cancer risk assessment methodology.

USEPA defines a reference dose (RfD) as *"an estimate of a daily oral exposure for a given duration to the human population (including susceptible subgroups) that is likely to be without an appreciable risk of adverse health effects over a lifetime."* It is derived from a benchmark dose limit (BMDL), a no-observed-adverse-effect level (NOAEL), a lowest-observed-adverse-effect level (LOAEL), or another suitable point of departure, with uncertainty/variability factors applied to reflect limitations of the data used. The term tolerable daily intake (TDI) has a meaning similar to the RfD, describing a *threshold dose*.

6.6.1.3 Exposure Assessment

a. Identify and Characterize Receptors Potentially at Risk

Receptors must be identified and characterized mainly in terms of how they use or occupy a site (differentiating inhabitants, workers, visitors, etc.). In analyzing receptors, the past, current and future uses of the site must be taken into account, including changes arising from current or future projects (such as modifications to zoning plans, construction of residential subdivisions and/or manufacturing plants, etc.).

Typical receptors are selected as child residents (ages 0 to 6 years), adult residents and non-resident workers. The childhood life stage is used in the assessment of exposure to non-carcinogens. Children have a higher ratio of environmental medium intake rate to body weight than adults and their behaviour increases their contact with the exposure pathway (e.g., playing with dirt – see Plate 6.7). For the assessment of exposure to carcinogens, the concept of an aggregate resident is applied. This approach averages dose across the childhood and adult life stages up to the age of 30 years. The non-resident worker assumes exposure of an adult for an occupational lifetime of 30 years.

[23] IRIS. 2010, online. Glossary of IRIS Terms. Integrated Risk Information System, US Environmental Protection Agency, Washington DC, USA.
[24] USEPA. 2005. Supplemental Guidance for Assessing Susceptibility from Early-Life Exposure to Carcinogens. Risk Assessment Forum, US Environmental Protection Agency. EPA/630/R03/003F.



Plate 6.7: Children are using this part of the old Berg Aukas plant as a slide

b. Identify Exposure Pathways to be Assessed

Exposure pathways are the media through which contaminants reach receptors. All potential pathways of exposure have to be investigated and a particular pathway can be removed from the assessment only if it is not 'complete'. This means that the pathway must be able to reach a receptor. For example, if groundwater is contaminated but the water yield of the aquifer is so low that the water cannot be used for any purpose, then the pathway would not be complete and exposure of potential receptors cannot occur. Table 6-4 indicates typical exposure pathways of chemicals of potential concern.

Table 6-4: Exposure Pathways to Consider in Assessing Exposure

Direct Exposure Pathways	Potential Concerns	Routes of Exposure
Surface Soil	Particulate matter (non-toxic)	Inhalation
	Particulate-associated contaminants	Inhalation, ingestion, dermal contact
Subsoil	Particulate-associated contaminants, occupational exposure, construction	Inhalation, ingestion, dermal contact
Surface water	Contaminants in surface water	Ingestion, dermal contact
Groundwater	Volatile and non-volatile contaminants	Inhalation, ingestion, dermal contact
Air	Contaminants as gas or on particulates	Inhalation
Indirect Exposure Pathways	**Potential Concerns**	**Routes of Exposure**
Surface water	Contamination into the food chain	Ingestion
Surface soil	Contamination into the food chain	Ingestion
Subsoil	Contamination into the food chain	Ingestion
	Contamination of subsurface soil	Ingestion
Groundwater	Contamination of groundwater	Ingestion

The food pathway considers ingestion of such commodities as vegetables grown in soil that is potentially contaminated by fall out dust (Plate 6.8), or irrigated with contaminated water; ingestion of products (meat, milk) from animals that consume contaminated water or which browse on forage growing in contaminated soil; or the consumption of aquatic species (fish, seafood, etc.) from contaminated waters.



a)



b)

Plate 6.8: a) Carrots being grown in highly contaminated soil at the Berg Aukas plant site, in spite of warnings by GSN not to grow root crops; b) cabbage being grown in soil contaminated by past spills from the Berg Aukas tailings

c. Integration of Receptors and Pathways of Exposure

Figure 6-4 shows an example of a scheme that can be followed to assess the links between potential exposure pathways and receptors. The example refers to contaminated soil. The dots indicate where an exposure pathway is complete, indicating routes of exposure and receptors. Direct exposure to contaminated soil can be developed further to include exposure of utility or construction workers. Similar schemes can be developed for other pathways of exposure, potential receptors and activities that may lead to exposure.

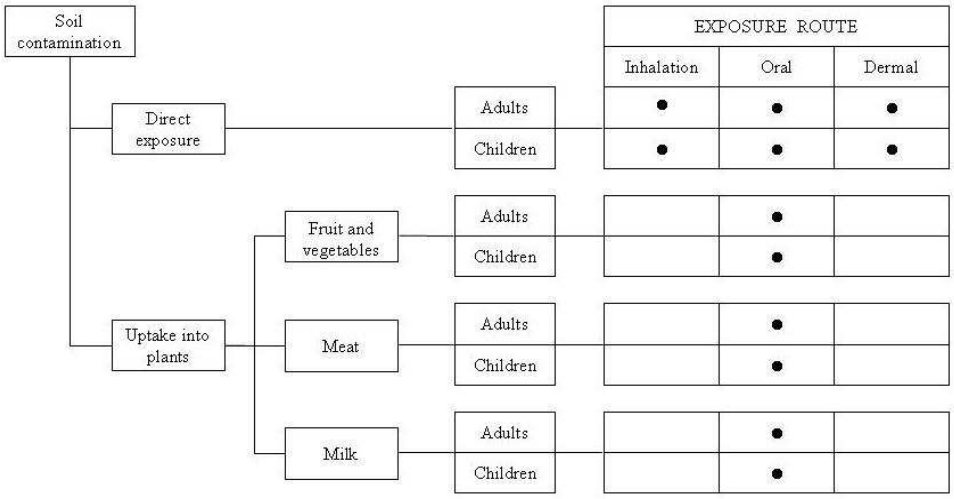
d. Determination of Exposure Frequency and Duration of Exposure

Exposure frequency and duration of exposure are parameters that depend on human behaviour and activity patterns. There may be large differences between different exposure scenarios and different population groups. It is recommended that surveys be conducted to estimate actual exposure patterns. In the absence of site-specific data it is recommended that the USEPA exposure factors[25;26]

[25] USEPA. 2009. Exposure Factors Handbook. National Center for Environmental Assessment, Office of Research and Development, US Environmental Protection Agency.
http://www.epa.gov/ncea.

be selected as a point of departure. These may be adjusted by an expert to be better representative of the scenario under investigation.

Figure 6-4: Example of Pathway-Receptor Integration Diagram.



e. Quantification of Exposure

USEPA provides general guidance on how to characterise exposures and risks when conducting risk assessments[27]. For exposure assessments, according to USEPA, it is suggested that intake and exposure values be selected so that the combination of all variables results in an estimate of the reasonable maximum exposure (RME) for that pathway. The RME is the maximum exposure that is reasonably expected to occur at a site. Under this approach, some intake variables (e.g., exposure frequency, duration of exposure and intake rate) may not be at their individual maximum values, but when in combination with other variables, will result in estimates of the RME[28]. USEPA guidance recommends estimating the high-end exposure by "*...identifying the most sensitive parameters and using maximum or near-maximum values for one or a few of these variables, leaving others at their mean values…*"[29]. This guidance applies when only limited information on the distribution of the exposure or dose factors is available. The recommendation is based on the fact that maximising all

[26] USEPA. 2008. Child-specific exposure factors handbook. National Center for Environmental Assessment, Washington, DC; EPA/600/R-06/096F. http://www.epa.gov/ncea.
27 USEPA, 1998. Risk Assessment Guidance for Superfund, Volume I: Human Health Evaluation Manual, Supplemental Guidance. Dermal Risk Assessment. Interim Guidance. (Peer Consultation Workshop Draft, November 6, 1998). US Environmental Protection Agency). Office of Emergency and Remedial Response.
28 USEPA, 1989. Risk Assessment Guidance for Superfund. Volume I. Human Health Evaluation Manual (Part A). Interim Final. EPA/540/1-89/002. US Environmental Protection Agency.
29 USEPA, 1992. Memorandum: Guidance on Risk Characterisation for Risk Managers and Risk Assessors. From: F Henry Habicht II. February 1992. US Environmental Protection Agency.

variables would result in an estimate that is above the range of actual values observed in the population.

Central tendency exposure (CTE) represents the most likely (lower risk) exposure scenario under which conditions the majority of individuals would be subjected. For example, the average CTE individual may ingest some 50 mg of soil per day while the RME may ingest 100 mg per day. Thus CTE exposure estimates would allow higher residual contaminant levels in soil (because of lower exposure of individuals) than concentrations derived from RME estimates (higher exposure levels). Calculated risks and the derivation of cleanup target levels derived for CTE and RME scenarios therefore apply to a range of concentrations that would cover the levels of a contaminant in soil.

e.1 Exposure Concentrations

Exposure concentrations will be estimated using information from site sampling or through a combination of sampling data and contaminant destination and transport models.

Sampling data may be used to estimate exposure concentrations through direct contact with the media. These cases may include direct contact with chemicals in soil or sampling done directly at the exposure point, such as a borehole used for drinking water. In these cases, the sampling data will yield the best estimate of real exposure concentrations. The sampled concentrations that will be used in this case will be defined by the expert.

In some cases it may not be appropriate to use only sampling data and contaminant fate and transport models may be required to estimate exposure concentrations. These models are recommended in the following cases:

- When the exposure points are spatially separated from sampling points. In this case models will be required to determine if mechanisms of release and transport to the exposure points are operating (for example, groundwater transport, air dispersion);
- When no information is available on the temporal distribution of data. Generally, data are collected over a relatively short period of time and give an indication of current conditions at the site. However, long-term and short-term exposures may be different. In that case it will be necessary to use forecasting models to predict the change in concentrations over time;
- In cases where sampling data are affected by the detection limit, models will be required to predict contaminant concentrations that could be toxic, but measured under the detection limit of the analytical method. For example, when a groundwater plume discharging into a river is diluted by the receiving water body, this may reduce concentrations of substances of interest to below levels that would be detected using laboratory analytical techniques. Nevertheless, the chemical could be sufficiently toxic or bio-accumulative to pose a health risk at concentrations below the analytical method's detection limit, in which case models for estimating exposure would be applied.

e.2 Dose Calculation

Quantification of dose can be complex and must be undertaken by an expert in human health risk assessment.

The generic Equation for calculating average daily dose from exposure to contaminants in air, soil or water is as follows:

$$ADD = (C \, x \, IR \, x \, EF \, x \, ED \, x \, BAF \, x \, CF) / (BW \, x \, AT) \qquad (6\text{-}1)$$

Where:

ADD	Average daily dose of a substance from intake of air, soil or water (mg/kg-day)
C	Concentration of substance in air (mg/m^3), soil (mg/kg) or water (mg/litre)
IR	Daily intake rate of air (m^3/day), soil (mg/day) or water (litres/day)
EF	Exposure frequency (days/year)
ED	Exposure duration (years)
BAF	Bioavailability factor for substances in air (default 1)
CF	Unit conversion factor: air 1, soil 10^{-6} kg/mg, water 1
BW	Body weight (kg)
AT	Averaging time (days)

Bioavailability as expressed in the BAF can play an important role in estimating the human exposure associated with exposure to toxic substances in the environment. Bioavailability defines the portion of chemical exposure (e.g., the quantity inhaled or ingested) that enters the bloodstream and that is assumed to be available to produce toxic effects in tissues. It is important to note that bioavailability depends on the chemical species, the medium of exposure and the tissue with which the chemical interacts.

In some cases, such as in quantification of cancer risk to account for mutagenic action in the early life stages of exposed individuals, the risk assessment requires calculation of an age-weighted dose.

For dermal contact, quantification of average daily absorbed dose follows the paradigm described by the United States Environmental Protection Agency[30].

[30] USEPA. 1992. Dermal Exposure Assessment: Principles and Applications. EPA/600/6-88/005Cc Office of Health and Environmental Assessment, US Environmental Protection Agency, Washington, DC.

The dermally-absorbed average daily intake from contaminants in water is described in Equation 6-2.

$$ADD = \left(DA_{event}\ x\ SA\ x\ EV\ x\ EF\ x\ ED\right) / \left(BW\ x\ AT\right) \quad (6\text{-}2)$$

Where:

ADD	Dermally-absorbed average daily intake of a contaminant from water or soil (mg/day)
DA_{event}	Absorbed dose per unit skin area per event (mg/cm^2-event)
SA	Total skin surface area (cm^2)
EV	Event frequency (events/day)
EF	Exposure frequency (days/year)
ED	Exposure duration (years)
BW	Body weight (kg)
AT	Averaging time

The absorbed dose per unit skin area from contaminants in water is controlled largely by the dermal permeability coefficient of a contaminant from water. Where dermal permeability coefficients of contaminants are not available from literature sources, these can be estimated from empirical relationships based on molecular weight and octanol-water partition coefficients of the substances[31]. The most recent USEPA guidance[32] on dermal risk assessment published a relationship for the absorbed dose per skin area per event that accounts for the lag time for absorption where exposure duration is shorter than the time required for reaching steady state. It accounts for the fact that short exposures, such as during body washing, have been shown to lead to higher absorption of the contaminants considered in this assessment than what would be predicted from conditions under steady-state.

The absorbed dose per unit skin area from contaminants in soil is determined by a soil adherence factor and a dermal absorption fraction that is substance-specific. The adherence factor describes the amount of soil that adheres to the skin per unit of surface area. It is influenced by soil properties and varies considerably across different parts of the body. It also varies with age and activity patterns.

[31] McKone TE and Howd RA, 1992. Estimating Dermal Uptake of Nonionic Organic Chemicals from Water and Soil: 1: Unified Fugacity-Based Models for Risk Assessments. Risk Analysis, 12(4):543-557.

[32] USEPA. 2004. Risk Assessment Guidance for Superfund Volume 1: Human Health Evaluation Manual (Part E, Supplemental Guidance for Dermal Risk Assessment) Final. EPA/540/R/99/005, OSWER 9285.7-02EP, PB99-963312, July 2004. Office of Superfund Remediation and Technology Innovation, US Environmental Protection Agency, Washington, DC.

The ability to quantify the absorption of contaminants from exposure to soil is limited. Chemical-specific information is available for only a few chemicals. McKone and Howd[33] developed an approach to calculate the overall mass transfer of organic chemicals from soil through the combined adhered soil layer using a thermodynamic fugacity model. For inorganic substances, speciation of the compound is critical to the dermal absorption and there are inadequate data to extrapolate a reasonable default value. Estimates have been made by various agencies

6.6.1.4 Characterization of Human Health Risks

a. Health Risks Associated with Criteria Pollutants

In the assessment of health effects due to exposure to the criteria pollutants (particulate matter (PM10), sulphur dioxide (SO_2), and nitrogen oxides (represented by NO_2)), mortality or hospitalisation rates for respiratory or cardiovascular causes are the measure of associated illness that is mostly applied in epidemiological studies. Air concentrations of compounds that exceed the ambient air quality guidelines or standards indicate that adverse health conditions may develop, but simple comparisons between exposure concentrations and ambient air quality guidelines are inadequate to quantify health outcomes. In general, predicted or measured impacts of industrial emissions on air quality are used as a basis to quantify impacts on health. This is achieved by calculating the potential increase in hospital admissions or in mortality due to specific causes, associated with increased air concentrations of specific toxic compounds. These calculations are based on results of studies reported in the international scientific literature in which statistical methods were used to compare changes in hospitalisation or mortality rates with changes in air quality.

It is important to note that it is common to observe increases in mortality or hospitalisation rates even when the available air concentrations do not exceed the environmental air quality guidelines. Ambient air quality guidelines are used for management of air quality and are not intended for risk quantification. Estimation of impacts of air pollutants on health may therefore not be restricted to areas in which the guideline concentrations are exceeded, but should also include areas in which concentrations are within limits. Current statistical methods use the concept of relative risk ratios (RR) to derive the potential percentage increase in effects.

The potential number of additional deaths or hospital admissions brought on by an increase in the concentration of a pollutant is calculated using the following approach of the World Health Organization[34]:

[33] McKone TE and Howd RA, 1992. Estimating Dermal Uptake of Nonionic Organic Chemicals from Water and Soil: 1: Unified Fugacity-Based Models for Risk Assessments. Risk Analysis, 12(4):543-557.
[34] WHO. 2004. Meta-analysis of Time Series Studies and Panel Studies of Particulate Matter (PM) and Ozone (O_3). EUR/04/5042688. Copenhagen: World Health Organization Regional Office for Europe.

$$E = AF \times P \times B / 1000 \quad (6\text{-}3)$$

Where:

E	Potential mortalities or morbidities per day or per year due to exposure to the pollutant
AF	The attributable fraction of mortalities or morbidities due to exposure to the pollutant
B	The population incidence of mortality or morbidity (e.g., deaths or hospitalisation rates per 1 000 people)
P	Size of the exposed population (number)

$$AF = RR - 1 \quad (6\text{-}4)$$

Where:

RR	The relative risk of mortality or morbidity due to exposure to the pollutant

The relative risk of death (RR) is calculated as follows:

$$RR = e^{(\Delta_{deaths} \times \Delta_p)} \quad (6\text{-}5)$$

Where:

Δ_{deaths}	Potential proportion change in mortality associated with a change in the pollutant concentration of 1 µg/m^3
Δ_p	The modelled change in the mean pollutant concentration in µg/m^3

Similar calculations can be made for morbidity cases.

b. Risk for Non-Carcinogenic Systemic Toxicants

The dose calculated using the equations presented should be compared to the reference dose (RfD) for non-carcinogenic chemicals for each exposure pathway. The ratio of these two values is the Hazard Quotient (HQ), which can be calculated using the following equation:

$$HQ = (ADD_I + ADD_O + ADD_D) / RfD \quad (6\text{-}6)$$

Where:

HQ	Hazard quotient for exposure to a substance in water (unitless)
ADD_I	Average daily dose of a substance due to inhalation of air (mg/kg-day)
ADD_O	Average daily dose of a substance due to oral intake of water (mg/kg-day)
ADD_D	Dermally-absorbed average daily dose of the substance from water, considering

	various dermal exposure scenarios (mg/kg-day)
RfD	Reference dose in mg/kg-day

The Hazard Index (HI) is the summation of the Hazard Quotients (HQs) associated with exposure to systemic toxicants that act on the same target organ systems.

c. Risk for Carcinogenic Chemicals

Calculated cancer risks refer to excess risk, i.e., risks due to exposure to a particular substance, over and above the background cancer risks to which members of the community may be exposed.

$$Cancer\ risk = (ADD_I + ADD_O + ADD_D)\, x\, Q^* \qquad (6\text{-}7)$$

Where:

Cancer risk	Cancer risk expressed as a unitless number
ADD_I	Average daily dose of a substance due to inhalation of air (mg/kg-day)
ADD_O	Average daily dose of a substance due to oral intake of water (µg/kg-day)
ADD_D	Dermally-absorbed average daily dose of a substance from water, including personal cleaning and washing of clothes
*Q**	Cancer slope factor $(mg/kg\text{-}day)^{-1}$

Individual cancer risk is expressed as a probability based on the number of cancer cases that may be expected in a population of a selected size, for example the number of cases in a million, in a hundred thousand, or in ten thousand. The actual population size in the study is not taken into account. Risk estimates obtained in this way are not estimates of actual cancer risk; the calculated numbers are upper bounds on actual cancer risk that are useful to regulators for setting priorities and for setting exposure limits. In cases where communities may be exposed to more than one cancer-causing agent, the calculated cancer risks associated with the individual substances are added to obtain an overall upper bound of cancer risk.

The concept of aggregate exposure quantification and risk assessment takes into account the number of individuals in the area that is being investigated, such as a regional district or suburb of a city. It may involve exposure to multiple cancer-causing agents through different routes of exposure, but it may focus on a single chemical and one route of exposure. The assessment presents the average probability of people developing chemical-exposure-induced cancer during their lifetime or the number of lifetime chemical-exposure-induced cancer cases for a specific aggregate population during a specified time period.

d. Acceptability of Risk

The level of total cancer risk that is of concern is a matter of personal, community, and regulatory judgement. In general, the USEPA[35] considers excess cancer risks that are below about 1 chance in a million ($1x10^{-6}$ or 1E-06) to be so small as to be negligible (*de minimis* lifetime risk), and risks above one in ten thousand ($1x10^{-4}$ or 1E-04) to be sufficiently large that some sort of remediation is desirable (*de manifestis* risk). In the judgement of cancer risk, the cancer classification of the substance, as published by IARC[36] and USEPA[37], must be taken into account.

The assessment of risk implications of HQs and HIs require understanding of the background toxicology and epidemiology, as well as the assumptions and uncertainties associated with reference doses and tolerable daily intakes of substances. There is no simple rule that may be applied in all assessments. A HQ or HI below 1 confirms that health risks are unlikely to occur, but values above 1 do not infer that adverse effects would in fact be observed. This requires interpretation by an expert in health risk assessment, which must take into account the entire body of scientific background information on which the assessment criteria are based.

6.6.1.5 Analysis of Uncertainties

It is often not possible, nor necessary, to conduct sophisticated statistical interpretations of estimates of exposure and risk. Generally, qualitative description of assumptions and uncertainties provide sufficient information to contextualize the outcome of the health risk assessment.

The risk assessment paradigm must follow standard international practice, as outlined in this Handbook. When applied under guidance of an expert, the outcome of the health risk assessment should have a high level of confidence. Toxicological parameters from credible, peer reviewed sources have known levels of confidence and if these data are considered in the assessment, the calculated risk can be presented with confidence. The risk assessment must state sources and the level of confidence in the reference data. The paradigm of risk assessment is designed to be on the side of caution, thus intended to overestimate rather than underestimate risk.

Data quality is controlled by formal QA/QC plans, stating data quality objectives and setting criteria for data acceptance. Interpretations shall be made only on data that have been signed off as credible on the basis of the QA/QC procedures.

In cases of limitations in the sampling and analytical process, for example sampling under difficult circumstances where samples might not be fully representative of the situation under study, or

35 USEPA. 1991. Role of the Baseline Risk Assessment in Superfund Remedy Selection Decisions, US Environmental Protection Agency. OSWER Directive 9355.0-30.
36 Integrated Risk Information System (IRIS), http://www.epa.gov/ncea/iris/index.html.
37 International Agency for Research on Cancer (IARC), http://www.iarc.fr/.

analysis of samples with multiple contaminant interferences, a sensitivity analysis must be undertaken of the parameters that may affect the data quality. This will assist in establishing the confidence interval in which the data can be presented.

6.6.2 Ecological Risk Assessment

6.6.2.1 Introduction to Quantitative Ecological Risk Assessment

The strategy for ecological risk assessment (ERA) is more complex than that for human health risk assessment and is fundamentally different in its inferential approach. The greater complexity is due largely to the large number of species and the diversity of routes of exposure that must be considered in ERAs.

The steps in the paradigm for ERA generally are similar to the assessment for human health risks, with slightly different uses of certain terminology. The paradigm uses the term 'stressor response' rather than 'dose response', because both physical and chemical parameters are addressed in ERA.

The paradigm divides ecological risk assessment into a number of logical steps, as is outlined below:

- ***Problem formulation (hazard assessment)*** is the identification of chemical and biological contaminants suspected to pose hazards to ecosystems and a description of the types of toxicity that they may evoke. This has been dealt with in Steps 1 to 3 in sections 6.3 to 6.5 above. In the USEPA's Framework for Ecological Risk Assessment, formulation of a conceptual model for assessing ecological risk is the output of the problem formulation phase of the assessment[38]. It presents a working hypothesis of how the site contaminants might affect the ecological components of the site. It includes descriptions of the source, the receiving environment, and the processes by which the receptors come to be exposed directly to the contaminants and, secondarily, to the effects of the contaminants on other environmental components.

Ecological receptors include all endpoint species or communities identified for a site.

- **Stressor-response assessment[39]** is an integration of exposure and response. Stressor-response assessment addresses the relationship between levels of biological exposure and the manifestation of adverse health effects ecological receptors. Calculation of stressor response and exposure estimates is the determination of what plants and animals are

[38] USEPA. 1992. Framework for Ecological Risk Assessment. US Environmental Protection Agency. Washington, DC. Report No EPA/630/R-92/001.

[39] USEPA. 2010. Online. Superfund Risk Assessment: Ecological: Stressor Response and Exposure Analysis. US Environmental Protection Agency. Washington, DC. http://www.epa.gov/oswer/riskassessment/superfund_stressor.htm.

exposed to, quantitative determination of the level of exposure and an interpretation of whether or not that level of exposure is likely to cause harmful ecological effects.

- **Exposure assessment** includes a description of the environmental pathways and distribution of hazardous substances and identification of potentially exposed ecological receptors. It requires the investigation and quantification of various parameters (e.g., area use, food ingestion rates, bioaccumulation rates, bioavailability, life-stage, body weight, and dietary composition) to determine the levels of exposure to a chemical contaminant by a selected plant or animal receptor.
- **Risk quantification** involves the calculation of hazard quotients (the ratio of chemical contaminant concentration to a selected screening benchmark).
- ***Uncertainty review*** identifies the nature and, when possible, the magnitude of the uncertainty and variability inherent in the characterisation of ecological risks. The results of ecological risk assessment often reflect greater scientific uncertainty than interpretations of human health risk assessment.

6.6.2.2 Stressor-Response Assessment for Ecological Receptors

The process of evaluating ecological risks of environmental contaminants comprises two tiers. Tier-1 is a screening assessment where concentrations of contaminants in the environment are compared to no-observed-adverse-effects-level (NOAEL)-based toxicological benchmarks that represent concentrations of chemicals in environmental media (water, sediment, soil, food, etc.). These concentrations are presumed to be non-hazardous to the surrounding and otherwise-exposed biota.

The second tier is a baseline ecological risk assessment where toxicological benchmarks are one of several lines of evidence used to support or refute the presence of adverse ecological effects[40]. See also Annexure C1.

Unlike some other endpoint assemblages, terrestrial wildlife is significantly exposed to contaminants in multiple media. They may drink or swim in contaminated water, ingest contaminated food and soil, and breathe contaminated air. In addition, because most wildlife is mobile, moving among and within habitats, exposure is not restricted to a single location. They may integrate contamination from several spatially discrete sources. Therefore, exposure models for terrestrial wildlife must include multiple media.

Guidance for ecological risk assessment has been published in a number of research papers[41;42;43] and other literature that may be consulted[44].

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[40] Sample BE, Opresko DM and Suter GW, 1996. Toxicological Benchmarks for Wildlife: 1996 Revision. Prepared for US Department of Energy. Report No ES/ER/TM-86/R3.
[41] Suter GW II. 1996. Guide for Developing Conceptual Models for Ecological Risk Assessments

6.6.2.3 Exposure Assessment

a. Identification of ecological receptors

Ecological receptors can include individual organisms, populations and/or communities that could be exposed to contaminants. Potential receptors can be identified after reviewing the destination, migration and real or potential release of contaminants. The investigator needs to identify terrestrial and aquatic areas, sensitive and protected habitats, farming, livestock, commercial game farming, fishing and aquaculture zones within the site or nearby and develop lists of species known or likely to exist in each habitat. Specific care must be taken to list the following:

- Endangered, threatened, rare or endemic species;
- Species protected by specific legislation;
- Species that might be consumed by people;
- Species that are indicators of the health of a community.

If the chemicals of potential concern at a site are known to be bio-accumulative (e.g. cadmium, mercury), it will be important to consider environmental fate with regard to the trophic relations among species in order to assess effects related to the food chain.

b. Identification of Exposure Pathways

Ecological receptors can be exposed to chemicals through direct or indirect contact. The main exposure pathways are presented in Table 6-5.

Environmental Restoration Risk Assessment Program, Oak Ridge National Laboratory. Oak Ridge, Tennessee. Report No ES/ER/TM-186.

[42] Sample B. E., Aplin M. S., Efroymson R. A., Suter G. W. II and Welsh C. J. E.. 1997. Methods and Tools for Estimation of the Exposure of Terrestrial Wildlife to Contaminants. Oak Ridge National Laboratory. Environmental Sciences Division Publication No. 4650. ORNL/TM-13391.

[43] Suter GW, Efroyson RA, Simple BE and Jones DS. 2000. Ecological Risk Assessment for Contaminated Sites. CRC Press, Boca Raton, Florida.

[44] Guidance for Ecological Risk Assessment at Hazardous Waste Sites and Permitted Facilities. State of California, California Environmental Protection Agency. Department of Toxic Substances Control, Human and Ecological Risk Division. July 4, 1996. http://www.dtsc.ca.gov/AssessingRisk/upload/overview.pdf.

Table 6-5: Ecological Risk Assessment. Possible Exposure Pathways by Media Susceptible to Contamination.

Medium	Exposure pathway	Observations
Surface water	Direct contact	Terrestrial organisms can be exposed through direct contact with contaminants present in surface water by walking or swimming in the water. Aquatic receptors can be exposed by osmotic exchange or by breathing in surface water.
	Contact through roots	Contaminants may come into direct contact with terrestrial plants through roots that are in contact with surface water.
	Ingestion	Terrestrial receptors can ingest contaminated water through drinking.
Sediment	Ingestion	Terrestrial organisms can ingest sediment occasionally and accidentally when they take their food from places that flood only periodically. Aquatic organisms can ingest sediment during regular feeding activity.
	Direct contact	Aquatic organisms can be exposed directly or through osmotic exchange, respiration or ventilation of interstitial water.
Groundwater	Contact through roots	Contaminants can enter into contact with terrestrial plants through roots that are in contact with groundwater.
Soil	Foliage deposition	Exposure of terrestrial plants to contaminants present in particles deposited on the surface of leaves and stems.
	Contact through roots	Contaminants in the soil can dissolve and be absorbed by plant roots.
	Ingestion	Accidental ingestion of contaminated soil by animals when feeding off plants grown in or covered with contaminated soil
	Direct contact	Many species live in burrows – often excavated in the soft substrate of tailings dams – and therefore complete their life cycles fully or partially in direct contact with contaminated material
Air	Inhalation of gases or vapour	Exposure via inhalation is most important for organisms that nest in contaminated soil, considering the limited amount of air present to dilute vapour and the absence of airflow to disperse gases.
	Inhalation of dust	Inhalation exposure to fugitive dust is particularly applicable to species living in the soil, which can be exposed through their activity in the soil or by the wind.
	Absorption through foliage (vapour)	Foliar absorption of organic vapours is limited to species with a relatively high vapour pressure.
	Foliage deposition (dust)	Exposure of terrestrial plants to contaminants present in particles deposited on the surface of leaves and stems.

Medium	Exposure pathway	Observations
Food Chain	Ingestion	Animals with the highest terrestrial and aquatic trophic levels include predators, which do not necessarily have to come into direct contact with a contaminated medium, but can be exposed by ingesting contaminated food.

c. Uptake of contaminants into animal and plant tissue

This factor is important in the assessment of exposure through indirect food pathways. Information may be obtained from direct analysis of food sources (e.g., fish, plants, etc), or concentrations may be estimated by applying mathematical multi-media uptake models, based on media transfer factors[45;46].

d. Quantification of Exposure for Terrestrial Receptors

d.1 Exposure factors

Exposure factors for wildlife are available in the USEPA Wildlife Exposure Factors Handbook[47]. This Handbook provides data, references, and guidance for conducting exposure assessments for wildlife species exposed to toxic chemicals in their environment. The information is applicable to wildlife in the USA, but may be used as a point of departure for deriving exposure factors applicable to the situation in Namibia.

d.2 Quantification of dose

Exposure of animals to contaminants usually occurs in one of three main ways: water ingestion, food ingestion or accidental ingestion of soil or sediment. Except for inhalation of criteria air pollutants such as sulphur dioxide, exposure to environmental toxicants via inhalation and skin contact generally are considered negligible compared to exposure through ingestion.

Assessment of exposure to a contaminant generally requires quantification of the dose ingested with contaminated water, food, soil or sediment[48].

[45] Staven LH, Napier BA, Rhoads K, and Streng DL. 2003. A Compendium of Transfer Factors for Agricultural and Animal Products. Pacific Northwest National Laboratory.
[46] Ecological Risk Analysis: Guidance, Tools, and Applications. ORNL. http://www.esd.ornl.gov/programs/ecorisk/biological_uptake.html.
[47] USEPA. 1993. Wildlife Exposure Factors Handbook. US Environmental Protection Agency, Washington, DC. EPA/600/R-93/187 (2 Volumes). http://cfpub.epa.gov/ncea/cfm/.
[48] Sample BE and Suter GW, 1994. Estimating Exposure of Terrestrial Wildlife to Contaminants. Prepared for US Department of Energy. Report No ES/ER/TM-86/R3.

$$ADD = ADD_F + ADD_W + ADD_S + ADD_{SD} \quad (6\text{-}8)$$

Where:

ADD	Average daily dose of a substance from all exposure pathways (mg/kg-day)
ADD_F	Average daily dose of the substance from food sources (mg/kg-day)
ADD_W	Average daily dose of the substance from intake of water (mg/kg-day)
ADD_S	Average daily dose of the substance from intake of soil (mg/kg-day)
ADD_{SD}	Average daily dose of the substance from intake of sediment (mg/kg-day)

Exposure estimates must be expressed in terms of a body-weight normalized daily dose. Information on bioavailability of individual toxicants is too limited to apply bioavailability factors in the estimation of dose. It is assumed that the bioavailability will be set at a default value of 1. The receptor's contact with the contaminated medium shall be estimated on information such as location of receptors in the Area of Study (influence), movement of receptors (for animals) and time spent in the contaminated zone.

Estimation of the daily contaminant dose of an individual from a particular medium is expressed in its simplest form by the following equation:

$$ADD_j = \sum_{i=1}^{m} \left(\frac{IR_i \, x \, C_{ij}}{BW} \right) \quad (6\text{-}9)$$

Where:

ADD_j	Average daily dose of contaminant j (mg/kg-day)
i	Environmental medium i (food, water or soil)
m	Total number of environmental media
IR_i	Consumption rate of medium i (kg/day or litre/day)
C_{ij}	Concentration of contaminant j in medium (mg/kg or mg/litre)
BW	Body weight of endpoint species (kg)

Few wildlife species consume diets that consist exclusively of one food type. To account for the intake of varying contaminant concentrations in different food types, exposure estimates must be weighted by the relative proportions of daily food intake from the different sources.

$$ADD_j = \sum_{i=1}^{m} \left(\frac{FIR_i \, x \, C_{ij}}{BW} \right) \quad (6\text{-}10)$$

Where:

ADD_j	Average individual daily dose of contaminant j (mg/kg-day)
i	Food type i (food, water or soil)
m	Total number of food types
FIR_i	Intake rate of food type i (kg/day)
C_{ij}	Concentration of contaminant j in food type i (mg/kg fresh weight)
BW	Body weight of endpoint species (kg)

The ingestion rate for each food type may be estimated from:

$$FIR_i = P_i \, x \, FIR \qquad (6\text{-}11)$$

Where:

FIR_i	Ingestion rate of each food type for an individual (kg/day)
P_i	Proportion of the i^{th} food type in the diet
FIR	The total food ingestion rate (kg/day)

If the affected (contaminated) area has similar habitat to the surrounding area that constitutes the home range, exposure to contaminants would be proportional with regard to area.

$$ADD_j = \left(\frac{A}{HR}\right)\sum_{i=1}^{m}\left(\frac{IR_i \, x \, C_{ij}}{BW}\right) \qquad (6\text{-}12)$$

Where:

ADD_j	Average daily dose of contaminant j (mg/kg-day)
A	Contaminated area (hectares)
HR	Home range size (hectares)
i	Environmental medium i (food, water or soil)
m	Total number of environmental media
IR_i	Consumption rate of medium i (kg/day or litre/day)
C_{ij}	Concentration of contaminant j in medium (mg/kg or mg/litre)
BW	Body weight of endpoint species (kg)

In cases where the site under consideration is highly modified and only a proportion of the contaminated area provides suitable habitat, an additional factor may be introduced to account for the lesser exposure:

$$ADD_j = P_h \left(\frac{A}{HR} \right) \sum_{i=1}^{m} \left(\frac{IR_i \, x C_{ij}}{BW} \right) \quad (6\text{-}13)$$

Where:

ADD_j	Average daily dose of contaminant j (mg/kg-day)
P_h	Proportion of suitable habitat in the contaminated area
A	Contaminated area (hectares)
HR	Home range size (hectares)
i	Environmental medium i (food, water or soil)
m	Total number of environmental media
IR_i	Consumption rate of medium i (kg/day or litre/day)
C_{ij}	Concentration of contaminant j in medium (mg/kg or mg/litre)
BW	Body weight of endpoint species (kg)

Where sites are heterogeneous, the proportional contribution of each area can be modelled to account for the factors of contaminant levels and quality and habitat.

$$ADD_j = \sum_{k=1}^{n} \left(\frac{A_k}{HR} \left[\sum_{i=1}^{m} \left(\frac{IR_i \, x C_{ijk}}{BW} \right) \right] \right) \quad (6\text{-}14)$$

Where:

ADD_j	Average daily dose of contaminant j (mg/kg-day)
n	The number of distinct contaminated areas
A_k	Area of a distinct contaminated habitat area
HR	Home range size (hectares)
i	Environmental medium i (food, water or soil)
m	Total number of environmental media
IR_i	Consumption rate of medium i (kg/day or litre/day)
C_{ijk}	Concentration of contaminant j in medium i in the k^{th} area (mg/kg or mg/litre)
BW	Body weight of endpoint species (kg)

The equation can be expanded further to account for wide-ranging wildlife to multiple contaminated areas.

6.6.2.4 Quantification of ecological risks

a. Risk Assessment Methodology for Birds and Mammals

In general, risk is quantified by estimating the ingestion of contaminants (ingested dose) by wildlife and comparing this dose to reference dose values (estimated for organisms of reference under laboratory conditions or from epidemiological studies) as referenced in Annexure C1. A hazard quotient can be calculated to assist in the assessment. After this comparison, an extrapolation is performed to estimate the probability of ecological effects on wildlife under natural conditions. The methodology may be applied to assess the risk to wild or domestic animals (livestock). Quantified chronic exposure values shall represent a level of exposure to a chemical contaminant with no adverse effects, i.e., not exceeding the no-observed-adverse-effect-level (NOAEL). The ecological effects of greatest concern are those that can affect population levels, in other words, those that affect development, reproduction and survival on a group basis.

The science of risk assessment in ecology has not evolved to the point where scientists can make standard risk calculations for common risk scenarios, as is done in human health evaluations. Risk characterization in ecological assessment is a process of applying professional judgement to determine whether adverse effects are occurring or may occur as a result of contamination associated with a site.

Because professional judgment is so important, specialized knowledge and experience in the various phases of ecological risk assessment is required. Thus, an interactive multidisciplinary team that includes biologists, ecologists and risk assessment specialists is a prerequisite for a successful ecological risk assessment.

b. Risk Assessment Methodology for Fish, Invertebrates and Plants

In the case of these receptors there is no reference to ‘dose’ by some route of exposure. The maximum contaminant concentration needs to be established for the medium in which these organisms live, which is then compared with a reference toxicity value for aquatic or relevant terrestrial organisms.

The stressor-response component of ecological risk assessment for aquatic receptors considers more factors than the toxicological effects of chemicals and physical stressors. Assessment is divided in the evaluation of a ‘driver component’ and a ‘response component’.

- The ‘driver component’ of the assessment considers water quality and habitat as the primary factors that would affect the integrity of the ecosystem. This is a generic assessment that is independent of the actual species and their sensitivities in the environmental setting and generally is on the conservative side, i.e., it tends to overestimate rather than underestimate risk.

- The 'response component' involves a practical site-specific assessment (field measurements) of the integrity of the ecosystem, compared against the expected state in the absence of impacts. The study uses effects-based criteria and always overrides the assessment based on chemical criteria, because it considers more direct measurements of adverse effects. The outcome of this holistic study is an integrated assessment of the local ecosystem integrity state.

6.6.2.5 Analysis of Uncertainties

Even more than is the case with human health risk assessment, it is not possible, nor necessary, to conduct sophisticated statistical interpretations of estimates of exposure and risk in ecological risk assessment. Generally, qualitative description of assumptions and uncertainties provide sufficient information to contextualize the outcome of the health risk assessment.

Ecological risk assessments are based on scientific data that are frequently difficult and complex, conflicting or ambiguous, or incomplete. Analysis of such data for risk assessment purposes depends on professional judgment based on scientific expertise. Professional judgment is necessary to:

- Design and conceptualize the risk assessment;
- Evaluate and select methods and models;
- Determine the relevance of available data to the risk assessment;
- Develop assumptions based on logic and scientific principles to fill data gaps; and
- Interpret the ecological significance of predicted or observed effects.

Data quality needs to be controlled by formal QA/QC plans, stating data quality objectives and setting criteria for data acceptance. Interpretations shall be made only on data that have been signed off as credible on the basis of the QA/QC procedures.

The ecological risk assessment paradigm must follow standard international practice, as outlined in this Handbook. When applied under guidance of an expert, the outcome of the risk assessment should provide good estimates of exposure and risk. Toxicological parameters from credible, peer reviewed sources have known levels of confidence and if these data are considered in the assessment, the calculated risk can be presented with confidence in stated confidence intervals. The risk assessment must state sources and the level of confidence in the reference data. The risk assessor shall be conservative in selecting values from other sources and shall detail the limitations of these values when applying these. The paradigm of ecological risk assessment is designed to be on the side of caution, thus intended to overestimate rather than underestimate risk.

In cases of limitations in the sampling and analytical process, for example sampling under difficult circumstances where samples might not be fully representative of the situation under study, or analysis of samples with multiple contaminant interferences, a sensitivity analysis must be undertaken of the parameters that may affect the data quality. This will assist in establishing the confidence interval in which the data can be presented.

Overall, the statement of confidence in the ecological risk assessment must be made by an expert in the field.

6.7 STEP 5 – Risk Statement

6.7.1 Human health risk assessment

This step in the assessment process requires that guidance be set on the acceptability of risk. It is a complicated step that has to consider the acceptability of health risks to humans and ecological receptors in balance with social implications and financial considerations. It requires multi-disciplinary expertise in cost-benefit analysis, taking into account regulatory requirements.

In particular, this step has to advise on the requirement or not for remedial action. It involves the application of multi-disciplinary science that has to take into account social, financial and environmental considerations.

An example of a Probability Index rating scheme is presented in Table 6-6.

Table 6-6: Example of a Probability Index Rating scheme.

Probability Index	Public Health	
	Excess Cancer Risk	Non-cancer Risk (HQ or HI max. value)
High	>1E-04	> 100
Medium	Between 1E-05 and 1E-04	Between 10 and 100
Low	Between 1.0E-6 and 1E-05	Between 1 and 10
Negligible	<1E-06	< 1

As discussed in Section 6.6.1.4d., the level of total cancer risk that is of concern is a matter of personal, community, and regulatory judgement. Table 6-6 reflects excess cancer risks that are below one in a million (1E-06) to be so small as to be negligible (*de minimis* lifetime risk). Risks above one in ten thousand (1E-04) are sufficiently large that some sort of corrective action is desirable (*de manifestis* risk). The description of such risks in Table 6-6 as “high” should be placed into context. In

the judgement of cancer risk, the cancer classification of the substance, as published by the IARC[49] and USEPA[50], as well as the particular cancer endpoint, must be taken into account. The Globally Harmonized System for classification and labelling of chemicals (GHS)[51] applies the cancer classification presented in Table 6-7.

Table 6-7: Classification Criteria for Hazard Categories of Carcinogens.

Hazard Category	Classification Criteria
1A	Known to have carcinogenic potential for humans, based largely on human evidence.
1B	Presumed to have carcinogenic potential for humans: • evidence from human studies that establish a causal relationship between human exposure to a chemical and the development of cancer (known human carcinogen), or • evidence from animal tests for which there is sufficient evidence to demonstrate animal carcinogenicity (presumed human carcinogen), and • on a case-by-case basis, scientific judgement may warrant a decision of presumed human carcinogenicity derived from studies showing limited evidence of carcinogenicity in humans together with limited evidence of carcinogenicity in animal tests.
2	Suspected human carcinogen: • evidence from human or animal studies (or both), but which is not sufficiently convincing for classification as a category 1 carcinogen, and • limited evidence of carcinogenicity in human studies or limited evidence of carcinogenicity in animal tests.

There is a factor 10 difference in the hazard rating between Category 1 and Category 2 carcinogens in the GHS, which indicates that there is no generalised hazard rating for the various categories of cancer classification. There are many examples that demonstrate limitations associated with generalisation of interpretations across carcinogens. For example, in cancer risk quantification for carcinogens that have mutagenic activity, cancer slope factors have to be adjusted to account for higher vulnerability in the early human life stages. Vinyl chloride is another example; there is a difference in cancer risk quantification between exposure from birth and exposure only in the adult life stage. The Probability Index in Table 6-6 must thus be applied with caution.

The rating of HQ and HI values for non-carcinogens is subject to similar limitations. The significance of a HQ of a substance depends on the level of certainty of the reference dose (RfD) or the tolerable daily intake (TDI). Uncertainty (safety) factors are applied to account for limitations in data and for the adjustment of animal data and epidemiology studies to apply to the most sensitive human receptors. These uncertainty factors may range between as low as 10 to as high as 10 000. Furthermore, RfDs are based on effects on the most sensitive health endpoints, the effects of which

[49] International Agency for Research on Cancer (IARC), http://www.iarc.fr/.
[50] Integrated Risk Information System (IRIS), http://www.epa.gov/ncea/iris/index.html.
[51] Globally Harmonized System of Classification and Labelling of Chemicals (GHS). Document ST/SG/AC.10/30/Rev 2. United Nations 2007.

may be reversible or irreversible. The severity of systemic toxicity of a particular toxicant, as reflected in exceedence of the RfD, depends on the slope of the dose-response relationship in the low-dose region and it is inappropriate to generalise interpretation of the value of a HQ for all non-carcinogens as has been done in the Probability Index in Table 6-6. The information in Table 6-6 must thus be regarded purely as an example of the methodology that may be followed for establishing a Probability Index in the assessment of environmental exposure to hazardous chemicals. The actual assignment of a Probability Index for a hazardous chemical shall be done by specialists in chemical toxicology, epidemiology and health risk assessment.

6.7.2 Ecological risk assessment

It has been pointed out in Section 6.6.2.4 a. that the science of risk assessment in ecology has not evolved to the point where scientists can make standard risk calculations for common risk scenarios, as is done in human health evaluations. Applying a generalised scheme for developing a Probability Index rating scheme for a diverse range of ecological receptors is thus a challenge. Risk characterization in ecological assessment requires a great deal of professional judgement to determine whether adverse effects are occurring or may occur as a result of contamination associated with a site. The HQ is only one of the factors that assist in ecological risk interpretation.

Table 6-8 presents an example of a Probability Index rating scheme for ecological receptors. The information in this table must be regarded purely as an example. Ecological risk assessment specialists shall interpret dose-response information of toxicants on particular ecological species and the health endpoints of concern. After assessment in detail, a Probability Index can be compiled for a particular stressor on the category of receptors of interest.

Table 6-8: Probability Index versus Ecological Risk Value or Hazard Quotient (HQ).

Probability Index	Ecological Risk (HQ)
High	> 100
Medium	From 10 to 100
Low	From 1 to 10
Negligible	< 1

6.7.3 Assessment of the severity of consequences

A generalised scheme for the assessment of severity of the consequences of exposure to environmental contamination is presented in Table 6-9.

Individual human cancer risk is expressed as a probability based on the number of cancer cases that may be expected in a population of a selected size, for example the number of cases in a million, in a hundred thousand, or in ten thousand. The actual population size in the study is not taken into

account. Risk estimates obtained in this way are not estimates of actual cancer risk; the calculated numbers are upper bounds on actual cancer risk that are useful to regulators for setting priorities and for setting exposure limits. In cases where communities may be exposed to more than one cancer-causing agent, the calculated cancer risks associated with the individual substances are added to obtain an overall upper bound of cancer risk.

The concept of aggregate exposure quantification and risk assessment takes into account the number of individuals in an area that is investigated, such as a regional district or a particular residential area in the vicinity of the contaminated site. It may involve exposure to multiple cancer-causing agents through different routes of exposure, but it may also focus on a single chemical and one route of exposure. The assessment presents the average probability of people developing chemical-exposure-induced cancer during their lifetime or the number of lifetime chemical-exposure-induced cancer cases for a specific aggregate population during a specified time period. The aggregate population may consist of different subpopulations subjected to different doses of cancer-causing agents.

Table 6-9: Example of a Severity of Consequences Index Rating.

		Severity of Consequences				
		Negligible	**Low**	**Moderate**	**High**	**Catastrophic**
PEOPLE	Public Health (nº of people that could come into contact with the contaminant)	None	For carcinogens, severity is based probabilistically on aggregate cancer risk assessment For non-carcinogens, it is based on specific target organ toxicity and the toxicity dose-response relationship, considering the level of confidence in the toxicity data			
THE ENVIRONMENT	Aquatic Life (surface area or length of water body/course affected by contamination)	No habitat loss	< 5 ha for wetlands and dams; OR < 0.5 km for rivers/coast	5 - 10 ha for wetlands and dams; OR 0.5 - 2 km for rivers/coast	> 10 ha for wetlands and dams or >2 km for rivers/coast	Not applicable
	Aquatic Life (loss of biodiversity)	No biodiversity loss	Some loss of biodiversity. Ecosystem under low threat. Effects would be reversible	Biodiversity low. Species limited to a few tolerant individuals. Ecosystem under stress. Possible irreversible impacts.	No biodiversity. No living creatures evident. Ecosystem dead. Irreversible effects.	Not applicable
	Terrestrial Fauna & Flora (total area of habitat affected)	No habitat loss	< 10 ha	10 - 100 ha	> 100 ha	Not applicable

		Severity of Consequences				
		Negligible	**Low**	**Moderate**	**High**	**Catastrophic**
	Terrestrial Fauna & Flora (biodiversity loss)	No biodiversity loss	Some loss of biodiversity. Ecosystem under low threat. Effects would be reversible	Biodiversity low. Species limited to a few tolerant individuals. Ecosystem under stress. Possible irreversible impacts.	No biodiversity. No living creatures evident. Ecosystem dead. Irreversible effects.	Not applicable
	Terrestrial Fauna & Flora (drinking water resources affected)	None contaminated	Many other sources of uncontaminated water within 10km radius	One or two alternative uncontaminated water sources within a 10km radius	Only source of water within a 10km radius is contaminated	Not applicable
	Protected or Environmentally Sensitive Areas (area or sites affected by contamination)	None	< 1 ha	1 - 10 ha; OR cultural heritage sites of local importance	>10 ha; OR cultural heritage sites of regional/national importance	Not applicable
ECONOMIC ACTIVITIES	Crop Farming (crop production type)	No toxic effects	Only certain species susceptible to contamination or pollution are affected e.g. salt intolerant spp, root vegetables etc	Only a few very tolerant species can be grown	No crops can be grown because of high levels of soil and crop contamination	Not applicable
	Crop production - yield and income	No effects on yield and/or income	Loss of 20% of yield and/or income due to contamination. Limited effect on livelihoods	Loss of 21-50% of crop yield and/or income due to contamination. Moderate impact on livelihoods	Loss of >50% of crop yield and/or income. Lands have to be abandoned. Major impact on livelihoods	
	Game Farming & Livestock Activity – grazing areas	No loss of grazing area or grazing quality	Loss of <20% of grazing area due to contamination	Loss of 21-50% of grazing land due to contamination	Loss of >50% 0f grazing area due to contamination	Not applicable

		Severity of Consequences				
		Negligible	**Low**	**Moderate**	**High**	**Catastrophic**
	Game Farming & Livestock Activity - production rate and income	No loss of income	<20% drop in production. Limited impact on livelihoods	Loss of 21-50% in production and/or income due to contamination. Some products cannot be sold or consumed. Moderate impact on livelihoods	Loss of >50% in production and/or income. Lands have to be abandoned. Major impact on livelihoods	
	Aquaculture and Fishing	No loss of income	<20% drop in production. Limited impact on livelihoods	Loss of 21-50% in production and/or income due to contamination. Some products cannot be sold or consumed. Moderate impact on livelihoods	Loss of >50% in production and/or income. Business has to be abandoned. Major impact on livelihoods	Not applicable
	Tourism - impacts of contamination on tourist facilities	Absent	1 tour operator or 1 tourist site	2-5 tour operators or tourist sites	>5 tour operators or tourist sites	Not applicable

Aggregate risk assessment provides a measure of the overall exposure-induced cancer cases in a community under assessment. The risk is estimated over a lifetime, assuming exposure from birth to 30 years. The number of probabilistically estimated cancer cases can be calculated according to Equation 6-15:

$$A_{cases} = \left(\sum_{k=1}^{n} (R_k N_k) \right) \Big/ n \qquad (6\text{-}15)$$

Where:

A_{cases}	Aggregate risk (number of cases)
R_k	Excess cancer risk in subpopulation k
N_k	Number of people in subpopulation k
n	Number of subpopulations

Calculation of aggregate cancer risk assessment provides the required information for assessing the severity of cancer risk by taking into consideration the exposed population size and different

exposures in different subpopulations. The severity rating cannot be generalised across all carcinogens and exposure levels. The severity of the consequence has to be calculated on a case-by-case basis. The methodology can be applied to predict the number of excess cancer cases that may be expected and decisions about severity can be taken on the estimated annual cancer incidence in a community in a site-specific scenario.

The severity of consequences resulting from exposure to non-carcinogens is not calculated following probabilistic risk assessment. The approach is deterministic and assumes that the health effects may occur in any or in all exposed individuals if a HQ for exposure to a particular toxic substance exceeds unity. The severity of the consequence will depend on the level of confidence in the reference dose that is applied in the assessment, the target organ and prognosis of the health outcome, whether the effect is reversible or not, and what the dose-response relationship is. Severity of the consequence therefore cannot be expressed probabilistically on the potential number of cases that may show in a population. Assessment of the severity of the consequence of exposure shall thus be assessed by specialists in toxicology, epidemiology and human health risk assessment.

Table 6-9 also lists criteria for assessment of the severity of consequences on the environment and economic activities. The numbers in the table must be taken as examples; site-specific assessments shall be conducted by specialists in the respective activity fields to determine appropriate criteria for the assignment of severity index ratings for consequences associated with the various activities that may be relevant in a specific assessment.

6.8 Peer Review of Detailed Risk Assessment Reports

Because of the complex methodology involved, DRAs for Chemical Contamination shall be prepared by experts in the multidisciplinary science of human and ecological health risk assessment.

The Handbook contains a checklist (Annex C2) to assist in reviewing the studies and to verify credible data quality and interpretation.

Peer review is an internationally accepted procedure that assists in the carrying out of environmental risk assessments that are robust and in accordance with the best available international practice. Peer reviewers shall be internationally recognized professionals with appropriated certification, such as the QEP Certification of the Institute of Professional Environmental Practice (IPEP) in the USA, or equivalent[52].

Peer review is not a procedure that is conducted to assess only data quality and validity of interpretations. The peer reviewer has to be involved in the project from its planning stage to the final conclusions, to add value throughout the planning and assessment process. Peer review is an interactive, transparent activity. Each comment of the peer reviewer has to be considered and

[52] IPEP. Institute of Professional Environmental Practice, Pittsburg, PA. http://www.ipep.org/.

responded to in writing by the project scientist, whether or not there has been agreement with the comment. The peer reviewer has to sign off the final project report, thereby confirming support for the credibility of the study and its conclusions and recommendations.

6.9 Calculating Site Specific Target Levels (SSTLs).

When the assessment of risks has been completed and remedial action goals are developed, ecological risks must be compared with human health risks to determine which will drive the selection of cleanup target levels and remedial options.

In the case of remedial action based on human health risk considerations, it is advised that site-specific cleanup target levels be derived using the methodology applied by the USEPA Mid-Atlantic Risk Assessment programme[53]. The USEPA approach follows multi-route risk-based equations to derive generic screening levels for the derivation of Tier-1 screening levels for assessment of contamination in environmental media. Different land-use scenarios are taken into account. It must again be emphasized that screening guidelines are not remediation goals or cleanup target levels.

By applying site-specific exposure parameters in the USEPA equations, cleanup target levels can be derived that will be representative of site-specific conditions. These shall take into account population characteristics, behaviour and activity patterns and shall be protective of human health under all potential exposure scenarios at the site.

Remediation requirements that are driven by ecological risks are more difficult to determine, because in many cases the balance between costs and benefits play a greater role than in remediation to protect human health. Decisions also depend on factors such as the presence of endangered or threatened species, species protected by specific legislation and rare and the consumption of species by humans. Corrective actions may involve development of alternative protected areas or relocation of species to other areas, which are generally not practical where humans are the affected receptors. The effects of degraded habitat as a result of causes other than site contamination may have a more serious adverse effect on ecological receptors in comparison with chemical drivers. Generally, the requirement for corrective action and setting environmental targets for such actions, requires specialist knowledge and experience in risk assessment and involves multidisciplinary contributions in the development and optimisation of remediation programmes.

[53] US Environmental Protection Agency (USEPA), Mid-Atlantic Risk Assessment (Serving Delaware, District of Columbia, Maryland, Pennsylvania, Virginia, and West Virginia). Risk-Based Concentration (RBC) Table. Online.
http://www.epa.gov/reg3hwmd/risk/human/index.htm.
http://www.epa.gov/reg3hwmd/risk/human/pdf/MAY_2010_FISH.pdf.

BOX 4

IMPORTANCE OF A DETAILED RISK ASSESSMENT: OAMITES MINE

The Geological Survey of Namibia was instructed by Cabinet to investigate possible effects of the Oamites abandoned mine site on human health due to an unusual high rate of respiratory problems among the ca. 2000 residents at the military base camp.

The two un-rehabilitated tailings dumps at Oamites contain 5.5 million tons of very fine grained rock material which consists mainly of quartz, feldspars, calcite and mica and contains significant traces of uranium and copper. Uranium occurs in Oamites tailings material as very small grains (<5 microns) in the form of uraninite (UO_2) and brannerite $(U,Ca,Ce)(Ti,Fe)_2O_6$.

A detailed investigation found that the respiratory health problems at Oamites can neither be attributed to radiation exposure nor to heavy metal contamination but to physical irritation of mucous membranes by the extensive exposure of residents to the tailings dust.



Dust from the Oamites tailings dump with the military camp buildings in the background

For mitigation, it was proposed to reprocess the tailings for uranium, followed by a safe final deposition of the remaining tailings. Laboratory tests at the GSN showed that uranium is extractable from the tailings by acid leaching. Based on these promising results, MME and MoD instructed GSN to investigate the metallurgical details and the feasibility of uranium extraction. However this was found to be uneconomic and therefore the study recommended that the tailings dumps should be properly rehabilitated using available waste rock material of the waste rock dumps at Oamites mine.

6. DETAILED RISK ASSESSMENT FOR CONTAMINATION

6.1 Methodology Background

The Detailed Risk Assessment (DRA) for contamination requires complex methodologies that must be applied by experts in health risk assessment and specialists with knowledge of toxicology, epidemiology and environmental science. This Handbook thus offers only general notions of the methods used to assess risks to human receptors, the environment and economic activities (Figure 6-1).

The original paradigm for regulatory human health risk assessment (HHRA) in the USA was developed by the USA National Research Council[1]. This model has been adopted and refined by the US Environmental Protection Agency (USEPA)[2;3] and other agencies around the world[4], and is used widely for quantitative health risk assessments. The paradigm essentially divides human health risk assessment (HHRA) into a number of logical steps, as follows:

- Hazard identification (formulation of the problem);
- Dose-response assessment (toxicological assessment);
- Exposure assessment;
- Risk characterization;
- Uncertainty review.

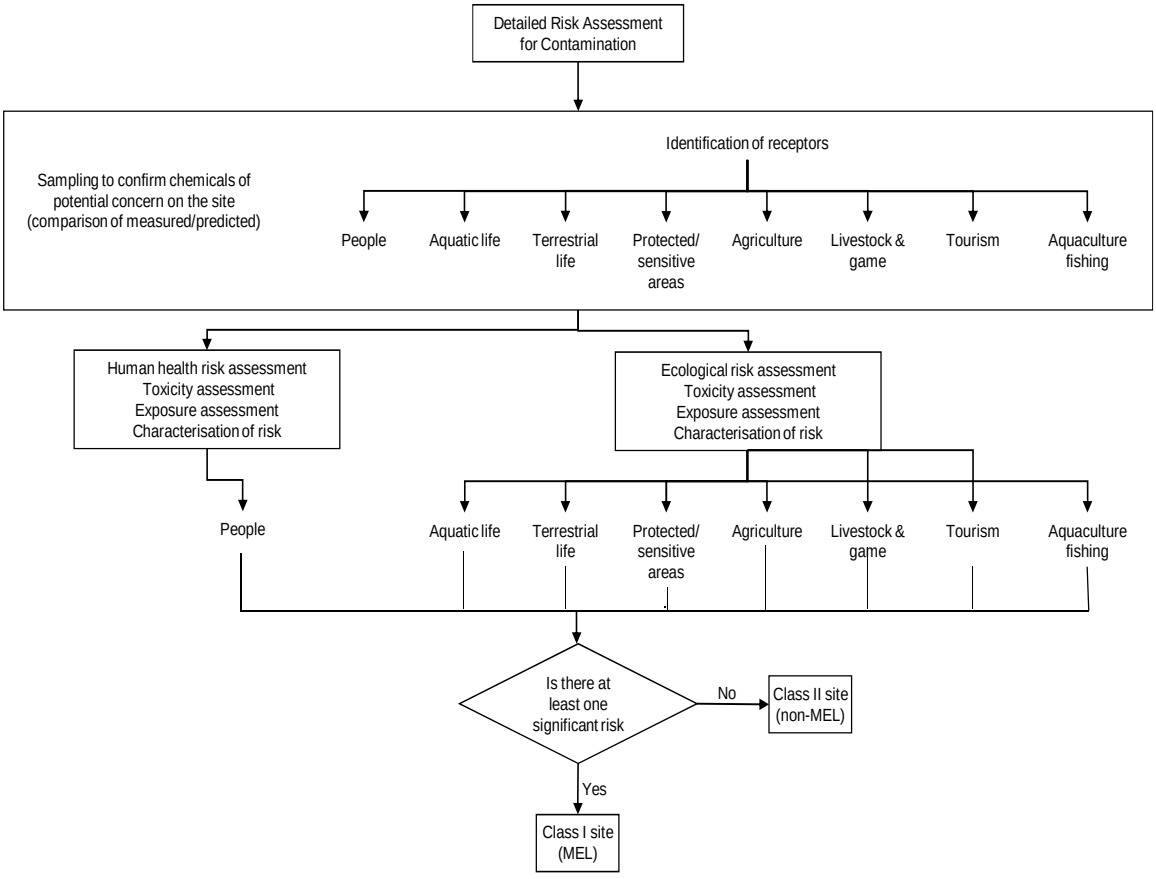
In its simplest form, ecological risk assessment (ERA) refers to the probability of an adverse effect occurring in an ecological system. In accordance with general risk assessment methodology, ecological risk assessment includes estimations of hazard and exposure due to an environmental stressor[5]. Compared to the framework for HHRA, the USEPA framework for ERA changes the first step from hazard identification to problem identification in a holistic context and the phrase 'dose-

[1] NRC, 1983. Risk Assessment in the Federal Government: Managing the Process. National Research Council, Committee on the Institutional Means for the Assessment of Risks to Public Health, National Academy Press, Washington, DC.
[2] USEPA, 1989. Risk Assessment Guidance for Superfund. Volume I. Human Health Evaluation Manual (Part A). Interim Final. EPA/540/1-89/002. US Environmental Protection Agency.
[3] USEPA, 1991. Risk Assessment Guidance for Superfund (RAGS), Volume I: Human Health Evaluation Manual (HHEM), Part B, Development of Risk-Based Preliminary Remediation Goals. US Environmental Protection Agency Office of Emergency and Remedial Response, Washington, DC. OERR 9285.7-01B. NTIS PB92-963333.
[4] IPCS, 1999. Environmental Health Criteria 210. Principles for the Assessment of Risks to Human Health from Exposure to Chemicals. World Health Organisation, Geneva.
[5] Landis W and Yu M-h, 1998. Introduction To Environmental Toxicology: Impacts Of Chemicals Upon Ecological Systems, Second Edition. CRC Press.

response' is replaced by 'stressor-response' to emphasize the possibility that physical changes (which are not measured in doses) as well as chemical contamination can stress ecosystems[6].

A DRA needs to be performed for all environmental media susceptible to chemical contamination (surface water, sediment, groundwater, soil, air) that could be present at a mine site. The DRA is likely to be different for each site and will depend on the results of the SRA.

Figure 6-1: Flowchart for Detailed Risk Assessment for Contamination



[6] US Environmental Protection Agency. 1998. Guidelines for Ecological Risk Assessment. USEPA EPA/630/R095/002F. U.S. Environmental Protection Agency, Risk Assessment Forum, Washington, DC, 175 pp.

6.2 DRA process for contamination

This section describes the steps to be taken for the Detailed Risk Assessment for Contamination, shown in Figure 6-2, namely:

Step 1 – Formulate the Problem (Hazard Identification): This requires identification of sources of contamination and compilation of a preliminary list of chemicals of potential concern, receptors and exposure pathways. These three elements are integrated into a conceptual model that illustrates contamination pathways from the source to the different environmental media (water, sediment, soil, air) and receptors of interest. It then defines the need for additional characterisation studies for the media susceptible to chemical contamination.

Step 2 – Collect Supplementary Information: This is based on a description of procedures for collecting supplementary information, which may include a site visit, sampling of different environmental media susceptible to chemical contamination and chemical analyses.

Step 3 – Confirm Chemicals of Potential Concern: Once the results of analyses have been obtained, chemicals of potential concern are assessed by comparing the analytical results with reference for different receptors (people, aquatic life, etc.). This comparison will yield one of the following situations:

- All results of the analyses are below reference concentrations, and therefore do not require additional assessment (proceed directly to Step 5).
- The results of the analyses present one or more values that exceed reference concentrations and therefore additional assessment is required (proceed to Step 4).

Step 4 – Risk Assessment: Assessment for Human Health and/or Ecological Factors (environment and economic activities) with regard to risk.

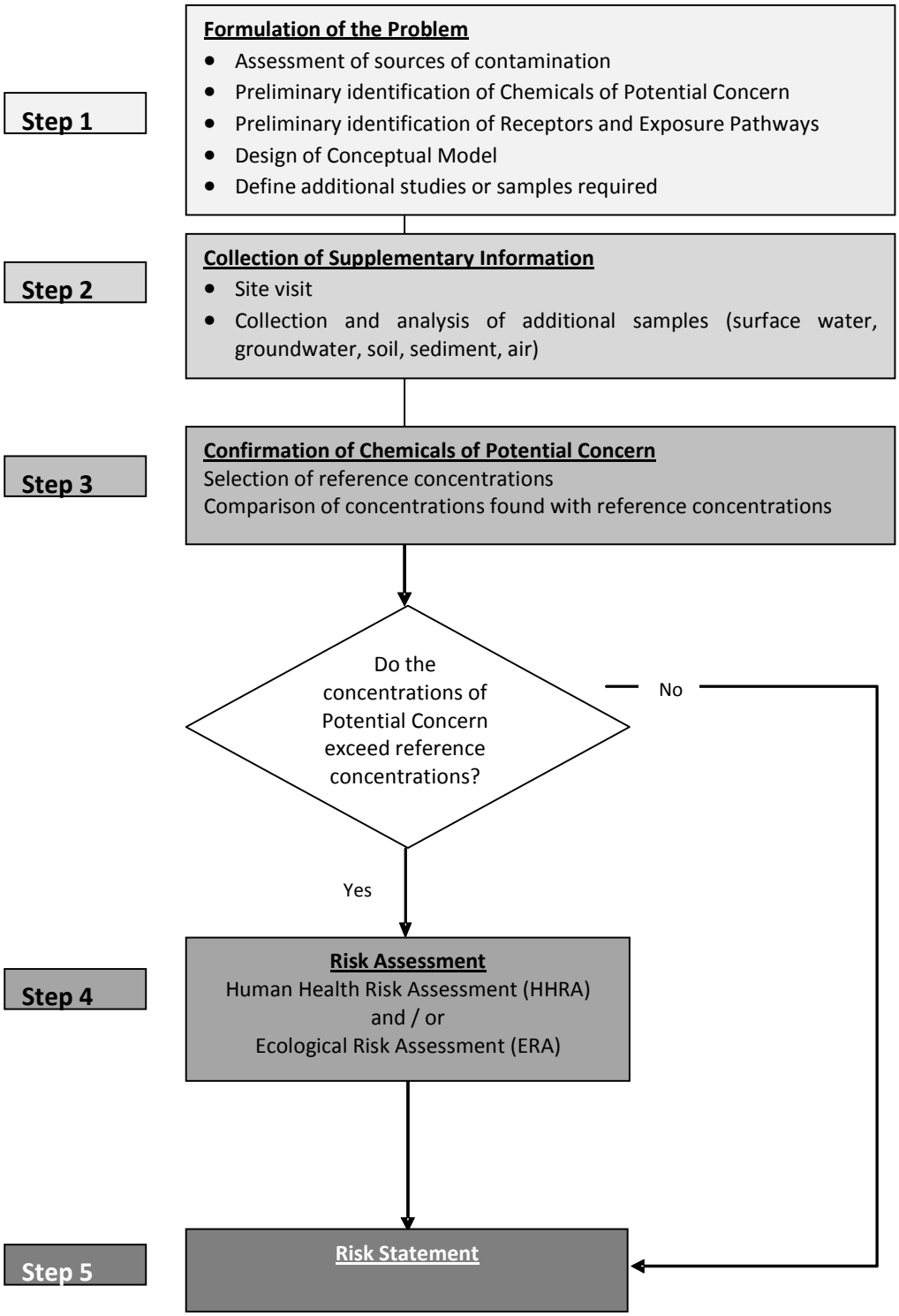
Step 5 – Risk Statement: Analysis of the quantified risk in terms of international perceptions of acceptable risk.

6.3 STEP 1- Formulate the Problem

6.3.1 Study Approach

The Detailed Risk Assessment (DRA) begins with the formulation of the problem, which is mainly qualitative and involves defining the nature of the problem and building preliminary hypotheses about how and why an effect has been observed or could potentially occur in future.

Figure 6-2: Steps in the Detailed Risk Assessment



Formulation of the problem should take into account:

- The source of contamination and preliminary identification of chemicals or pollutants of potential concern;
- Potential receptors that could be exposed to the contamination; and
- Pathways by which these receptors could come into contact with chemicals of potential concern.

These three elements are integrated into a conceptual model (Figure 4-3 in Chapter 4), which illustrates the contamination pathways from the source to the environmental media (water, sediment, soil, air) and receptors of interest.

It is important to note that the analysis must consider past, present and potential future use of the land, and relevant associated exposure pathways. For example, the likelihood of the land use changing in future (e.g., from agricultural to industrial) shall be assessed based on:

- Current or programmed planning instruments[7];
- The land use pattern in the zone where the site is located; and
- Information from government stakeholders such as MRLGH, MME, MET, Ministry of Youth Namibian Defence Force, Namibia Planning Advisory Board, National Planning Commission, etc.

Where land use is dynamic i.e. changing through time, past, current and future use shall be included in the risk assessment.

The process of formulating and understanding the problem will determine the need for additional characterization of the media susceptible to contamination. In formulating the problem, it is important to take into account results of the SRA in order to identify receptors and sources of pollution to be considered in the DRA. It is imperative that human health and ecological risk assessors coordinate their activities and communicate throughout the whole process so that all relevant data are accessible to all parties concerned.

The sections below describe the steps involved in formulating the problem.

6.3.2 Assessment of Sources of Contamination

A source of contamination corresponds to the area in which a hazardous substance may have been deposited, stored or disposed of, and the point of release of substances that could represent a risk to potential receptors. For SD/AMS, sources of contamination are those associated with

[7] Regional Development Plans, Municipal Zoning Plans, Sectional Plans, definition of City Limits, Strategic Environmental Assessments etc., as may be available and applicable.

installations, deposits and/or works of the mine site identified in the SRA. Table 6-1 presents a list of potential sources of contamination associated with installations and media susceptible to contamination. The list is provided as guidance and may not be completely representative of all mine sites.

Table 6-1: Potential Sources of Contamination and Media Susceptible to Contamination

Activity	Form of Contamination	Medium Susceptible to Contamination
Underground workings	Mine drainage	Surface water /sediment Groundwater
Open pits	Pit drainage or seepage Dust	Surface water /sediment Groundwater
Processing plants	Drainage or seepage due to runoff of hazardous waste Suspension of hazardous waste from wind action Processing stack emissions (past)	Surface water /sediment Groundwater Soil Air
Tailings dams, impoundments and deposits	Drainage or seepage from the deposit Tailings transported by rainwater or suspended by wind	Surface water /sediment Groundwater Soil Air
Heap leach residue dump	Drainage or seepage from the residue dump	Surface water /sediment Groundwater Soil
Waste rock Low grade ore	Drainage or seepage from deposit Dust	Surface water /sediment Groundwater Soil Air
Small scale process waste (smelter dust, discarded solutions, etc.), industrial waste	Drainage or seepage from the deposit Transport or suspension of hazardous waste due to rain or wind	Surface water /sediment Groundwater Soil Air
Associated infrastructure	Drainage or seepage due to the presence of hazardous waste (PCBs, oils, reagents, etc.) Transport or suspension of hazardous waste (asbestos, other)	Surface water /sediment Groundwater Soil Air

6.3.3 Preliminary Identification of Chemicals of Potential Concern

Chemicals of potential concern will vary with the type of mining and processes carried out on the site under assessment. Table 6-2 provides a guide to some of the elements of potential concern, but these will vary with the specific geology of the mine and the method used in ore processing. Therefore, sampling and analytical surveys must follow advice of specialists familiar with all activities at the site. Selection of target substances for analysis must be guided by an understanding of potential impacts on human health and the environment and must satisfy the requirements of the study that intends to address the issues under investigation.

Table 6-2: Types of Mineral and Chemicals of Potential Concern

Type of Mineral Found in SD/AMS in Namibia	Elements of Potential Concern*
Polymetallics (Cu, Pb, Zn, Cd, As)	Cu, Pb, Zn, As, Cd, Be, Ag, Mo, Sb, Ge, Co, Ni
Gold	SO_4, Fe, (Hg), (CN) (depending on the process used)
Uranium	U, Rn, Ra, V, B, Mn. Full radionuclide analysis
Tin	Sn
Fluorspar	F
Pyrite	SO_4, Fe, acid generation potential
Rare Earths and Rare Metals (Lithium, Niobium, Tantalum, Wolframite)	Thorium
Phosphate	PO_4
Graphite	SO_4, Fe
Manganese	Mn
Vanadium	V, Zn, Cd, As, Hg, Pb, Cu
Coal	SO_4, Fe, Se, B, Mn

*Full cation and anion analysis recommended. Also note that organic contamination (oils and grease) from underground fuel storage tanks may be present.

6.3.4 Preliminary Identification of Receptors and Exposure Pathways

Receptors can be humans (people), animals, or ecosystems that could be at risk as a result of exposure to contaminants. The aim of the preliminary identification of receptors is to determine which human or ecological receptors are most likely to be exposed to contamination and/or are more susceptible to contaminants of potential concern (see Chapter 3).

In the DRA, experts must define the receptors in accordance with the results of the SRA, using the receptor classification scheme that was applied in the SRA, namely:

- People
- Environment

  - Aquatic Life
  - Terrestrial Life (fauna and flora)
  - Protected or Environmentally Sensitive Areas
- Economic activities
  - Agriculture (crop farming)
  - Game Farming and Livestock Activities
  - Aquaculture and Fishing
  - Tourism.

It is important to take into account that the DRA must be performed only for the types of receptors indicated in the SRA. In other words, if the SRA results for a given mine site were to indicate that there are no risks associated with the receptors 'environment' and 'economic activities' and there is no uncertainty on those assessment results, then there would be no need to conduct a DRA for those receptors. However, if there is any uncertainty about the site's SRA for human receptors, then it should be necessary to conduct a DRA for that receptor.

Exposure pathways represent the environmental media through which receptors could come into contact with chemicals of potential concern. Routes of exposure are the mechanisms of intake of contaminants into the human body, for example ingestion, inhalation and dermal contact. For humans, pathways and routes of exposure may include ingestion of contaminated water or foodstuffs, skin contact with contaminated soil or water, and/or inhalation of vapour or dust. During the formulation of the problem, the exposure pathways associated with human and ecological receptors shall be assessed in preliminary form in order to ensure that the collection of samples which may be required, will provide the information necessary to corroborate or refute the importance of any potential exposure pathways.

6.3.5 Designing a Conceptual Model

Based on the information obtained from the site, the expert shall design a conceptual model to plan the risk assessment, including supplementary sample collection activities. The conceptual model shall illustrate the relationship between chemicals of potential concern and potential receptors. This model must also highlight important features of the site to allow subsequent steps in the assessment to focus on the most significant environmental issues. This model shall be reviewed regularly as more detailed information about the site is obtained. The conceptual model consists of a schematic diagram that shall cover no less than the following aspects:

- Identification of primary sources of contamination on site (e.g., release of acid drainage from an underground mine).
- Indication of how the chemicals can move from a source into the environment (e.g., a chemical released from a tailings deposit can seep into soil and penetrate the water table, or the tailings themselves can be transported by wind).

- Identification of potential exposure pathways and routes of exposure (e.g., ingestion of contaminated water, skin contact, inhalation of particulate matter).
- Identification of direct receptors (e.g., local residents, visitors, ecosystems, crops, etc.) that could come into contact with the contaminated medium.
- Identification of indirect receptors, e.g. people who may consume agricultural products (crops, livestock) which have been contaminated.

6.3.6 Requirements for Additional Studies and Sampling

After the problem has been formulated and is clear in detail, the need for specific additional studies and sampling of media susceptible to contamination must be defined in order to complete the characterization of the SD/AMS. For example, it may be necessary to collect samples, where applicable, of fish and/or other human and animal food sources.

The following section presents more detail on sampling and supporting methodologies.

6.4 STEP 2 - Collect Supplementary Information

6.4.1 Visit to the SD/AMS

Experts involved in the studies shall visit the SD/AMS to collect information on receptors, exposure pathways and media susceptible to contamination. This information will be useful in defining the Sampling Plan that would characterize the area under assessment. The visit shall cover no less than the following areas:

- Areas with confirmed contamination.
- Areas between the source of contamination and areas that could be affected.
- Areas located along known or potential animal migration routes that could spread the contamination to other locations.
- Suitable areas of reference.

An area of reference is an area that has similar hydrological, geological, meteorological and ecosystem characteristics to the area under investigation, but which is not affected by the site's contaminants, such as an area up gradient or up wind from the mine site.

Field information shall be collected through direct observation, supported by interviews with inhabitants in the Area of Study and its surroundings, with local authorities and with organizations having interests or involved in activities in the area.

For receptors denominated 'people', information to be gathered during the initial visit shall focus on the following aspects:

- Locating nearby and other populations potentially exposed to contaminants from the site under assessment.
- Identifying groundwater wells, surface water intake works and major water supply infrastructure.
- Determining the distance between sources of drinking water supply and contaminated areas.
- Identifying the existence of farming activities in the Area of Study that provide food to the population. This addresses the possibility that residents may consume food commodities grown in contaminated soil or irrigated with contaminated water.
- Determining the existence of livestock activity in the Area of Study. In this case, the assessment shall consider the possibility that animals are consuming fodder crops contaminated by dust, and/or irrigated with contaminated water and/or drinking contaminated water.
- Determining the existence of commercial game farming in the Area of Study. In this case the focus shall be primarily on the assessment of reproductive effects of contaminants on wildlife.
- Determining the existence of fishing and aquaculture activities as a source of food for the population. This refers to the possibility that the population is consuming aquatic life forms (fish, shellfish, etc.) from contaminated water.
- Assessing the possibility that contaminants or contaminated foods are transported to other populations beyond the Area of Study that could be affected in future.
- Identifying rivers, dams and/or other water bodies that are used for recreation.

With regard to ecological receptors, the site visit shall be planned to directly assess characteristics and conditions in the area, and therefore the field team shall include a biologist or ecologist familiar with local flora and fauna, preferably someone also experienced in ecological risk assessment. Prior to the field visit, the following information must be available, at minimum:

- Present and historical use of the site and neighbouring properties.
- Past, present and possible future water use.
- Presence of sensitive ecosystems on site and adjoining land.
- Presence of endemic and endangered species.
- Local and/or regional maps indicating vegetation, sampling points (where applicable), land use, conservation areas, surface water, etc.

The ecologist/biologist with specialist knowledge needs to identify and describe flora and fauna species of ecological importance and their populations (protected species and other species that

sustain them, endemic species, etc.), revise current or potential impact indicators and locate a suitable reference habitat. This information must be collected and mapped.

Some impact indicators (for example, changes in community structure or species diversity) may not be evident during a relatively short field visit. However, the absence of certain ecosystem features may be noted during these visits, as well as evidence of potential impacts. For example, the absence of certain piscivorous birds typically found close to river banks can point to potential ecological impacts (i.e. no fish).

The date of the field visit needs to be selected with special care, as the presence or abundance of certain plants and animals is closely related to seasonal factors. It is also important to bear in mind different species' activity patterns (diurnal/nocturnal, early morning/late afternoon, etc.).

The visit to each of the areas involved shall include observation walks around the entire area occupied by the installations, works and deposits of the SD/AMS, in areas down gradient where contaminants could accumulate, at any surface water courses, etc. During these visits the occurrence of major habitat types should be logged and mapped.

6.4.2 Collection and Analysis of Supplementary Samples

Once the problem under investigation has been formulated and the site visit conducted, the team can start collecting and analyzing supplementary samples (surface water, groundwater, sediment, soil, air) to build a physical-chemical characterization of potentially contaminated media at the SD/AMS. A detailed Sampling Plan shall be prepared for each sector to be assessed, which shall include, but not be limited to, the following:

- Statement of data quality objectives;
- Sampling design, determination of the appropriate number of samples and selection of sampling points;
- Sampling methodology;
- Laboratory analyses required;
- Statistical analysis of results;
- Quality assurance and quality control of sampling (QA/QC).



Plate 6.1: Taking radiation measurements on an abandoned tailings dam

6.4.2.1 Selection of Sampling Points and Sample Size

a. Sampling points

Table 6-3 presents a conceptual Sampling Plan for media susceptible to contamination: surface water, sediment, groundwater, soil and air, for the works and installations of the SD/AMS. An expert has to be consulted to identify the process nodes and areas where samples have to be collected for analysis and to advise on the parameters that have to be determined.

Background samples must be taken to determine the background concentration of chemicals to be assessed, i.e., their naturally occurring levels in surface water, groundwater and soil. These samples should be taken in the areas of reference that are free from the influence of site contamination, but which are similar in terms of geology, topography, meteorology and other physical characteristics.

b. Sample Size

Generally, the sample size (number of samples that must be taken) and location of sampling points must be determined at the same time. To determine a suitable number of samples for the detailed risk assessment of each site, the following aspects shall be considered:

- Number of areas of concern (areas with contaminants present).
- Methods that will be used to interpret the results.
- Practical considerations related to logistics and cost.

The final number of samples and sampling points should be determined by an expert in statistical sampling design, taking into account the purpose and sensitivity of the investigation.

c. Criteria for sampling points and size

This section offers general guidance for selecting sampling points and deciding on the number of samples that have to be collected. These recommendations are for guidance only; the expert directing the study shall determine the exact criteria in each case. Generally, for sampling of liquids and solids it is advisable to collect as many samples as practically possible and to combine these into a smaller number of composite samples for analysis. Typically, ten individual samples can be combined into one composite sample. Samples collected in this manner are more representative than single point samples. Composite samples are prepared by combining equal volumes or masses of individual samples to form a single sample for analysis.

Table 6-3: Conceptual Sampling Plan for Media Susceptible to Contamination

Activity	Surface Water	Sediment	Groundwater	Soil	Air
Underground mine workings	Sample of drainage from the mine Sample of water from receiving body (river/dam) Sample from water course upstream of mine	Sample of bottom sediment in receiving water body and upstream	Sample of water from boreholes in the Area of Study Installation of new monitoring wells when water table level is less than 20 meters	Not required	Not required
Open pit workings	Sample of water accumulated in the pit	Not required	Sample of water from boreholes in the Area of Study	Not required	Not required
Processing plants	Sample of receiving water body (river/dam) Sample from water course upstream of mine	Sample of bottom sediment in receiving water body and upstream	Sample of water from boreholes in the Area of Study Installation of new monitoring wells when water table level is less than 20 meters	Sample of shallow soil (<250mm depth)	Not applicable
Tailings dams	Sample of receiving water body (river/dam) Sample from water course upstream of mine	Sample of bottom sediment in receiving water body and upstream	Sample of water from boreholes in the Area of Study Installation of new monitoring wells when water table level is less than 20 meters	Sample of shallow soil (<250mm depth) in tailings deposit	Sample of airborne contaminants at locations in the area of receptors, taking predominant wind direction into account
Heap leach residues	Sample of receiving water body (river/dam) Sample from water course upstream of mine	Sample of bottom sediment in receiving water body and upstream	Sample of water from boreholes in the Area of Study Installation of new monitoring wells when water table level is less than 20 meters	Sample of heap leach residues	Not required

Activity	Surface Water	Sediment	Groundwater	Soil	Air
Waste rock / sterile rock/ low grade ore deposits	Sample of receiving water body (river/dam) Sample from water course upstream of mine	Sample of bottom sediment in receiving water body and upstream	Sample of water from boreholes in the Area of Study. Installation of new monitoring wells when water table level is less than 20 meters.	Sample of material deposited	Not required
Industrial waste (hazardous, non-hazardous)	Sample of receiving water body (river/dam) Sample from water course upstream of mine	Sample of bottom sediment in receiving water body and upstream	Sample of water from boreholes in the Area of Study Installation of new monitoring wells when water table level is less than 20 meters	Sample of shallow soil (<250mm depth) in waste deposition area.	Sample of airborne contaminants at locations in the area of receptors, taking predominant wind direction into account
Small scale process waste (smelter dust, discarded solutions, etc)	Sample of receiving water body (river/dam) Sample from water course upstream of mine	Sample of bottom sediment in receiving water body and upstream	Sample of water from boreholes in the Area of Study. Installation of new monitoring wells when water table level is less than 20 meters.	Sample of shallow soil (<250mm depth)	Sample of airborne contaminants at locations in the area of receptors, taking predominant wind direction into account

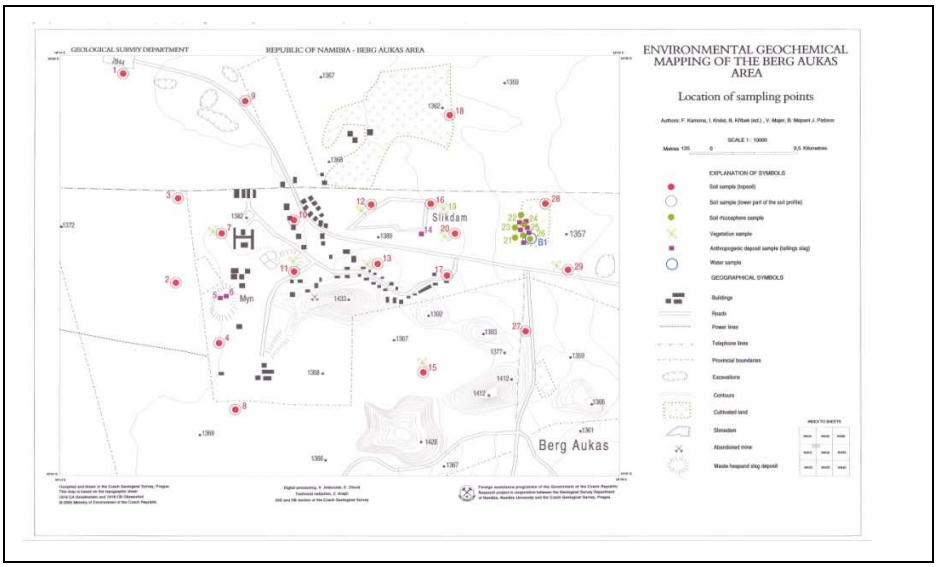


Plate 6.2: Location of soil, water and vegetation sampling points at Berg Aukas

c.1 Surface water

The following guidelines serve as a broad framework, which may be amended under certain site conditions:

- Collect samples of drainage from the mine site (underground mine, open pit, processing plant, heap leach residues, deposits of waste rock, low grade ore and waste deposits).
- Collect samples from the water body/ies upstream from each of the sources (to determine background levels). There may be more than one water course involved.
- Collect samples from the receiving water body/ies immediately downstream from the drainage discharge point. There may be more than one water course affected.
- Collect samples from the receiving water body every 500 m or in places where the water may be used within the Area of Study (consumption, irrigation, etc.), up to a distance to be determined by the expert.
- Collect a composite sample for every 500 m^2 of surface area for dams and ponds.
- Collect a composite sample for every 500 m^2 of water accumulated in a pit.

For sampling of surface water bodies, both perennial and seasonal receiving water bodies shall be taken into account, so long as there is water in the latter. If there is no flowing water in a water course, take a composite sample of the sediment (see below).

c.2 Sediment

Composite sediment samples shall be collected from the same locations where surface water sampling is conducted or from dry river beds, if there is currently no flow.



Plate 6.3: Collecting water samples from contaminated river at Otjihase Mine

c.3 Groundwater

Sampling points for groundwater comprise existing boreholes within the Area of Study. At least one sample shall be taken from each existing well.

Where groundwater is found less than 20 meters from the surface, monitoring wells may need to be installed for sampling, depending on the specific risks present in the SD/AMS. The number of wells and their location shall be determined by an environmental specialist and hydrogeologist.

c.4 Soil

For tailings deposits, heap leach residues, low grade ore, and dumps containing any other kinds of waste, a sampling grid shall be established according to the size of the deposit. The grid may be square, rectangular, triangular or hexagonal, depending on the form of the area to be sampled. The following shall be taken into account in this regard:

- At least 5 to 10 composite samples from different points around the deposit shall be collected.
- Samples shall be taken at a depth of 250mm, unless there is evidence of deep-soil contamination. Surface soil is understood to represent soil to a depth of no more than 250mm.

Soil samples in the processing plant area shall be collected as required in the field. At a minimum, one composite sample of surface soil shall be taken at points where evidence of contamination is observed.



Plate 6.4: Collecting and recording tailings samples at Oamites Mine

c.5 Air

Air monitoring programmes require that data be collected over a period of at least a year, to cover seasonal variations in meteorological conditions. Short-term monitoring programmes may be implemented for special investigations, but careful correlation with meteorological conditions must be established, with recording of wind directions, wind speeds, temperature and rain events as a minimum requirement. The location of a monitoring station shall be determined by the location of sources of air contamination and potential receptors, with due consideration to meteorological conditions. An air dispersion modelling specialist must be consulted for selecting the most appropriate location for the monitoring station(s). It is recommended that PM10s are monitored for the purposes of the HHRA and Total Suspended Particulates for the ERA. Sampling for other contaminants shall be determined by the expected source profile characteristic of the mining and processing activities.





Plates 6.5a and 6.5b: Different air quality monitoring instruments. Plate 6.5a shows a dust bucket to measure particulates; Plate 6.5b is a PM10 pump sampler.

d. Assessment of Background Levels

Background concentration is defined as the concentration of a substance in the environment in a defined geographic area, which derives from no anthropogenic sources. Obviously, around mine sites the concentrations of chemicals, and especially metals, may be naturally high, as this is the reason for the mine being there in the first place. Because of this fact, it is important to consider background data to determine whether the concentrations detected in the environment are a natural feature of the area or derive from anthropogenic activities.

In analyzing risk, it is important to determine the specific background concentrations of the mine site under assessment, as the concentration of naturally occurring metals in the environment can vary widely from one site to another and from one medium to another (water, soil and sediment). The following criteria need to be taken into account when deciding the location for background sampling:

- The sampling location must be inside the local geographic area.
- It must have the same rock deposits and surface geography found in the Area of Study.
- It must be representative of the concentration of elements attributable to natural sources.
- It must not include point source concentrations.

The number of samples required to determine background concentrations will depend on the characteristics of a particular site. In principle, background samples should be collected in 1 to 3 representative sectors for each medium (soil, water, air, etc.). However, the factors listed below may increase the number of sectors or samples that would be required to characterize background:

- Contamination of more than one medium.
- Heterogeneous geological material.
- Extensiveness of the area of interest, with variable terrain.
- Variation in concentrations of chemicals of potential concern is high compared to background.
- In cases where contamination is suspected on site, but the difference between on-site concentrations and background concentration is small.

6.4.2.2 Sampling Methodology

Instead of providing a list of sampling and analytical methods for assessing contamination in environmental media, this section provides references and links to website sources where comprehensive lists of methodologies are available online. Methodologies are being continually updated and it is prudent to consult the latest standard international documents. The most prominent sources are presented below.

- British Columbia Environmental Laboratory Manual for the Analysis of Water, Wastewater, Sediment, Biological Materials and Discrete Ambient Air Samples. 2007 Edition. http://freedownloadbooks.net/Environmental-sampling-and-analysis-lab-manual-rapidshare-pdf.html.
- FACT SHEET #29: Voluntary Remediation Program (VRP). http://deq.state.wy.us/volremedi/index.asp
- Sampling and Analysis Plans, 2007. http://deq.state.wy.us/volremedi/downloads/Current%20Fact%20Sheets/FS_29.pdf
- ASTM International (ASTM) http://www.astm.org/Standards/D5013.htm

  Searchable website providing comprehensive references to ASTM documents. The documents have to be ordered from ASTM.
- ASTM Standards on Environmental Sampling, 3rd Edition 2006

  This 3rd Edition provides access to 118 of the latest ASTM Standards on Environmental Sampling. The standards cover: Planning for sampling, screening samples in the field to indicate the need for additional sampling, interpreting data based on a specific sampling plan, various sampling techniques for a variety of environmental media, valuable information on different types of sampling equipment, sample holding times, preservation techniques, and QA/QC specifications. http://www.constructionbook.com/astm-standards-on-environmental-sampling-3rd-edition
- J Russell Boulding and Jon S Ginn, 2003. Practical Handbook of Soil, Vadose Zone, and Ground-Water Contamination. http://books.google.co.za/books

  This book serves as a comprehensive guide for conducting complex site investigations and identifying methods for effective soil and ground water cleanup. A list of applicable ASTM methods is provided.
- US Environmental Protection Agency (USEPA) Test Methods

  Test methods are approved procedures for measuring the presence and concentration of chemical pollutants and physical parameters.

  The Test Methods Collections page provides links to numerous sources of methods and guidelines. http://www.epa.gov/osa/fem/methcollectns.htm

  The Index to EPA Test Methods provides information on locating and obtaining test methods and provides both chemical names and numeric indices. The Index to EPA Test Methods can be accessed from: http://www.epa.gov/ne/info/testmethods/

Some methods are published as a part of official EPA publications. In these cases, the Test Method Index will list the EPA publication number. Many, but not all, of these publications are available in the National Service Center for Environmental Publications (NSCEP) catalogue Web site: http://www.epa.gov/nscep/

A web search can be conducted using the method number using on the search page at: http://www.epa.gov/epahome/search.html

Many test methods are published in Title 40 of the Code of Federal Regulations. This resource is available online at: http://www.gpoaccess.gov/ecfr/

- Environment, Health And Safety Online

  This is a free website that lists links to all USEPA Test Methods. Go to: http://www.ehso.com/testmethods.php

- International Standards Organization (ISO)

  Section 13: Environment Health Protection Safety provides access to ISO Methods for characterisation of contamination in air, soil and water.
  http://www.iso.org/iso/iso_catalogue/catalogue_ics/catalogue_ics_browse.htm?ICS1=13

6.4.2.3 Laboratory analysis

The parameters to be analyzed in environmental media will depend on the type of mining and metallurgical process at the investigation site, and the nature of the contamination. Generally, the assessment is divided into the classes of inorganic cations and anions, semi-volatile organic compounds and volatile organic compounds. Analytical methods are available from the standard database sources listed under Sampling Methodology above. Analytical laboratories often adapt methods for convenience to become 'in-house' procedures. This is acceptable as long as the laboratory has documented the procedure and recorded deviations from the original method. Methods must go through a validation process.

Chemicals that pose a greater ecological risk rather than a human health risk may need to be analysed in more detail than would otherwise be required. In addition, minimum required detection limits may be lower for ecological concerns than for human health concerns in some cases. Certain water quality parameters, such as pH, hardness, salinity and oxygen levels, are also more important for ecological assessments.

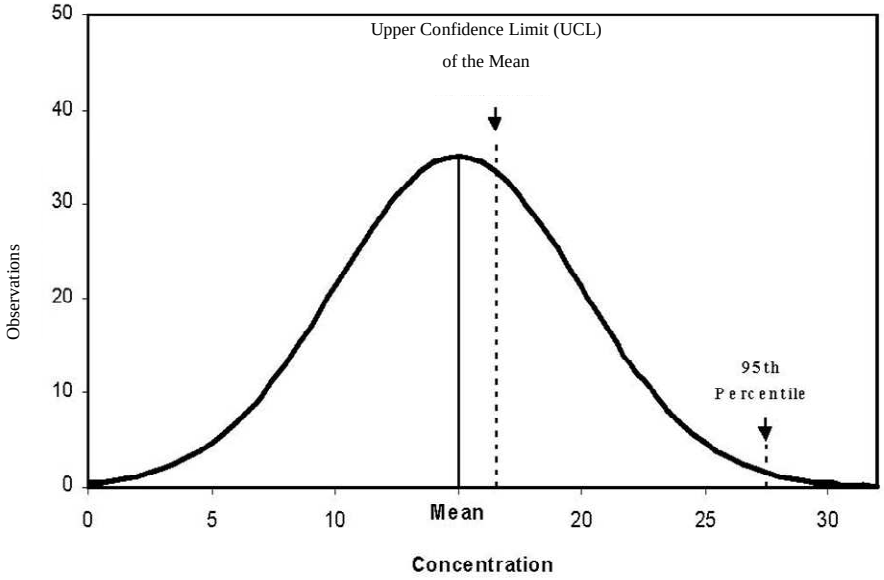
Special attention needs to be paid to the competence of the laboratory and methods of analysis to ensure that the detection limits of the analytical method are lower than the guideline concentrations for contaminants in the media under assessment.

Note that the laboratory facilities in Namibia are limited and may not be able to undertake all of the desired analyses or to the detection level required. Samples therefore may have to be sent to South Africa or overseas.

6.4.2.4 Statistical Analysis of the Results

A variety of factors come into play when assessing contamination risks, many of which have no definite natural distribution. A good example of this is the variation in concentrations of substances in a medium such as soil or water. The more samples that are analyzed, the better the information that will be generated of the range of potential results and typical concentrations (in statistics, this is known as the central limit theorem; see Figure 6-3).

Figure 6-3: Statistical Analysis of Laboratory Results. Comparison of UCL and 95th Percentile[8]



As the number of samples increases, the upper confidence limit (UCL) of the mean approaches the true mean, while the 95%-ile (95 percentile) of the distribution stays in the upper extreme of the distribution. The concentrations of contaminants at a site are usually characterized with statistical values such as:

- Range;
- Mean;
- Mean with 95% level of confidence (95% Upper Confidence Limit of the Mean (UCLM));
- 90th percentile;
- Percentage of samples that exceed the standard.

[8] Figure taken from the document "Supplemental Guidance to RAGS: Calculating the Concentration Term," US EPA, 1992

Risk assessors commonly use the mean with a confidence level of 95% as well as the 90th percentile, as it is preferable to overestimate rather than underestimate risks.

While it is possible to calculate these statistical parameters with a limited set of data, it does not always make sense to do so when the number of samples is insufficient (e.g., when the subset of contaminated locations is too small). For example, calculating the 90th percentile with less than 20 samples available generally does not yield a good estimation of the parameter. On the other hand, it is preferable to have 10-15 replicas for calculating the mean with a level of confidence of 95%. If less than 10 samples are available, it is possible to calculate this value and that of the mean; however, given the uncertainty of the statistical distribution, it will be more prudent to use the maximum value, with its associated risk, as an estimation of the level of contamination.

Good professional judgment is required in these cases; for example, if the bulk of the area presents a relatively low level of contamination but there are specific areas that are highly contaminated due to a particular activity (e.g., a loading area where concentrate was transferred to trucks and spills occurred), then the loading area shall be defined as 'Area of Environmental Concern (AEC) No. 1' and the next as 'AEC No. 2', as these are two different distribution 'populations' for the contaminants. Thus, separate risks will be calculated for each AEC. Furthermore, remediation decisions may be different for each AEC; for example, it may be decided to clean AEC No. 1, but to take a different approach to AEC No. 2.

The expert shall use his/her judgment in selecting the source of information to obtain values which best represent the different variables. For example, the consumption frequency of fish from a contaminated body of water is best based on information obtained through interviews with local inhabitants rather than through statistical data taken from a generic report on regional fish consumption patterns.

6.4.2.5 Quality Assurance and Quality Control of Sampling (QA/QC)

For quality assurance and quality control of sampling activities, the investigator shall take into account sampling protocols, sampling equipment and materials, quality control samples, sample containers and sample preservation procedures.

a. Sampling Protocol

The sampling protocol for risk analysis needs to include the following:

- Objectives of the study;
- Sample numbering system;
- Procedures for collecting, preserving, handling and transporting samples;
- Analytical strategies that will be used.

b. Sampling Equipment and Materials

The equipment and materials used for the collection, storage, preservation and transport of samples must not alter the samples. For example, some material used to build monitoring wells for taking groundwater samples may absorb certain chemical compounds, preventing them from appearing in the collected sample.

c. Quality Control Simples

Samples must be taken for quality control (trip blank, field blank, equipment blank, replicate sample, split sample). These samples shall be stored, transported and analyzed in exactly the same way as samples taken to characterize the site.

It is recommended that all of these quality control samples be identified in the same way as the samples taken to characterize the site, so that the laboratory is not aware of which samples are quality control ones.

Field Blank. This sample is taken to confirm that no contaminant has inadvertently been introduced from the site into the samples during the sampling and transport process. Field blanks may be containers of de-ionized water or background soil that are taken from the laboratory to the site in closed containers and then transferred to other clean containers at the sampling location. This action has to reflect as closely as possible the sample handling procedures during sampling.

Trip blank. This consists of containers of de-ionized water or background soil samples prepared in the lab. The trip blanks are kept closed in the same cooler as the other samples at each stage of the process, from the time the containers are sent to the field until they are accepted by the lab. During the entire process, the samples shall remain closed to avoid contamination during sample transport or during storage in the lab. At least one trip blank is required for each batch of samples sent to the analytical laboratory. Trip blanks are analysed only in cases where field blanks show unexpected contamination or high concentrations of the substances under investigation.

Equipment Blank. An equipment blank is a sample of analyte-free media which has been used to rinse the sampling equipment. It is collected after completion of decontamination and prior to sampling. This blank is useful in documenting adequate decontamination of sampling equipment.

Replicate (Duplicate) Sample. These are independent samples that are collected as close as possible to the same point in space and time. They are two separate samples taken from the same source, stored in separate containers, and analyzed independently. These duplicates are useful in documenting the precision of the sampling process. It must be understood that duplicate sampling does not add statistical significance to the analytical results, because a larger number of samples is required for calculation of mean values and confidence intervals.

Split Sample. Aliquots of sample taken from the same container and analyzed independently. In cases where aliquots of samples are impossible to obtain, field duplicate samples shall be taken for the matrix duplicate analysis. These are usually taken after mixing or compositing and are used to document intra- or inter-laboratory precision.

d. Sample containers

Sample containers must be selected according to the sampling and analytical objectives. For water, soil and sediment samples, containers may be of glass or amber glass bottles of different sizes, glass jars, plastic bottles or plastic bags (for soils and sediments). For certain applications the lids of glass bottles must be Teflon-lined. Teflon-lined septa are used on bottles for sampling of volatile substances. Care must be taken in the selection of plastic sampling bottles, because certain plastics may contaminate samples. Volatile substances could also be lost as a result of diffusion through plastics.



Plate 6.6: Labelling and recording soil samples

Air samples for volatile organics may be collected in Tedlar® bags or Summa canisters. These techniques are specialized and their limitations must be recognized. In many cases air sampling requires techniques other than collection in bags or canisters.

The choice of sample containers is critical for maintaining sample integrity and to avoid contamination. An expert must be consulted for advice on appropriate sample containers.

e. Preservation of Samples

Suitable procedures need to be established to preserve the samples from collection to analysis in the laboratory, so as not to alter the chemical concentrations present in the medium from which they were extracted. Advice on preservation is given by ASTM[9] and SquiRT Tables[10].

[9] ASTM Standards on Environmental Sampling, 3rd Edition 2006
This 3rd Edition provides access to 118 of the latest ASTM Standards on Environmental Sampling.
http://www.constructionbook.com/astm-standards-on-environmental-sampling-3rd.

The following are some common sample preservation techniques used for different matrices:

- Generally, water, soil and sediment samples must be transported and stored under cold conditions (4°C).
- Preservation of water samples may be done under acidic or alkaline conditions. Depending on the analytes of interest, acidic preservation uses sulphuric acid or nitric acid to pH < 2. Alkaline preservation uses sodium hydroxide to pH > 12. If the interest is in dissolved species (not suspended matter), samples must be filtered prior to preservation.
- Soil and sediment samples are not preserved by addition of acid or alkaline solutions.
- Biological samples must be kept cold (<4°C) and analyzed within 24 hours of collection, **OR** they must be kept frozen until they are analyzed.
- Holding times of samples depend on the sample matrix and analytes of interest. The appropriate holding time must be clarified with the analytical laboratory and must be documented in the sampling and analytical procedures. Advice on holding times is provided in ASTM Standards on Environmental Sampling, 3rd Edition 2006 and in the SquiRT Tables referred to above.

f. *Chain of Custody*

The possession and handling of samples from the time they are collected until they are analyzed in the laboratory shall be managed under chain of custody with sample details recorded on a chain of custody form.

The purpose of the chain of custody form is to control and document the transfer of samples from the point of collection to the analytical laboratory. The form is signed each time when a sample or batch of samples is relinquished by one person and accepted by another. Dates and times are recorded and important observations noted, for example, leaking of bottles or when samples are not cold. Each person in the chain of custody keeps a copy of the signed chain of custody form for quality assurance records.

It is common practice to combine the chain of custody form with an analytical request form. The laboratory then receives not only the sample detail on the chain of custody form, but also a clear instruction for the analyses that are required.

[10] Guidelines for preserving samples and for analytical technique options are available in the Screening Quick Reference Tables (SQuiRTs) present screening concentrations for inorganic and organic contaminants in various environmental media Buchman MF 2008. NOAA Screening Quick Reference Tables, NOAA OR&R Report 08-1, Seattle WA, Office of Response and Restoration Division, National Oceanic and Atmospheric Administration, 34 pages.
http://response.restoration.noaa.gov/.

6.5 STEP 3 – Assessment of Chemicals of Potential Concern

The 'tiered approach' in contaminated site investigations was introduced to simplify the assessment process where multiple chemicals are present in environmental media. The tiered approach does not affect the actual level of risk to humans and ecological receptors in any way; the higher Tiers in the assessment involve more extensive investigations to reduce uncertainties in the risk assessment process, thereby removing 'non-issues' from the study list, thus reducing the data sets to a more manageable size and focusing the study on those toxicants that are of critical concern.

Chemicals of Potential Concern are assessed in Tier-1 by comparison with selected reference concentrations for contaminants in environmental media. These reference values are usually conservative and do not take into account site-specific conditions. The assessment assumes that exposure may occur and pathways and receptors are not considered in detail in Tier-1. Chemicals that are present in the environmental medium (air, soil, sediment of water) at concentrations below their respective reference concentrations are not of concern and are removed from the study list. The assessment then continues only for those substances that are present at concentrations above the screening guidelines.

Screening guidelines are not remediation goals or remediation target levels, but serve to identify potential concerns and the need for further investigation of site contamination. The cleanup level for contaminants in environmental media is a site-specific criterion that a remedial action has to satisfy in order to keep exposure to potential receptors at or below a risk-based 'action level'.

Where concentrations of chemicals are equal to or less than background concentrations, these should not be included in the human health and/or ecological risk analysis, even when they are higher than the guideline concentrations. This is because it is impractical to attempt to reduce risk through remediation when contaminant concentrations are found to be lower than background levels.

The process of evaluating ecological risks of environmental contaminants comprises two Tiers. Tier-1 is a screening assessment where concentrations of contaminants in the environment are compared to no-observed-adverse-effects-level (NOAEL)-based toxicological benchmarks that represent concentrations of chemicals in environmental media (water, sediment, soil, food, etc.). These concentrations are presumed to be non-hazardous to the surrounding biota. The second tier (Tier-2) is a baseline ecological risk assessment, where toxicological benchmarks are one of several lines of evidence used to support or refute the presence of ecological effects.

Annexure C1 presents a summary of sources of guideline concentrations.

6.6 STEP 4 – Risk Assessment

6.6.1 Quantitative human health risk assessment

6.6.1.1 Introduction

A site-specific risk assessment is undertaken when concentrations of compounds are higher than the guideline concentrations.

The original paradigm for regulatory human health risk assessment in the USA was developed by the USA National Research Council[11]. This model has been adopted and refined by the US Environmental Protection Agency (USEPA)[12; 13] and other agencies around the world[14], and is widely used for quantitative health risk assessments. The paradigm essentially divides human health risk assessment into a number of logical steps, as is outlined below:

- ***Hazard assessment*** is the identification of chemical and biological contaminants suspected to pose hazards and a description of the types of toxicity that they may evoke. This has been dealt with in Steps 1 to 3 (sections 6.3 – 6.5) above.
- ***Dose-response assessment*** (toxicological assessment) addresses the relationship between levels of biological exposure and the manifestation of adverse health effects in humans, and/or how humans can be expected to respond to different doses or concentrations of contaminants. This is a quantitative assessment that distinguishes between carcinogens and non-carcinogens. Risk quantification for carcinogens uses a cancer slope factor (CSF) for each substance, whereas non-carcinogens are characterised by reference doses (RfDs) and tolerable daily intake (TDI) values, as defined below:
- ***Exposure assessment*** includes a description of the environmental pathways and distribution of hazardous substances, identification of potentially exposed individuals or communities, the routes of direct and indirect exposure, and an estimate of concentrations and duration of the exposure. Determination of the intake of a substance (i.e., dose), expressed in mg per kg body weight per day (mg/kg-day), is the critical outcome of an exposure assessment.
- ***Risk characterization*** involves the integration of each component described above, with the purpose of determining whether specific exposures to an individual or a community might lead to adverse health effects. Risks are indicated by numbers such as a hazard quotient of larger or smaller than one, or a cancer risk of one in a hundred thousand or one in a million.
- ***Uncertainty review*** identifies the nature and, when possible, the magnitude of the uncertainty and variability inherent in the characterisation of risks. The results of any risk

[11] NRC. 1983. Risk Assessment in the Federal Government: Managing the Process. National Research Council, Committee on the Institutional Means for the Assessment of Risks to Public Health, National Academy Press, Washington, DC.
[12] USEPA. 1989. Risk Assessment Guidance for Superfund. Volume I. Human Health Evaluation Manual (Part A). Interim Final. EPA/540/1-89/002. US Environmental Protection Agency.
[13] USEPA. 1991. Risk Assessment Guidance for Superfund (RAGS), Volume I: Human Health Evaluation Manual (HHEM), Part B, Development of Risk-Based Preliminary Remediation Goals. US Environmental Protection Agency Office of Emergency and Remedial Response, Washington, DC. OERR 9285.7-01B. NTIS PB92-963333.
[14] IPCS. 1999. Environmental Health Criteria 210. Principles for the Assessment of Risks to Human Health from Exposure to Chemicals. World Health Organisation, Geneva.

assessment reflect scientific uncertainty associated with limitations in available data and assumptions that are made in the absence of such data, and the variability in exposure and toxicological response expected, given the diversity within the human population. Uncertainty review demonstrates the level of confidence in the outcome of the risk assessment and indicates whether additional data might be required, or whether elements of the precautionary principle have to be applied.

The approach to derive cleanup or remediation target levels is essentially a 'backwards' health risk assessment, working from levels of acceptable health risk for specific land-use options, through the exposure scenario and toxicological information, to contaminant concentrations in the environmental media relating to the acceptable risk levels.

The land use determines potential exposure pathways and routes of exposure to site contaminants, and defines the human and ecological receptors. These parameters, together with the toxicity profiles of contaminants, determine the maximum levels of exposure to which humans and ecological receptors may be subjected before health effects could potentially develop. To define the receptors, exposure pathways, and the frequency and duration of exposure, the assessor must take into account past, current and future land use patterns by consulting zoning plans, conducting interviews or consulting historical documents for each area under assessment.

6.6.1.2 Dose-Response Assessment (Toxicological Assessment for Humans)

Toxicological information is available from various databases and literature sources. The most prominent are the USEPA Integrated Risk Information System (IRIS)[15], the Agency for Toxic Substances and Disease Registry (ATSDR)[16], International Agency for Research on Cancer (IARC)[17], International Toxicity Estimates for Risk (ITER)[18], California Office of Environmental Health Hazard Assessment (OEHHA)[19], Health Canada[20], Baars *et al., 2001*[21], and World Health Organization (WHO)[22].

[15] Integrated Risk Information System (IRIS), http://www.epa.gov/ncea/iris/index.html.
[16] Agency for Toxic Substances and Disease Registry (ATSDR), http://www.atsdr.cdc.gov/.
[17] International Agency for Research on Cancer (IARC), http://www.iarc.fr/.
[18] International Toxicity Estimates for Risk, http://toxnet.nlm.nih.gov/cgi-bin/sis/htmlgen?iter.
[19] California Office of Environmental Health Hazard Assessment (OEHHA), http://oehha.ca.gov/about.html.
[20] Health Canada, Environment & Workplace Health, Reports & Publications. http://www.hc-sc.gc.ca/ewh-semt/pubs/.
[21] Baars AJ, Theelen RMC, Janssen PJCM, Hesse JM, Van Apeldoorn ME, Meijerink MCM, Verdam L & Zeilmaker MJ. 2001. Re-evaluation of human-toxicological maximum permissible risk levels. Bilthoven, The Netherlands: National Institute of Public Health and the Environment, March 2001, p 47-57. RIVM report no. 711701025. http://www.rivm.nl/bibliotheek/rapporten/711701025.pdf or at http://www.rivm.nl/en/.
[22] International Programme on Chemical Safety, Environmental Health Criteria. Geneva: World Health Organization.

The cancer slope factor per USEPA definition[23] *is "an upper bound, approximating a 95 per cent confidence limit, on the increased cancer risk from a lifetime exposure to an agent. This estimate, usually expressed in units of proportion (of a population) affected per mg/kg-day, is generally reserved for use in the low-dose region of the dose-response relationship, that is, for exposures corresponding to risks less than 1 in 100".* Dose is expressed as intake in milligrams of a substance per kilogram body weight per day. The slope factor therefore has the units $(mg/kg\text{-}day)^{-1}$.

USEPA[24] has identified several carcinogens that act via a mutagenic mode of action, and to account for their early-life exposures, default age-dependent adjustment factors (ADAFs) of 10 for ages 0-to-2 and 3 for ages 2-to-16 years have been introduced by USEPA in the cancer risk assessment methodology.

USEPA defines a reference dose (RfD) as *"an estimate of a daily oral exposure for a given duration to the human population (including susceptible subgroups) that is likely to be without an appreciable risk of adverse health effects over a lifetime."* It is derived from a benchmark dose limit (BMDL), a no-observed-adverse-effect level (NOAEL), a lowest-observed-adverse-effect level (LOAEL), or another suitable point of departure, with uncertainty/variability factors applied to reflect limitations of the data used. The term tolerable daily intake (TDI) has a meaning similar to the RfD, describing a *threshold dose*.

6.6.1.3 Exposure Assessment

a. Identify and Characterize Receptors Potentially at Risk

Receptors must be identified and characterized mainly in terms of how they use or occupy a site (differentiating inhabitants, workers, visitors, etc.). In analyzing receptors, the past, current and future uses of the site must be taken into account, including changes arising from current or future projects (such as modifications to zoning plans, construction of residential subdivisions and/or manufacturing plants, etc.).

Typical receptors are selected as child residents (ages 0 to 6 years), adult residents and non-resident workers. The childhood life stage is used in the assessment of exposure to non-carcinogens. Children have a higher ratio of environmental medium intake rate to body weight than adults and their behaviour increases their contact with the exposure pathway (e.g., playing with dirt – see Plate 6.7). For the assessment of exposure to carcinogens, the concept of an aggregate resident is applied. This approach averages dose across the childhood and adult life stages up to the age of 30 years. The non-resident worker assumes exposure of an adult for an occupational lifetime of 30 years.

[23] IRIS. 2010, online. Glossary of IRIS Terms. Integrated Risk Information System, US Environmental Protection Agency, Washington DC, USA.
[24] USEPA. 2005. Supplemental Guidance for Assessing Susceptibility from Early-Life Exposure to Carcinogens. Risk Assessment Forum, US Environmental Protection Agency. EPA/630/R03/003F.



Plate 6.7: Children are using this part of the old Berg Aukas plant as a slide

b. Identify Exposure Pathways to be Assessed

Exposure pathways are the media through which contaminants reach receptors. All potential pathways of exposure have to be investigated and a particular pathway can be removed from the assessment only if it is not 'complete'. This means that the pathway must be able to reach a receptor. For example, if groundwater is contaminated but the water yield of the aquifer is so low that the water cannot be used for any purpose, then the pathway would not be complete and exposure of potential receptors cannot occur. Table 6-4 indicates typical exposure pathways of chemicals of potential concern.

Table 6-4: Exposure Pathways to Consider in Assessing Exposure

Direct Exposure Pathways	Potential Concerns	Routes of Exposure
Surface Soil	Particulate matter (non-toxic)	Inhalation
	Particulate-associated contaminants	Inhalation, ingestion, dermal contact
Subsoil	Particulate-associated contaminants, occupational exposure, construction	Inhalation, ingestion, dermal contact
Surface water	Contaminants in surface water	Ingestion, dermal contact
Groundwater	Volatile and non-volatile contaminants	Inhalation, ingestion, dermal contact
Air	Contaminants as gas or on particulates	Inhalation
Indirect Exposure Pathways	**Potential Concerns**	**Routes of Exposure**
Surface water	Contamination into the food chain	Ingestion
Surface soil	Contamination into the food chain	Ingestion
Subsoil	Contamination into the food chain	Ingestion
	Contamination of subsurface soil	Ingestion
Groundwater	Contamination of groundwater	Ingestion

The food pathway considers ingestion of such commodities as vegetables grown in soil that is potentially contaminated by fall out dust (Plate 6.8), or irrigated with contaminated water; ingestion of products (meat, milk) from animals that consume contaminated water or which browse on forage growing in contaminated soil; or the consumption of aquatic species (fish, seafood, etc.) from contaminated waters.



a)



b)

Plate 6.8: a) Carrots being grown in highly contaminated soil at the Berg Aukas plant site, in spite of warnings by GSN not to grow root crops; b) cabbage being grown in soil contaminated by past spills from the Berg Aukas tailings

c. Integration of Receptors and Pathways of Exposure

Figure 6-4 shows an example of a scheme that can be followed to assess the links between potential exposure pathways and receptors. The example refers to contaminated soil. The dots indicate where an exposure pathway is complete, indicating routes of exposure and receptors. Direct exposure to contaminated soil can be developed further to include exposure of utility or construction workers. Similar schemes can be developed for other pathways of exposure, potential receptors and activities that may lead to exposure.

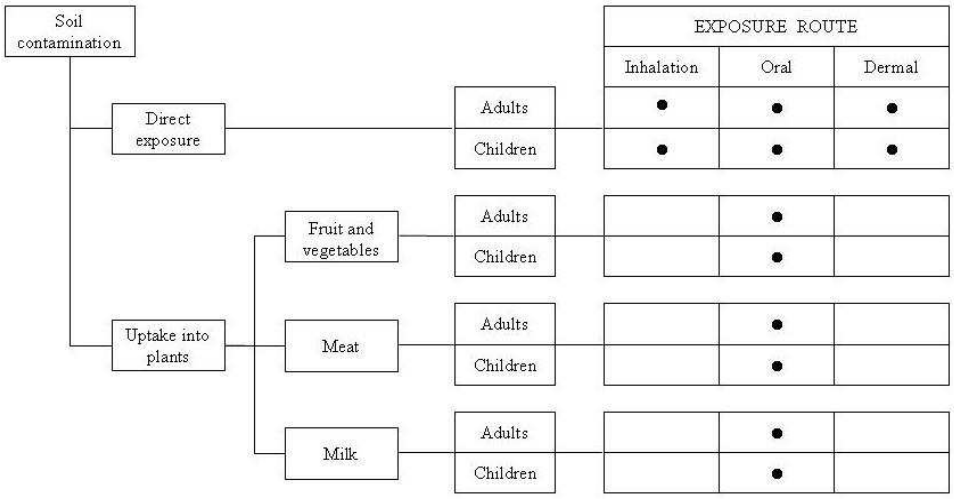
d. Determination of Exposure Frequency and Duration of Exposure

Exposure frequency and duration of exposure are parameters that depend on human behaviour and activity patterns. There may be large differences between different exposure scenarios and different population groups. It is recommended that surveys be conducted to estimate actual exposure patterns. In the absence of site-specific data it is recommended that the USEPA exposure factors[25;26]

[25] USEPA. 2009. Exposure Factors Handbook. National Center for Environmental Assessment, Office of Research and Development, US Environmental Protection Agency.
http://www.epa.gov/ncea.

be selected as a point of departure. These may be adjusted by an expert to be better representative of the scenario under investigation.

Figure 6-4: Example of Pathway-Receptor Integration Diagram.



e. Quantification of Exposure

USEPA provides general guidance on how to characterise exposures and risks when conducting risk assessments[27]. For exposure assessments, according to USEPA, it is suggested that intake and exposure values be selected so that the combination of all variables results in an estimate of the reasonable maximum exposure (RME) for that pathway. The RME is the maximum exposure that is reasonably expected to occur at a site. Under this approach, some intake variables (e.g., exposure frequency, duration of exposure and intake rate) may not be at their individual maximum values, but when in combination with other variables, will result in estimates of the RME[28]. USEPA guidance recommends estimating the high-end exposure by "*...identifying the most sensitive parameters and using maximum or near-maximum values for one or a few of these variables, leaving others at their mean values…*"[29]. This guidance applies when only limited information on the distribution of the exposure or dose factors is available. The recommendation is based on the fact that maximising all

[26] USEPA. 2008. Child-specific exposure factors handbook. National Center for Environmental Assessment, Washington, DC; EPA/600/R-06/096F. http://www.epa.gov/ncea.
27 USEPA, 1998. Risk Assessment Guidance for Superfund, Volume I: Human Health Evaluation Manual, Supplemental Guidance. Dermal Risk Assessment. Interim Guidance. (Peer Consultation Workshop Draft, November 6, 1998). US Environmental Protection Agency). Office of Emergency and Remedial Response.
28 USEPA, 1989. Risk Assessment Guidance for Superfund. Volume I. Human Health Evaluation Manual (Part A). Interim Final. EPA/540/1-89/002. US Environmental Protection Agency.
29 USEPA, 1992. Memorandum: Guidance on Risk Characterisation for Risk Managers and Risk Assessors. From: F Henry Habicht II. February 1992. US Environmental Protection Agency.

variables would result in an estimate that is above the range of actual values observed in the population.

Central tendency exposure (CTE) represents the most likely (lower risk) exposure scenario under which conditions the majority of individuals would be subjected. For example, the average CTE individual may ingest some 50 mg of soil per day while the RME may ingest 100 mg per day. Thus CTE exposure estimates would allow higher residual contaminant levels in soil (because of lower exposure of individuals) than concentrations derived from RME estimates (higher exposure levels). Calculated risks and the derivation of cleanup target levels derived for CTE and RME scenarios therefore apply to a range of concentrations that would cover the levels of a contaminant in soil.

e.1 Exposure Concentrations

Exposure concentrations will be estimated using information from site sampling or through a combination of sampling data and contaminant destination and transport models.

Sampling data may be used to estimate exposure concentrations through direct contact with the media. These cases may include direct contact with chemicals in soil or sampling done directly at the exposure point, such as a borehole used for drinking water. In these cases, the sampling data will yield the best estimate of real exposure concentrations. The sampled concentrations that will be used in this case will be defined by the expert.

In some cases it may not be appropriate to use only sampling data and contaminant fate and transport models may be required to estimate exposure concentrations. These models are recommended in the following cases:

- When the exposure points are spatially separated from sampling points. In this case models will be required to determine if mechanisms of release and transport to the exposure points are operating (for example, groundwater transport, air dispersion);
- When no information is available on the temporal distribution of data. Generally, data are collected over a relatively short period of time and give an indication of current conditions at the site. However, long-term and short-term exposures may be different. In that case it will be necessary to use forecasting models to predict the change in concentrations over time;
- In cases where sampling data are affected by the detection limit, models will be required to predict contaminant concentrations that could be toxic, but measured under the detection limit of the analytical method. For example, when a groundwater plume discharging into a river is diluted by the receiving water body, this may reduce concentrations of substances of interest to below levels that would be detected using laboratory analytical techniques. Nevertheless, the chemical could be sufficiently toxic or bio-accumulative to pose a health risk at concentrations below the analytical method's detection limit, in which case models for estimating exposure would be applied.

e.2 Dose Calculation

Quantification of dose can be complex and must be undertaken by an expert in human health risk assessment.

The generic Equation for calculating average daily dose from exposure to contaminants in air, soil or water is as follows:

$$ADD = (C \, x \, IR \, x \, EF \, x \, ED \, x \, BAF \, x \, CF) / (BW \, x \, AT) \qquad (6\text{-}1)$$

Where:

ADD	Average daily dose of a substance from intake of air, soil or water (mg/kg-day)
C	Concentration of substance in air (mg/m^3), soil (mg/kg) or water (mg/litre)
IR	Daily intake rate of air (m^3/day), soil (mg/day) or water (litres/day)
EF	Exposure frequency (days/year)
ED	Exposure duration (years)
BAF	Bioavailability factor for substances in air (default 1)
CF	Unit conversion factor: air 1, soil 10^{-6} kg/mg, water 1
BW	Body weight (kg)
AT	Averaging time (days)

Bioavailability as expressed in the BAF can play an important role in estimating the human exposure associated with exposure to toxic substances in the environment. Bioavailability defines the portion of chemical exposure (e.g., the quantity inhaled or ingested) that enters the bloodstream and that is assumed to be available to produce toxic effects in tissues. It is important to note that bioavailability depends on the chemical species, the medium of exposure and the tissue with which the chemical interacts.

In some cases, such as in quantification of cancer risk to account for mutagenic action in the early life stages of exposed individuals, the risk assessment requires calculation of an age-weighted dose.

For dermal contact, quantification of average daily absorbed dose follows the paradigm described by the United States Environmental Protection Agency[30].

[30] USEPA. 1992. Dermal Exposure Assessment: Principles and Applications. EPA/600/6-88/005Cc Office of Health and Environmental Assessment, US Environmental Protection Agency, Washington, DC.

The dermally-absorbed average daily intake from contaminants in water is described in Equation 6-2.

$$ADD = \left(DA_{event}\ x\ SA\ x\ EV\ x\ EF\ x\ ED\right) / \left(BW\ x\ AT\right) \quad (6\text{-}2)$$

Where:

ADD	Dermally-absorbed average daily intake of a contaminant from water or soil (mg/day)
DA_{event}	Absorbed dose per unit skin area per event (mg/cm^2-event)
SA	Total skin surface area (cm^2)
EV	Event frequency (events/day)
EF	Exposure frequency (days/year)
ED	Exposure duration (years)
BW	Body weight (kg)
AT	Averaging time

The absorbed dose per unit skin area from contaminants in water is controlled largely by the dermal permeability coefficient of a contaminant from water. Where dermal permeability coefficients of contaminants are not available from literature sources, these can be estimated from empirical relationships based on molecular weight and octanol-water partition coefficients of the substances[31]. The most recent USEPA guidance[32] on dermal risk assessment published a relationship for the absorbed dose per skin area per event that accounts for the lag time for absorption where exposure duration is shorter than the time required for reaching steady state. It accounts for the fact that short exposures, such as during body washing, have been shown to lead to higher absorption of the contaminants considered in this assessment than what would be predicted from conditions under steady-state.

The absorbed dose per unit skin area from contaminants in soil is determined by a soil adherence factor and a dermal absorption fraction that is substance-specific. The adherence factor describes the amount of soil that adheres to the skin per unit of surface area. It is influenced by soil properties and varies considerably across different parts of the body. It also varies with age and activity patterns.

[31] McKone TE and Howd RA, 1992. Estimating Dermal Uptake of Nonionic Organic Chemicals from Water and Soil: 1: Unified Fugacity-Based Models for Risk Assessments. Risk Analysis, 12(4):543-557.

[32] USEPA. 2004. Risk Assessment Guidance for Superfund Volume 1: Human Health Evaluation Manual (Part E, Supplemental Guidance for Dermal Risk Assessment) Final. EPA/540/R/99/005, OSWER 9285.7-02EP, PB99-963312, July 2004. Office of Superfund Remediation and Technology Innovation, US Environmental Protection Agency, Washington, DC.

The ability to quantify the absorption of contaminants from exposure to soil is limited. Chemical-specific information is available for only a few chemicals. McKone and Howd[33] developed an approach to calculate the overall mass transfer of organic chemicals from soil through the combined adhered soil layer using a thermodynamic fugacity model. For inorganic substances, speciation of the compound is critical to the dermal absorption and there are inadequate data to extrapolate a reasonable default value. Estimates have been made by various agencies

6.6.1.4 Characterization of Human Health Risks

a. Health Risks Associated with Criteria Pollutants

In the assessment of health effects due to exposure to the criteria pollutants (particulate matter (PM10), sulphur dioxide (SO_2), and nitrogen oxides (represented by NO_2)), mortality or hospitalisation rates for respiratory or cardiovascular causes are the measure of associated illness that is mostly applied in epidemiological studies. Air concentrations of compounds that exceed the ambient air quality guidelines or standards indicate that adverse health conditions may develop, but simple comparisons between exposure concentrations and ambient air quality guidelines are inadequate to quantify health outcomes. In general, predicted or measured impacts of industrial emissions on air quality are used as a basis to quantify impacts on health. This is achieved by calculating the potential increase in hospital admissions or in mortality due to specific causes, associated with increased air concentrations of specific toxic compounds. These calculations are based on results of studies reported in the international scientific literature in which statistical methods were used to compare changes in hospitalisation or mortality rates with changes in air quality.

It is important to note that it is common to observe increases in mortality or hospitalisation rates even when the available air concentrations do not exceed the environmental air quality guidelines. Ambient air quality guidelines are used for management of air quality and are not intended for risk quantification. Estimation of impacts of air pollutants on health may therefore not be restricted to areas in which the guideline concentrations are exceeded, but should also include areas in which concentrations are within limits. Current statistical methods use the concept of relative risk ratios (RR) to derive the potential percentage increase in effects.

The potential number of additional deaths or hospital admissions brought on by an increase in the concentration of a pollutant is calculated using the following approach of the World Health Organization[34]:

[33] McKone TE and Howd RA, 1992. Estimating Dermal Uptake of Nonionic Organic Chemicals from Water and Soil: 1: Unified Fugacity-Based Models for Risk Assessments. Risk Analysis, 12(4):543-557.
[34] WHO. 2004. Meta-analysis of Time Series Studies and Panel Studies of Particulate Matter (PM) and Ozone (O_3). EUR/04/5042688. Copenhagen: World Health Organization Regional Office for Europe.

$$E = AF \times P \times B / 1000 \quad (6\text{-}3)$$

Where:

E	Potential mortalities or morbidities per day or per year due to exposure to the pollutant
AF	The attributable fraction of mortalities or morbidities due to exposure to the pollutant
B	The population incidence of mortality or morbidity (e.g., deaths or hospitalisation rates per 1 000 people)
P	Size of the exposed population (number)

$$AF = RR - 1 \quad (6\text{-}4)$$

Where:

RR	The relative risk of mortality or morbidity due to exposure to the pollutant

The relative risk of death (RR) is calculated as follows:

$$RR = e^{(\Delta_{deaths} \times \Delta_p)} \quad (6\text{-}5)$$

Where:

Δ_{deaths}	Potential proportion change in mortality associated with a change in the pollutant concentration of 1 µg/m^3
Δ_p	The modelled change in the mean pollutant concentration in µg/m^3

Similar calculations can be made for morbidity cases.

b. Risk for Non-Carcinogenic Systemic Toxicants

The dose calculated using the equations presented should be compared to the reference dose (RfD) for non-carcinogenic chemicals for each exposure pathway. The ratio of these two values is the Hazard Quotient (HQ), which can be calculated using the following equation:

$$HQ = (ADD_I + ADD_O + ADD_D) / RfD \quad (6\text{-}6)$$

Where:

HQ	Hazard quotient for exposure to a substance in water (unitless)
ADD_I	Average daily dose of a substance due to inhalation of air (mg/kg-day)
ADD_O	Average daily dose of a substance due to oral intake of water (mg/kg-day)
ADD_D	Dermally-absorbed average daily dose of the substance from water, considering

	various dermal exposure scenarios (mg/kg-day)
RfD	Reference dose in mg/kg-day

The Hazard Index (HI) is the summation of the Hazard Quotients (HQs) associated with exposure to systemic toxicants that act on the same target organ systems.

c. Risk for Carcinogenic Chemicals

Calculated cancer risks refer to excess risk, i.e., risks due to exposure to a particular substance, over and above the background cancer risks to which members of the community may be exposed.

$$Cancer\ risk = (ADD_I + ADD_O + ADD_D)\, x\, Q^* \qquad (6\text{-}7)$$

Where:

Cancer risk	Cancer risk expressed as a unitless number
ADD_I	Average daily dose of a substance due to inhalation of air (mg/kg-day)
ADD_O	Average daily dose of a substance due to oral intake of water (µg/kg-day)
ADD_D	Dermally-absorbed average daily dose of a substance from water, including personal cleaning and washing of clothes
*Q**	Cancer slope factor $(mg/kg\text{-}day)^{-1}$

Individual cancer risk is expressed as a probability based on the number of cancer cases that may be expected in a population of a selected size, for example the number of cases in a million, in a hundred thousand, or in ten thousand. The actual population size in the study is not taken into account. Risk estimates obtained in this way are not estimates of actual cancer risk; the calculated numbers are upper bounds on actual cancer risk that are useful to regulators for setting priorities and for setting exposure limits. In cases where communities may be exposed to more than one cancer-causing agent, the calculated cancer risks associated with the individual substances are added to obtain an overall upper bound of cancer risk.

The concept of aggregate exposure quantification and risk assessment takes into account the number of individuals in the area that is being investigated, such as a regional district or suburb of a city. It may involve exposure to multiple cancer-causing agents through different routes of exposure, but it may focus on a single chemical and one route of exposure. The assessment presents the average probability of people developing chemical-exposure-induced cancer during their lifetime or the number of lifetime chemical-exposure-induced cancer cases for a specific aggregate population during a specified time period.

d. Acceptability of Risk

The level of total cancer risk that is of concern is a matter of personal, community, and regulatory judgement. In general, the USEPA[35] considers excess cancer risks that are below about 1 chance in a million ($1x10^{-6}$ or 1E-06) to be so small as to be negligible (*de minimis* lifetime risk), and risks above one in ten thousand ($1x10^{-4}$ or 1E-04) to be sufficiently large that some sort of remediation is desirable (*de manifestis* risk). In the judgement of cancer risk, the cancer classification of the substance, as published by IARC[36] and USEPA[37], must be taken into account.

The assessment of risk implications of HQs and HIs require understanding of the background toxicology and epidemiology, as well as the assumptions and uncertainties associated with reference doses and tolerable daily intakes of substances. There is no simple rule that may be applied in all assessments. A HQ or HI below 1 confirms that health risks are unlikely to occur, but values above 1 do not infer that adverse effects would in fact be observed. This requires interpretation by an expert in health risk assessment, which must take into account the entire body of scientific background information on which the assessment criteria are based.

6.6.1.5 Analysis of Uncertainties

It is often not possible, nor necessary, to conduct sophisticated statistical interpretations of estimates of exposure and risk. Generally, qualitative description of assumptions and uncertainties provide sufficient information to contextualize the outcome of the health risk assessment.

The risk assessment paradigm must follow standard international practice, as outlined in this Handbook. When applied under guidance of an expert, the outcome of the health risk assessment should have a high level of confidence. Toxicological parameters from credible, peer reviewed sources have known levels of confidence and if these data are considered in the assessment, the calculated risk can be presented with confidence. The risk assessment must state sources and the level of confidence in the reference data. The paradigm of risk assessment is designed to be on the side of caution, thus intended to overestimate rather than underestimate risk.

Data quality is controlled by formal QA/QC plans, stating data quality objectives and setting criteria for data acceptance. Interpretations shall be made only on data that have been signed off as credible on the basis of the QA/QC procedures.

In cases of limitations in the sampling and analytical process, for example sampling under difficult circumstances where samples might not be fully representative of the situation under study, or

35 USEPA. 1991. Role of the Baseline Risk Assessment in Superfund Remedy Selection Decisions, US Environmental Protection Agency. OSWER Directive 9355.0-30.
36 Integrated Risk Information System (IRIS), http://www.epa.gov/ncea/iris/index.html.
37 International Agency for Research on Cancer (IARC), http://www.iarc.fr/.

analysis of samples with multiple contaminant interferences, a sensitivity analysis must be undertaken of the parameters that may affect the data quality. This will assist in establishing the confidence interval in which the data can be presented.

6.6.2 Ecological Risk Assessment

6.6.2.1 Introduction to Quantitative Ecological Risk Assessment

The strategy for ecological risk assessment (ERA) is more complex than that for human health risk assessment and is fundamentally different in its inferential approach. The greater complexity is due largely to the large number of species and the diversity of routes of exposure that must be considered in ERAs.

The steps in the paradigm for ERA generally are similar to the assessment for human health risks, with slightly different uses of certain terminology. The paradigm uses the term 'stressor response' rather than 'dose response', because both physical and chemical parameters are addressed in ERA.

The paradigm divides ecological risk assessment into a number of logical steps, as is outlined below:

- ***Problem formulation (hazard assessment)*** is the identification of chemical and biological contaminants suspected to pose hazards to ecosystems and a description of the types of toxicity that they may evoke. This has been dealt with in Steps 1 to 3 in sections 6.3 to 6.5 above. In the USEPA's Framework for Ecological Risk Assessment, formulation of a conceptual model for assessing ecological risk is the output of the problem formulation phase of the assessment[38]. It presents a working hypothesis of how the site contaminants might affect the ecological components of the site. It includes descriptions of the source, the receiving environment, and the processes by which the receptors come to be exposed directly to the contaminants and, secondarily, to the effects of the contaminants on other environmental components.

Ecological receptors include all endpoint species or communities identified for a site.

- **Stressor-response assessment[39]** is an integration of exposure and response. Stressor-response assessment addresses the relationship between levels of biological exposure and the manifestation of adverse health effects ecological receptors. Calculation of stressor response and exposure estimates is the determination of what plants and animals are

[38] USEPA. 1992. Framework for Ecological Risk Assessment. US Environmental Protection Agency. Washington, DC. Report No EPA/630/R-92/001.

[39] USEPA. 2010. Online. Superfund Risk Assessment: Ecological: Stressor Response and Exposure Analysis. US Environmental Protection Agency. Washington, DC. http://www.epa.gov/oswer/riskassessment/superfund_stressor.htm.

exposed to, quantitative determination of the level of exposure and an interpretation of whether or not that level of exposure is likely to cause harmful ecological effects.

- **Exposure assessment** includes a description of the environmental pathways and distribution of hazardous substances and identification of potentially exposed ecological receptors. It requires the investigation and quantification of various parameters (e.g., area use, food ingestion rates, bioaccumulation rates, bioavailability, life-stage, body weight, and dietary composition) to determine the levels of exposure to a chemical contaminant by a selected plant or animal receptor.
- **Risk quantification** involves the calculation of hazard quotients (the ratio of chemical contaminant concentration to a selected screening benchmark).
- ***Uncertainty review*** identifies the nature and, when possible, the magnitude of the uncertainty and variability inherent in the characterisation of ecological risks. The results of ecological risk assessment often reflect greater scientific uncertainty than interpretations of human health risk assessment.

6.6.2.2 Stressor-Response Assessment for Ecological Receptors

The process of evaluating ecological risks of environmental contaminants comprises two tiers. Tier-1 is a screening assessment where concentrations of contaminants in the environment are compared to no-observed-adverse-effects-level (NOAEL)-based toxicological benchmarks that represent concentrations of chemicals in environmental media (water, sediment, soil, food, etc.). These concentrations are presumed to be non-hazardous to the surrounding and otherwise-exposed biota.

The second tier is a baseline ecological risk assessment where toxicological benchmarks are one of several lines of evidence used to support or refute the presence of adverse ecological effects[40]. See also Annexure C1.

Unlike some other endpoint assemblages, terrestrial wildlife is significantly exposed to contaminants in multiple media. They may drink or swim in contaminated water, ingest contaminated food and soil, and breathe contaminated air. In addition, because most wildlife is mobile, moving among and within habitats, exposure is not restricted to a single location. They may integrate contamination from several spatially discrete sources. Therefore, exposure models for terrestrial wildlife must include multiple media.

Guidance for ecological risk assessment has been published in a number of research papers[41;42;43] and other literature that may be consulted[44].

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[40] Sample BE, Opresko DM and Suter GW, 1996. Toxicological Benchmarks for Wildlife: 1996 Revision. Prepared for US Department of Energy. Report No ES/ER/TM-86/R3.
[41] Suter GW II. 1996. Guide for Developing Conceptual Models for Ecological Risk Assessments

6.6.2.3 Exposure Assessment

a. Identification of ecological receptors

Ecological receptors can include individual organisms, populations and/or communities that could be exposed to contaminants. Potential receptors can be identified after reviewing the destination, migration and real or potential release of contaminants. The investigator needs to identify terrestrial and aquatic areas, sensitive and protected habitats, farming, livestock, commercial game farming, fishing and aquaculture zones within the site or nearby and develop lists of species known or likely to exist in each habitat. Specific care must be taken to list the following:

- Endangered, threatened, rare or endemic species;
- Species protected by specific legislation;
- Species that might be consumed by people;
- Species that are indicators of the health of a community.

If the chemicals of potential concern at a site are known to be bio-accumulative (e.g. cadmium, mercury), it will be important to consider environmental fate with regard to the trophic relations among species in order to assess effects related to the food chain.

b. Identification of Exposure Pathways

Ecological receptors can be exposed to chemicals through direct or indirect contact. The main exposure pathways are presented in Table 6-5.

Environmental Restoration Risk Assessment Program, Oak Ridge National Laboratory. Oak Ridge, Tennessee. Report No ES/ER/TM-186.

[42] Sample B. E., Aplin M. S., Efroymson R. A., Suter G. W. II and Welsh C. J. E.. 1997. Methods and Tools for Estimation of the Exposure of Terrestrial Wildlife to Contaminants. Oak Ridge National Laboratory. Environmental Sciences Division Publication No. 4650. ORNL/TM-13391.

[43] Suter GW, Efroyson RA, Simple BE and Jones DS. 2000. Ecological Risk Assessment for Contaminated Sites. CRC Press, Boca Raton, Florida.

[44] Guidance for Ecological Risk Assessment at Hazardous Waste Sites and Permitted Facilities. State of California, California Environmental Protection Agency. Department of Toxic Substances Control, Human and Ecological Risk Division. July 4, 1996. http://www.dtsc.ca.gov/AssessingRisk/upload/overview.pdf.

Table 6-5: Ecological Risk Assessment. Possible Exposure Pathways by Media Susceptible to Contamination.

Medium	Exposure pathway	Observations
Surface water	Direct contact	Terrestrial organisms can be exposed through direct contact with contaminants present in surface water by walking or swimming in the water. Aquatic receptors can be exposed by osmotic exchange or by breathing in surface water.
	Contact through roots	Contaminants may come into direct contact with terrestrial plants through roots that are in contact with surface water.
	Ingestion	Terrestrial receptors can ingest contaminated water through drinking.
Sediment	Ingestion	Terrestrial organisms can ingest sediment occasionally and accidentally when they take their food from places that flood only periodically. Aquatic organisms can ingest sediment during regular feeding activity.
	Direct contact	Aquatic organisms can be exposed directly or through osmotic exchange, respiration or ventilation of interstitial water.
Groundwater	Contact through roots	Contaminants can enter into contact with terrestrial plants through roots that are in contact with groundwater.
Soil	Foliage deposition	Exposure of terrestrial plants to contaminants present in particles deposited on the surface of leaves and stems.
	Contact through roots	Contaminants in the soil can dissolve and be absorbed by plant roots.
	Ingestion	Accidental ingestion of contaminated soil by animals when feeding off plants grown in or covered with contaminated soil
	Direct contact	Many species live in burrows – often excavated in the soft substrate of tailings dams – and therefore complete their life cycles fully or partially in direct contact with contaminated material
Air	Inhalation of gases or vapour	Exposure via inhalation is most important for organisms that nest in contaminated soil, considering the limited amount of air present to dilute vapour and the absence of airflow to disperse gases.
	Inhalation of dust	Inhalation exposure to fugitive dust is particularly applicable to species living in the soil, which can be exposed through their activity in the soil or by the wind.
	Absorption through foliage (vapour)	Foliar absorption of organic vapours is limited to species with a relatively high vapour pressure.
	Foliage deposition (dust)	Exposure of terrestrial plants to contaminants present in particles deposited on the surface of leaves and stems.

Medium	Exposure pathway	Observations
Food Chain	Ingestion	Animals with the highest terrestrial and aquatic trophic levels include predators, which do not necessarily have to come into direct contact with a contaminated medium, but can be exposed by ingesting contaminated food.

c. Uptake of contaminants into animal and plant tissue

This factor is important in the assessment of exposure through indirect food pathways. Information may be obtained from direct analysis of food sources (e.g., fish, plants, etc), or concentrations may be estimated by applying mathematical multi-media uptake models, based on media transfer factors[45;46].

d. Quantification of Exposure for Terrestrial Receptors

d.1 Exposure factors

Exposure factors for wildlife are available in the USEPA Wildlife Exposure Factors Handbook[47]. This Handbook provides data, references, and guidance for conducting exposure assessments for wildlife species exposed to toxic chemicals in their environment. The information is applicable to wildlife in the USA, but may be used as a point of departure for deriving exposure factors applicable to the situation in Namibia.

d.2 Quantification of dose

Exposure of animals to contaminants usually occurs in one of three main ways: water ingestion, food ingestion or accidental ingestion of soil or sediment. Except for inhalation of criteria air pollutants such as sulphur dioxide, exposure to environmental toxicants via inhalation and skin contact generally are considered negligible compared to exposure through ingestion.

Assessment of exposure to a contaminant generally requires quantification of the dose ingested with contaminated water, food, soil or sediment[48].

[45] Staven LH, Napier BA, Rhoads K, and Streng DL. 2003. A Compendium of Transfer Factors for Agricultural and Animal Products. Pacific Northwest National Laboratory.
[46] Ecological Risk Analysis: Guidance, Tools, and Applications. ORNL. http://www.esd.ornl.gov/programs/ecorisk/biological_uptake.html.
[47] USEPA. 1993. Wildlife Exposure Factors Handbook. US Environmental Protection Agency, Washington, DC. EPA/600/R-93/187 (2 Volumes). http://cfpub.epa.gov/ncea/cfm/.
[48] Sample BE and Suter GW, 1994. Estimating Exposure of Terrestrial Wildlife to Contaminants. Prepared for US Department of Energy. Report No ES/ER/TM-86/R3.

$$ADD = ADD_F + ADD_W + ADD_S + ADD_{SD} \quad (6\text{-}8)$$

Where:

ADD	Average daily dose of a substance from all exposure pathways (mg/kg-day)
ADD_F	Average daily dose of the substance from food sources (mg/kg-day)
ADD_W	Average daily dose of the substance from intake of water (mg/kg-day)
ADD_S	Average daily dose of the substance from intake of soil (mg/kg-day)
ADD_{SD}	Average daily dose of the substance from intake of sediment (mg/kg-day)

Exposure estimates must be expressed in terms of a body-weight normalized daily dose. Information on bioavailability of individual toxicants is too limited to apply bioavailability factors in the estimation of dose. It is assumed that the bioavailability will be set at a default value of 1. The receptor's contact with the contaminated medium shall be estimated on information such as location of receptors in the Area of Study (influence), movement of receptors (for animals) and time spent in the contaminated zone.

Estimation of the daily contaminant dose of an individual from a particular medium is expressed in its simplest form by the following equation:

$$ADD_j = \sum_{i=1}^{m} \left(\frac{IR_i \, x \, C_{ij}}{BW} \right) \quad (6\text{-}9)$$

Where:

ADD_j	Average daily dose of contaminant j (mg/kg-day)
i	Environmental medium i (food, water or soil)
m	Total number of environmental media
IR_i	Consumption rate of medium i (kg/day or litre/day)
C_{ij}	Concentration of contaminant j in medium (mg/kg or mg/litre)
BW	Body weight of endpoint species (kg)

Few wildlife species consume diets that consist exclusively of one food type. To account for the intake of varying contaminant concentrations in different food types, exposure estimates must be weighted by the relative proportions of daily food intake from the different sources.

$$ADD_j = \sum_{i=1}^{m} \left(\frac{FIR_i \, x \, C_{ij}}{BW} \right) \quad (6\text{-}10)$$

Where:

ADD_j	Average individual daily dose of contaminant j (mg/kg-day)
i	Food type i (food, water or soil)
m	Total number of food types
FIR_i	Intake rate of food type i (kg/day)
C_{ij}	Concentration of contaminant j in food type i (mg/kg fresh weight)
BW	Body weight of endpoint species (kg)

The ingestion rate for each food type may be estimated from:

$$FIR_i = P_i \, x \, FIR \qquad (6\text{-}11)$$

Where:

FIR_i	Ingestion rate of each food type for an individual (kg/day)
P_i	Proportion of the i^{th} food type in the diet
FIR	The total food ingestion rate (kg/day)

If the affected (contaminated) area has similar habitat to the surrounding area that constitutes the home range, exposure to contaminants would be proportional with regard to area.

$$ADD_j = \left(\frac{A}{HR}\right)\sum_{i=1}^{m}\left(\frac{IR_i \, x \, C_{ij}}{BW}\right) \qquad (6\text{-}12)$$

Where:

ADD_j	Average daily dose of contaminant j (mg/kg-day)
A	Contaminated area (hectares)
HR	Home range size (hectares)
i	Environmental medium i (food, water or soil)
m	Total number of environmental media
IR_i	Consumption rate of medium i (kg/day or litre/day)
C_{ij}	Concentration of contaminant j in medium (mg/kg or mg/litre)
BW	Body weight of endpoint species (kg)

In cases where the site under consideration is highly modified and only a proportion of the contaminated area provides suitable habitat, an additional factor may be introduced to account for the lesser exposure:

$$ADD_j = P_h \left(\frac{A}{HR} \right) \sum_{i=1}^{m} \left(\frac{IR_i \, x C_{ij}}{BW} \right) \quad (6\text{-}13)$$

Where:

ADD_j	Average daily dose of contaminant j (mg/kg-day)
P_h	Proportion of suitable habitat in the contaminated area
A	Contaminated area (hectares)
HR	Home range size (hectares)
i	Environmental medium i (food, water or soil)
m	Total number of environmental media
IR_i	Consumption rate of medium i (kg/day or litre/day)
C_{ij}	Concentration of contaminant j in medium (mg/kg or mg/litre)
BW	Body weight of endpoint species (kg)

Where sites are heterogeneous, the proportional contribution of each area can be modelled to account for the factors of contaminant levels and quality and habitat.

$$ADD_j = \sum_{k=1}^{n} \left(\frac{A_k}{HR} \left[\sum_{i=1}^{m} \left(\frac{IR_i \, x C_{ijk}}{BW} \right) \right] \right) \quad (6\text{-}14)$$

Where:

ADD_j	Average daily dose of contaminant j (mg/kg-day)
n	The number of distinct contaminated areas
A_k	Area of a distinct contaminated habitat area
HR	Home range size (hectares)
i	Environmental medium i (food, water or soil)
m	Total number of environmental media
IR_i	Consumption rate of medium i (kg/day or litre/day)
C_{ijk}	Concentration of contaminant j in medium i in the k^{th} area (mg/kg or mg/litre)
BW	Body weight of endpoint species (kg)

The equation can be expanded further to account for wide-ranging wildlife to multiple contaminated areas.

6.6.2.4 Quantification of ecological risks

a. Risk Assessment Methodology for Birds and Mammals

In general, risk is quantified by estimating the ingestion of contaminants (ingested dose) by wildlife and comparing this dose to reference dose values (estimated for organisms of reference under laboratory conditions or from epidemiological studies) as referenced in Annexure C1. A hazard quotient can be calculated to assist in the assessment. After this comparison, an extrapolation is performed to estimate the probability of ecological effects on wildlife under natural conditions. The methodology may be applied to assess the risk to wild or domestic animals (livestock). Quantified chronic exposure values shall represent a level of exposure to a chemical contaminant with no adverse effects, i.e., not exceeding the no-observed-adverse-effect-level (NOAEL). The ecological effects of greatest concern are those that can affect population levels, in other words, those that affect development, reproduction and survival on a group basis.

The science of risk assessment in ecology has not evolved to the point where scientists can make standard risk calculations for common risk scenarios, as is done in human health evaluations. Risk characterization in ecological assessment is a process of applying professional judgement to determine whether adverse effects are occurring or may occur as a result of contamination associated with a site.

Because professional judgment is so important, specialized knowledge and experience in the various phases of ecological risk assessment is required. Thus, an interactive multidisciplinary team that includes biologists, ecologists and risk assessment specialists is a prerequisite for a successful ecological risk assessment.

b. Risk Assessment Methodology for Fish, Invertebrates and Plants

In the case of these receptors there is no reference to ‘dose’ by some route of exposure. The maximum contaminant concentration needs to be established for the medium in which these organisms live, which is then compared with a reference toxicity value for aquatic or relevant terrestrial organisms.

The stressor-response component of ecological risk assessment for aquatic receptors considers more factors than the toxicological effects of chemicals and physical stressors. Assessment is divided in the evaluation of a ‘driver component’ and a ‘response component’.

- The ‘driver component’ of the assessment considers water quality and habitat as the primary factors that would affect the integrity of the ecosystem. This is a generic assessment that is independent of the actual species and their sensitivities in the environmental setting and generally is on the conservative side, i.e., it tends to overestimate rather than underestimate risk.

- The 'response component' involves a practical site-specific assessment (field measurements) of the integrity of the ecosystem, compared against the expected state in the absence of impacts. The study uses effects-based criteria and always overrides the assessment based on chemical criteria, because it considers more direct measurements of adverse effects. The outcome of this holistic study is an integrated assessment of the local ecosystem integrity state.

6.6.2.5 Analysis of Uncertainties

Even more than is the case with human health risk assessment, it is not possible, nor necessary, to conduct sophisticated statistical interpretations of estimates of exposure and risk in ecological risk assessment. Generally, qualitative description of assumptions and uncertainties provide sufficient information to contextualize the outcome of the health risk assessment.

Ecological risk assessments are based on scientific data that are frequently difficult and complex, conflicting or ambiguous, or incomplete. Analysis of such data for risk assessment purposes depends on professional judgment based on scientific expertise. Professional judgment is necessary to:

- Design and conceptualize the risk assessment;
- Evaluate and select methods and models;
- Determine the relevance of available data to the risk assessment;
- Develop assumptions based on logic and scientific principles to fill data gaps; and
- Interpret the ecological significance of predicted or observed effects.

Data quality needs to be controlled by formal QA/QC plans, stating data quality objectives and setting criteria for data acceptance. Interpretations shall be made only on data that have been signed off as credible on the basis of the QA/QC procedures.

The ecological risk assessment paradigm must follow standard international practice, as outlined in this Handbook. When applied under guidance of an expert, the outcome of the risk assessment should provide good estimates of exposure and risk. Toxicological parameters from credible, peer reviewed sources have known levels of confidence and if these data are considered in the assessment, the calculated risk can be presented with confidence in stated confidence intervals. The risk assessment must state sources and the level of confidence in the reference data. The risk assessor shall be conservative in selecting values from other sources and shall detail the limitations of these values when applying these. The paradigm of ecological risk assessment is designed to be on the side of caution, thus intended to overestimate rather than underestimate risk.

In cases of limitations in the sampling and analytical process, for example sampling under difficult circumstances where samples might not be fully representative of the situation under study, or analysis of samples with multiple contaminant interferences, a sensitivity analysis must be undertaken of the parameters that may affect the data quality. This will assist in establishing the confidence interval in which the data can be presented.

Overall, the statement of confidence in the ecological risk assessment must be made by an expert in the field.

6.7 STEP 5 – Risk Statement

6.7.1 Human health risk assessment

This step in the assessment process requires that guidance be set on the acceptability of risk. It is a complicated step that has to consider the acceptability of health risks to humans and ecological receptors in balance with social implications and financial considerations. It requires multi-disciplinary expertise in cost-benefit analysis, taking into account regulatory requirements.

In particular, this step has to advise on the requirement or not for remedial action. It involves the application of multi-disciplinary science that has to take into account social, financial and environmental considerations.

An example of a Probability Index rating scheme is presented in Table 6-6.

Table 6-6: Example of a Probability Index Rating scheme.

Probability Index	Public Health	
	Excess Cancer Risk	Non-cancer Risk (HQ or HI max. value)
High	>1E-04	> 100
Medium	Between 1E-05 and 1E-04	Between 10 and 100
Low	Between 1.0E-6 and 1E-05	Between 1 and 10
Negligible	<1E-06	< 1

As discussed in Section 6.6.1.4d., the level of total cancer risk that is of concern is a matter of personal, community, and regulatory judgement. Table 6-6 reflects excess cancer risks that are below one in a million (1E-06) to be so small as to be negligible (*de minimis* lifetime risk). Risks above one in ten thousand (1E-04) are sufficiently large that some sort of corrective action is desirable (*de manifestis* risk). The description of such risks in Table 6-6 as “high” should be placed into context. In

the judgement of cancer risk, the cancer classification of the substance, as published by the IARC[49] and USEPA[50], as well as the particular cancer endpoint, must be taken into account. The Globally Harmonized System for classification and labelling of chemicals (GHS)[51] applies the cancer classification presented in Table 6-7.

Table 6-7: Classification Criteria for Hazard Categories of Carcinogens.

Hazard Category	Classification Criteria
1A	Known to have carcinogenic potential for humans, based largely on human evidence.
1B	Presumed to have carcinogenic potential for humans: • evidence from human studies that establish a causal relationship between human exposure to a chemical and the development of cancer (known human carcinogen), or • evidence from animal tests for which there is sufficient evidence to demonstrate animal carcinogenicity (presumed human carcinogen), and • on a case-by-case basis, scientific judgement may warrant a decision of presumed human carcinogenicity derived from studies showing limited evidence of carcinogenicity in humans together with limited evidence of carcinogenicity in animal tests.
2	Suspected human carcinogen: • evidence from human or animal studies (or both), but which is not sufficiently convincing for classification as a category 1 carcinogen, and • limited evidence of carcinogenicity in human studies or limited evidence of carcinogenicity in animal tests.

There is a factor 10 difference in the hazard rating between Category 1 and Category 2 carcinogens in the GHS, which indicates that there is no generalised hazard rating for the various categories of cancer classification. There are many examples that demonstrate limitations associated with generalisation of interpretations across carcinogens. For example, in cancer risk quantification for carcinogens that have mutagenic activity, cancer slope factors have to be adjusted to account for higher vulnerability in the early human life stages. Vinyl chloride is another example; there is a difference in cancer risk quantification between exposure from birth and exposure only in the adult life stage. The Probability Index in Table 6-6 must thus be applied with caution.

The rating of HQ and HI values for non-carcinogens is subject to similar limitations. The significance of a HQ of a substance depends on the level of certainty of the reference dose (RfD) or the tolerable daily intake (TDI). Uncertainty (safety) factors are applied to account for limitations in data and for the adjustment of animal data and epidemiology studies to apply to the most sensitive human receptors. These uncertainty factors may range between as low as 10 to as high as 10 000. Furthermore, RfDs are based on effects on the most sensitive health endpoints, the effects of which

[49] International Agency for Research on Cancer (IARC), http://www.iarc.fr/.
[50] Integrated Risk Information System (IRIS), http://www.epa.gov/ncea/iris/index.html.
[51] Globally Harmonized System of Classification and Labelling of Chemicals (GHS). Document ST/SG/AC.10/30/Rev 2. United Nations 2007.

may be reversible or irreversible. The severity of systemic toxicity of a particular toxicant, as reflected in exceedence of the RfD, depends on the slope of the dose-response relationship in the low-dose region and it is inappropriate to generalise interpretation of the value of a HQ for all non-carcinogens as has been done in the Probability Index in Table 6-6. The information in Table 6-6 must thus be regarded purely as an example of the methodology that may be followed for establishing a Probability Index in the assessment of environmental exposure to hazardous chemicals. The actual assignment of a Probability Index for a hazardous chemical shall be done by specialists in chemical toxicology, epidemiology and health risk assessment.

6.7.2 Ecological risk assessment

It has been pointed out in Section 6.6.2.4 a. that the science of risk assessment in ecology has not evolved to the point where scientists can make standard risk calculations for common risk scenarios, as is done in human health evaluations. Applying a generalised scheme for developing a Probability Index rating scheme for a diverse range of ecological receptors is thus a challenge. Risk characterization in ecological assessment requires a great deal of professional judgement to determine whether adverse effects are occurring or may occur as a result of contamination associated with a site. The HQ is only one of the factors that assist in ecological risk interpretation.

Table 6-8 presents an example of a Probability Index rating scheme for ecological receptors. The information in this table must be regarded purely as an example. Ecological risk assessment specialists shall interpret dose-response information of toxicants on particular ecological species and the health endpoints of concern. After assessment in detail, a Probability Index can be compiled for a particular stressor on the category of receptors of interest.

Table 6-8: Probability Index versus Ecological Risk Value or Hazard Quotient (HQ).

Probability Index	Ecological Risk (HQ)
High	> 100
Medium	From 10 to 100
Low	From 1 to 10
Negligible	< 1

6.7.3 Assessment of the severity of consequences

A generalised scheme for the assessment of severity of the consequences of exposure to environmental contamination is presented in Table 6-9.

Individual human cancer risk is expressed as a probability based on the number of cancer cases that may be expected in a population of a selected size, for example the number of cases in a million, in a hundred thousand, or in ten thousand. The actual population size in the study is not taken into

account. Risk estimates obtained in this way are not estimates of actual cancer risk; the calculated numbers are upper bounds on actual cancer risk that are useful to regulators for setting priorities and for setting exposure limits. In cases where communities may be exposed to more than one cancer-causing agent, the calculated cancer risks associated with the individual substances are added to obtain an overall upper bound of cancer risk.

The concept of aggregate exposure quantification and risk assessment takes into account the number of individuals in an area that is investigated, such as a regional district or a particular residential area in the vicinity of the contaminated site. It may involve exposure to multiple cancer-causing agents through different routes of exposure, but it may also focus on a single chemical and one route of exposure. The assessment presents the average probability of people developing chemical-exposure-induced cancer during their lifetime or the number of lifetime chemical-exposure-induced cancer cases for a specific aggregate population during a specified time period. The aggregate population may consist of different subpopulations subjected to different doses of cancer-causing agents.

Table 6-9: Example of a Severity of Consequences Index Rating.

		Severity of Consequences				
		Negligible	**Low**	**Moderate**	**High**	**Catastrophic**
PEOPLE	Public Health (nº of people that could come into contact with the contaminant)	None	For carcinogens, severity is based probabilistically on aggregate cancer risk assessment For non-carcinogens, it is based on specific target organ toxicity and the toxicity dose-response relationship, considering the level of confidence in the toxicity data			
THE ENVIRONMENT	Aquatic Life (surface area or length of water body/course affected by contamination)	No habitat loss	< 5 ha for wetlands and dams; OR < 0.5 km for rivers/coast	5 - 10 ha for wetlands and dams; OR 0.5 - 2 km for rivers/coast	> 10 ha for wetlands and dams or >2 km for rivers/coast	Not applicable
	Aquatic Life (loss of biodiversity)	No biodiversity loss	Some loss of biodiversity. Ecosystem under low threat. Effects would be reversible	Biodiversity low. Species limited to a few tolerant individuals. Ecosystem under stress. Possible irreversible impacts.	No biodiversity. No living creatures evident. Ecosystem dead. Irreversible effects.	Not applicable
	Terrestrial Fauna & Flora (total area of habitat affected)	No habitat loss	< 10 ha	10 - 100 ha	> 100 ha	Not applicable

		Severity of Consequences				
		Negligible	**Low**	**Moderate**	**High**	**Catastrophic**
	Terrestrial Fauna & Flora (biodiversity loss)	No biodiversity loss	Some loss of biodiversity. Ecosystem under low threat. Effects would be reversible	Biodiversity low. Species limited to a few tolerant individuals. Ecosystem under stress. Possible irreversible impacts.	No biodiversity. No living creatures evident. Ecosystem dead. Irreversible effects.	Not applicable
	Terrestrial Fauna & Flora (drinking water resources affected)	None contaminated	Many other sources of uncontaminated water within 10km radius	One or two alternative uncontaminated water sources within a 10km radius	Only source of water within a 10km radius is contaminated	Not applicable
	Protected or Environmentally Sensitive Areas (area or sites affected by contamination)	None	< 1 ha	1 - 10 ha; OR cultural heritage sites of local importance	>10 ha; OR cultural heritage sites of regional/national importance	Not applicable
ECONOMIC ACTIVITIES	Crop Farming (crop production type)	No toxic effects	Only certain species susceptible to contamination or pollution are affected e.g. salt intolerant spp, root vegetables etc	Only a few very tolerant species can be grown	No crops can be grown because of high levels of soil and crop contamination	Not applicable
	Crop production - yield and income	No effects on yield and/or income	Loss of 20% of yield and/or income due to contamination. Limited effect on livelihoods	Loss of 21-50% of crop yield and/or income due to contamination. Moderate impact on livelihoods	Loss of >50% of crop yield and/or income. Lands have to be abandoned. Major impact on livelihoods	
	Game Farming & Livestock Activity – grazing areas	No loss of grazing area or grazing quality	Loss of <20% of grazing area due to contamination	Loss of 21-50% of grazing land due to contamination	Loss of >50% 0f grazing area due to contamination	Not applicable

		Severity of Consequences				
		Negligible	**Low**	**Moderate**	**High**	**Catastrophic**
	Game Farming & Livestock Activity - production rate and income	No loss of income	<20% drop in production. Limited impact on livelihoods	Loss of 21-50% in production and/or income due to contamination. Some products cannot be sold or consumed. Moderate impact on livelihoods	Loss of >50% in production and/or income. Lands have to be abandoned. Major impact on livelihoods	
	Aquaculture and Fishing	No loss of income	<20% drop in production. Limited impact on livelihoods	Loss of 21-50% in production and/or income due to contamination. Some products cannot be sold or consumed. Moderate impact on livelihoods	Loss of >50% in production and/or income. Business has to be abandoned. Major impact on livelihoods	Not applicable
	Tourism - impacts of contamination on tourist facilities	Absent	1 tour operator or 1 tourist site	2-5 tour operators or tourist sites	>5 tour operators or tourist sites	Not applicable

Aggregate risk assessment provides a measure of the overall exposure-induced cancer cases in a community under assessment. The risk is estimated over a lifetime, assuming exposure from birth to 30 years. The number of probabilistically estimated cancer cases can be calculated according to Equation 6-15:

$$A_{cases} = \left(\sum_{k=1}^{n} (R_k N_k) \right) \Big/ n \qquad (6\text{-}15)$$

Where:

A_{cases}	Aggregate risk (number of cases)
R_k	Excess cancer risk in subpopulation k
N_k	Number of people in subpopulation k
n	Number of subpopulations

Calculation of aggregate cancer risk assessment provides the required information for assessing the severity of cancer risk by taking into consideration the exposed population size and different

exposures in different subpopulations. The severity rating cannot be generalised across all carcinogens and exposure levels. The severity of the consequence has to be calculated on a case-by-case basis. The methodology can be applied to predict the number of excess cancer cases that may be expected and decisions about severity can be taken on the estimated annual cancer incidence in a community in a site-specific scenario.

The severity of consequences resulting from exposure to non-carcinogens is not calculated following probabilistic risk assessment. The approach is deterministic and assumes that the health effects may occur in any or in all exposed individuals if a HQ for exposure to a particular toxic substance exceeds unity. The severity of the consequence will depend on the level of confidence in the reference dose that is applied in the assessment, the target organ and prognosis of the health outcome, whether the effect is reversible or not, and what the dose-response relationship is. Severity of the consequence therefore cannot be expressed probabilistically on the potential number of cases that may show in a population. Assessment of the severity of the consequence of exposure shall thus be assessed by specialists in toxicology, epidemiology and human health risk assessment.

Table 6-9 also lists criteria for assessment of the severity of consequences on the environment and economic activities. The numbers in the table must be taken as examples; site-specific assessments shall be conducted by specialists in the respective activity fields to determine appropriate criteria for the assignment of severity index ratings for consequences associated with the various activities that may be relevant in a specific assessment.

6.8 Peer Review of Detailed Risk Assessment Reports

Because of the complex methodology involved, DRAs for Chemical Contamination shall be prepared by experts in the multidisciplinary science of human and ecological health risk assessment.

The Handbook contains a checklist (Annex C2) to assist in reviewing the studies and to verify credible data quality and interpretation.

Peer review is an internationally accepted procedure that assists in the carrying out of environmental risk assessments that are robust and in accordance with the best available international practice. Peer reviewers shall be internationally recognized professionals with appropriated certification, such as the QEP Certification of the Institute of Professional Environmental Practice (IPEP) in the USA, or equivalent[52].

Peer review is not a procedure that is conducted to assess only data quality and validity of interpretations. The peer reviewer has to be involved in the project from its planning stage to the final conclusions, to add value throughout the planning and assessment process. Peer review is an interactive, transparent activity. Each comment of the peer reviewer has to be considered and

[52] IPEP. Institute of Professional Environmental Practice, Pittsburg, PA. http://www.ipep.org/.

responded to in writing by the project scientist, whether or not there has been agreement with the comment. The peer reviewer has to sign off the final project report, thereby confirming support for the credibility of the study and its conclusions and recommendations.

6.9 Calculating Site Specific Target Levels (SSTLs).

When the assessment of risks has been completed and remedial action goals are developed, ecological risks must be compared with human health risks to determine which will drive the selection of cleanup target levels and remedial options.

In the case of remedial action based on human health risk considerations, it is advised that site-specific cleanup target levels be derived using the methodology applied by the USEPA Mid-Atlantic Risk Assessment programme[53]. The USEPA approach follows multi-route risk-based equations to derive generic screening levels for the derivation of Tier-1 screening levels for assessment of contamination in environmental media. Different land-use scenarios are taken into account. It must again be emphasized that screening guidelines are not remediation goals or cleanup target levels.

By applying site-specific exposure parameters in the USEPA equations, cleanup target levels can be derived that will be representative of site-specific conditions. These shall take into account population characteristics, behaviour and activity patterns and shall be protective of human health under all potential exposure scenarios at the site.

Remediation requirements that are driven by ecological risks are more difficult to determine, because in many cases the balance between costs and benefits play a greater role than in remediation to protect human health. Decisions also depend on factors such as the presence of endangered or threatened species, species protected by specific legislation and rare and the consumption of species by humans. Corrective actions may involve development of alternative protected areas or relocation of species to other areas, which are generally not practical where humans are the affected receptors. The effects of degraded habitat as a result of causes other than site contamination may have a more serious adverse effect on ecological receptors in comparison with chemical drivers. Generally, the requirement for corrective action and setting environmental targets for such actions, requires specialist knowledge and experience in risk assessment and involves multidisciplinary contributions in the development and optimisation of remediation programmes.

[53] US Environmental Protection Agency (USEPA), Mid-Atlantic Risk Assessment (Serving Delaware, District of Columbia, Maryland, Pennsylvania, Virginia, and West Virginia). Risk-Based Concentration (RBC) Table. Online.
http://www.epa.gov/reg3hwmd/risk/human/index.htm.
http://www.epa.gov/reg3hwmd/risk/human/pdf/MAY_2010_FISH.pdf.

BOX 4

IMPORTANCE OF A DETAILED RISK ASSESSMENT: OAMITES MINE

The Geological Survey of Namibia was instructed by Cabinet to investigate possible effects of the Oamites abandoned mine site on human health due to an unusual high rate of respiratory problems among the ca. 2000 residents at the military base camp.

The two un-rehabilitated tailings dumps at Oamites contain 5.5 million tons of very fine grained rock material which consists mainly of quartz, feldspars, calcite and mica and contains significant traces of uranium and copper. Uranium occurs in Oamites tailings material as very small grains (<5 microns) in the form of uraninite (UO_2) and brannerite $(U,Ca,Ce)(Ti,Fe)_2O_6$.

A detailed investigation found that the respiratory health problems at Oamites can neither be attributed to radiation exposure nor to heavy metal contamination but to physical irritation of mucous membranes by the extensive exposure of residents to the tailings dust.



Dust from the Oamites tailings dump with the military camp buildings in the background

For mitigation, it was proposed to reprocess the tailings for uranium, followed by a safe final deposition of the remaining tailings. Laboratory tests at the GSN showed that uranium is extractable from the tailings by acid leaching. Based on these promising results, MME and MoD instructed GSN to investigate the metallurgical details and the feasibility of uranium extraction. However this was found to be uneconomic and therefore the study recommended that the tailings dumps should be properly rehabilitated using available waste rock material of the waste rock dumps at Oamites mine.

INTRODUCTION TO GEOCHEMICAL AND REACTIVE TRANSPORT MODELING

Ondra Sracek

Principal types of geochemical modeling:

1. Speciation (for exemple, for lead);

2. Inverse geochemical modeling;

3. Direct geochemical modeling;

4. Reactive transport modeling (for example, with oxidation of pyrite, organic matter decay etc.);

A standard program, which includes all types of modeling indicated above, is PHREEQC-2 (Parkhurst and Appelo, 1999; available from U.S. Geological Survey), but includes only transport in 1-D; there are programs like PHT3D and PHAST, which couple PHREEQC-2 and a program of transport in 3-D (generally MT3D);

ad (1) can be performed with only one sample of water, program divides total concentrations between free ions and complexes, for example, lead can present as:

$Pb_{total} = Pb^{2+} + PbSO_4^0 + PbHCO_3^+ + PbCO_3^0$ etc.

and calculates saturation indices SI for different minerals, for example SI_{gypsum} for mineral gypsum

$SI_{gypsum} = [Ca^{2+}]\,[SO_4^{2-}]/K_{sp}$ where K_{sp} is solubility product for specified temperature and [ ] are activities

SI = 0 equilibrium

SI < 0 undersaturation, a mineral can dissolve

SI > 0 supersaturation, a mineral can precipite

problems: kinetic factors are not considered, there can be precipitation of solid solutions instead of pure mineral phases, in most cases data for formation of organic complexes are not available;

Exemple: speciation of arsenic-input

```
DATABASE C:\PROGRAM FILES\USGS\PHREEQC INTERACTIVE 2.8\phreeqc.dat
SOLUTION 1-1
    temp      11.1
    pH        6.87
    pe        1.39
    redox     pe
    units     mg/kgw
    Alkalinity  138.1 as HCO3
    Cl        5.37
    S         169.54 as SO4
    P         0.026 as HPO4
    Na        16.3
    K         5.13
    Mg        24.44
    Ca        50.46
    Fe        9.27
    Mn        0.445
    Al        1.32
    Si        15
    As        0.091
    Zn        0.083
    N(5)      0.9 as NO3
    N(-3)     0.46  as NH4
```

Exemple: continuation

```
SOLUTION_MASTER_SPECIES
As                H3AsO4  -1.0    74.9216         74.9216
    As(+3)        H3AsO3   0.0    74.9216
    As(+5)        H3AsO4  -1.0    74.9216
SOLUTION_SPECIES 1 # Do not change this number it is used by the program!
    H3AsO4 = H3AsO4
        log_k       0
        delta_h     0           kcal
    H3AsO4 + 2e- + 2H+ = H3AsO3 + H2O
        log_k       19.444
        delta_h     -30.015     kcal
    ..
    ..
    ..
    ..
PHASES
    Scorodite
    FeAsO4:2H2O = Fe+3 + AsO4-3 + 2H2O
        log_k       -20.249
    Arsenolite
    As4O6 + 6H2O = 4H3AsO3
        log_k       -2.801
        delta_h 14.330 kcal
    ..
```

Exemple-output:

	Species	Molality	Activity	log Molality	log Activity	log Gamma
Al		4.892e-05				
	Al(OH)4-	3.688e-05	3.352e-05	-4.433	-4.475	-0.042
	Al(OH)2+	8.492e-06	7.717e-06	-5.071	-5.113	-0.042
	Al(OH)3	2.729e-06	2.734e-06	-5.564	-5.563	0.001
As(3)		8.084e-08				
	H3AsO3	8.062e-08	8.078e-08	-7.094	-7.093	0.001
	H2AsO3-	2.268e-10	2.061e-10	-9.644	-9.686	-0.042
	H4AsO3+	5.941e-15	5.399e-15	-14.226	-14.268	-0.042
	HAsO3-2	9.430e-16	6.432e-16	-15.025	-15.192	-0.166
	AsO3-3	2.638e-22	1.116e-22	-21.579	-21.953	-0.374
As(5)		1.134e-06				
	HAsO4-2	7.007e-07	4.780e-07	-6.154	-6.321	-0.166
	H2AsO4-	4.330e-07	3.935e-07	-6.363	-6.405	-0.042
	AsO4-3	1.484e-11	6.273e-12	-10.829	-11.203	-0.374

etc.

Exemple-output (continuation):

Phase	SI	log IAP	log KT	
Al(OH)3(a)	1.09	12.84	11.75	Al(OH)3
Albite	0.46	-18.47	-18.93	NaAlSi3O8
Alunite	7.63	8.03	0.40	KAl3(SO4)2(OH)6
Anhydrite	-1.77	-6.10	-4.33	CaSO4
Anorthite	0.86	-19.27	-20.13	CaAl2Si2O8
Aragonite	-1.19	-9.45	-8.26	CaCO3
Arsenolite	-25.06	-28.37	-3.31	As4O6
As2S3(am)	-108.19	-155.18	-46.99	As2S3
Calcite	-1.04	-9.45	-8.41	CaCO3

etc.

ad (2) inverse geochemical modeling is used for interpretation of processes, which have already happened, we enter chemistry of water at 2 hydraulically connected points and composition of solid phase between these points; program produces reactions, which may explain changes of water chemistry:

Water 1 + reactants = Water 2 + products

Problems: stoichiometry of minerals in solid phase is not often well known, solution may be non-unique and program produces several possible models;

Exemple: data from PRB, Milovice, Czech Republic

```
DATABASE C:\PROGRAM FILES\USGS\PHREEQC INTERACTIVE 2.8\phreeqc.dat
TITLE PRB-inverse modeling 0-21 cm
SOLUTION 1 Entry
units mg/kgw
temp  13.2
pH 7.33
pe 5.427
Alkalinity  402.6 as HCO3
Ca  169
Na  18.4
Cl 55
Fe   1.2
N(5)  12
density 1
SOLUTION 2 Outflow
units mg/kgw
temp  12.4
pH 7.56
pe -2.797
Alkalinity 317.2 as HCO3
Ca  131
Na  18.2
Cl  53
Fe   42
N(5)  0.1
density 1
```

Exemple (continuation):

```
INVERSE_MODELING
-solutions 1 2
-uncertainty 0.149
-range
-balances
  pH   0.1
  Na
  Cl
-phases
calcite precip
siderite precip
Fe dissolv
N2(g)    precip
  H2(g)    precip
Fe6(OH)12CO3  precip
PHASES
Fe
Fe + 2.0H2O = 1.0Fe++ + 2.0OH- + H2
-log_k 0
Fe6(OH)12CO3
Fe6(OH)12CO3 + 12.0H+ = 4.0Fe++ + 2.0Fe+++ + 1.0CO3-2 + 12.0H2O
log_k -376
END
```

Exemple-output (transfer coeffcients in mmol/L):

Phase	mole transfers:	Minimum	Maximum
Calcite	-1.829e-03	-2.009e-03	-1.449e-03
Fe	1.916e-03	1.640e-03	2.205e-03
N2(g)	-4.248e-04	-4.892e-04	-3.604e-04
Fe6(OH)12CO3	-2.163e-04	-2.629e-04	-1.572e-04

Redox mole transfers:

Fe(3)	-4.150e-04
H(0)	3.833e-03
N(0)	-8.496e-04

ad (3) this type of modeling is used for prediction of water chemistry, we enter initial water composition and reactive phases (minerals, gases etc.), then program calculates predicted water chemistry:

Water 1 + reactants = Predicted water 2 + products

Problems: as in case (1), kinetic data are often missing and also adsorption data are frequently limited;

this modeling can be performed in batch mode or in column mode, but modeling in column mode already belongs to group (4), e.g., to the modeling of reactive transport;

Exemple-neutralization of AMD by calcite: input

```
SOLUTION 1-1
        temp      11.1
        pH        2.4
        pe        10.2
        redox     pe
        units     mmol/kgw
        S(6)      14.95
        Na        0.2
        Mg        1.1
        Fe        6.3
        Al        1.32
EQUILIBRIUM_PHASES
Calcite  0   10
Gypsum  0   0
Fe(OH)3(a) 0   0
Siderite 0    0
END
```

Output:

Phase	SI	log	Moles in assemblage Initial	Final	Delta
Calcite	0.00		1.000e+01	9.986e+00	-1.443e-02
Fe(OH)3(a)	0.00		0.000e+00	9.554e-05	9.554e-05
Gypsum	-0.02		0.000e+00	0.000e+00	
Siderite	0.00		0.000e+00	6.139e-03	6.139e-03

pH = 6.709
pe = 2.828

Elements	Molality
Al	1.320e-03
C	8.293e-03
Ca	1.443e-02
Fe	6.517e-05
Mg	1.100e-03
Na	2.000e-04
S	1.495e-02

ad (4) in this case geochemical module is connected to transport module; so called split operator approach is used: advection-dispersion equation (ADE) is solved first and then geochemical step calculation is performed,

there are special reactive transport programs (TOUGH AMD, SULFIDOX etc.) which may include, for example, oxidation of pyrite or decay of organic matter;

A necessary condition: flow parameters (flow direction, velocity) has to be determined before reactive transport modeling!

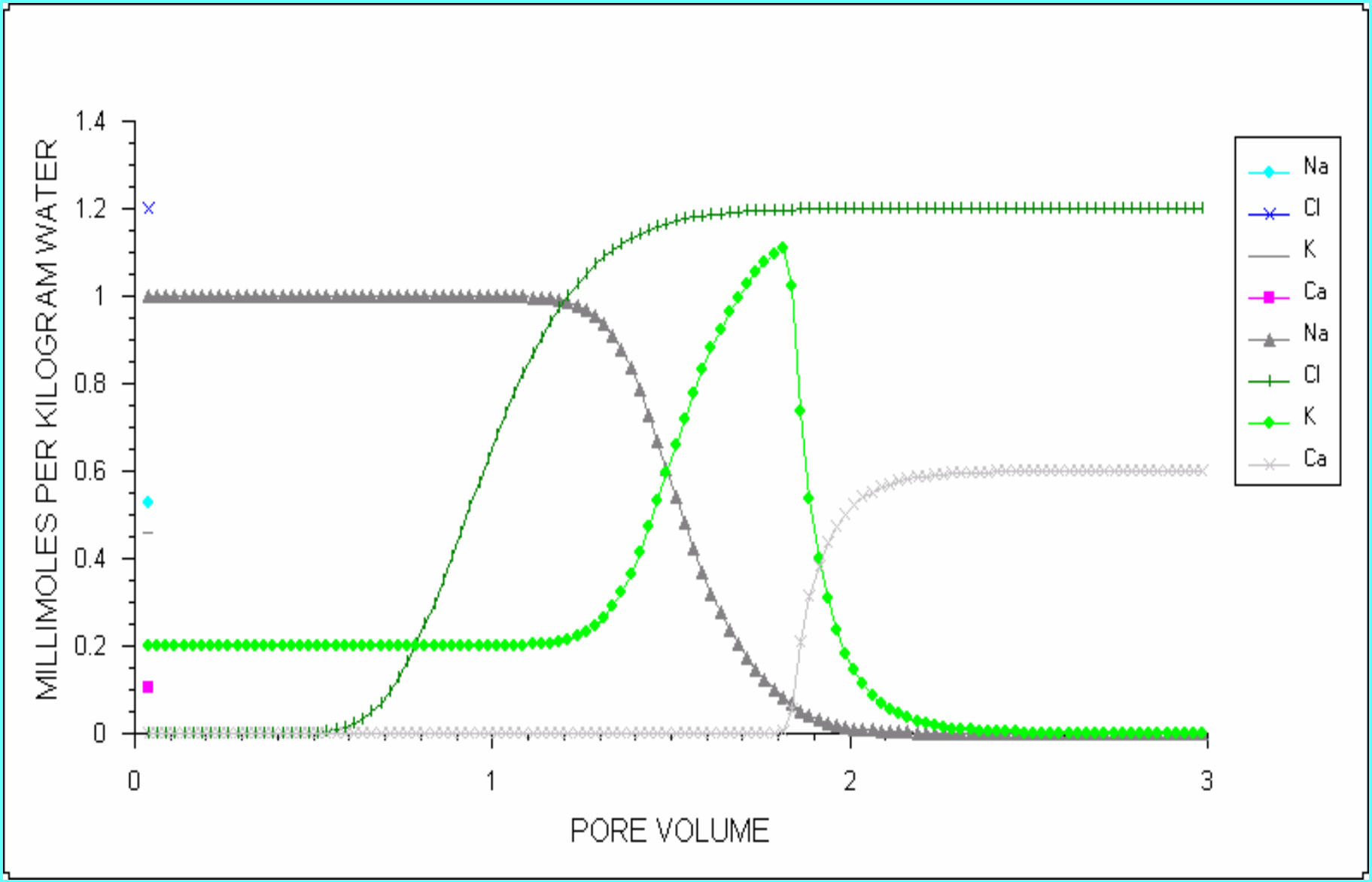
Exemple-cation exchange in a column, input:

```
TITLE Transport and ion exchange.
SOLUTION 0  CaCl2
        units           mmol/kgw
        temp            25.0
        pH              7.0     charge
        pe              12.5    O2(g)   -0.68
        Ca              0.6
        Cl              1.2
SOLUTION 1-40  Initial solution for column
        units           mmol/kgw
        temp            25.0
        pH              7.0     charge
        pe              12.5    O2(g)   -0.68
        Na              1.0
        K               0.2
        N(5)            1.2
EXCHANGE 1-40
        equilibrate 1
        X               0.0011
PRINT
        -reset          false
SELECTED_OUTPUT
        -file           ex11adv.sel
        -totals         Na Cl K Ca
```

Exemple-input (continuation):

```
TRANSPORT
        -cells          40
        -length          0.002
        -shifts         120
        -time_step       720.0
        -flow_direction  forward
        -boundary_cond   flux    flux
        -diffc          0.0e-9
        -dispersivity    0.002
        -correct_disp    true
        -punch           40
        -punch_frequency 1
        -print          40
        -print_frequency 20
END
```

Exemple-output for the end of column (1 pore volume, PV)



CONCLUSIONS

- Speciation modeling is used for calculation of free ions, complexes, and saturation indices values, it requires good thermodynamic database;

- inverse geochemical modeling is used for interpretation of water chemistry changes between hydraulically connected points, data on solid phase composition are necessary;

- direct geochemical modeling is used for prediction of water chemistry after pre-determined reactions, can be performed in batch or in column (this is already reactive transport modeling);

7. CLASSIFICATION AND PRIORITIZATION OF SD/AMS ACCORDING TO RISKS

7.1 Classification of SD/AMS

SD/AMS will be classified as **MELs** when they pose at least one significant risk to at least one receptor. A significant risk will be understood as any that occupies the 'red zone' of the Risk Matrix. Such sites are designated as **Class I**.

SD/AMS that present no significant risks will be classified as **non-MELs**. In other words, all risks associated with these sites are located in the 'green zone' of the Risk Matrix. These sites are designated as **Class II**.

7.2 Prioritization of SD/AMS

Once the risk assessment of the SD/AMS has been completed and the sites have been classified into Class I and II, a single list can be prepared for each class that ranks sites from highest to lowest level of risk.

7.2.1 Prioritization of Class I SD/AMS (MEL)

The aim of prioritizing MELs is to provide the State with adequate tools and grounds for making effective remediation decisions. Remediation may be carried out by the State itself or by the site owner, depending on the applicable legislation.

MELs (Class I) are grouped into nine groups numbered from 1 to 9, in accordance with the location of most significant risks. The highest risk group, Group 9, are MELs whose highest risks are located in cell a9. Sites from this group will be highest on the list of prioritized sites. Following this are the MELs in Group 8 (those with the highest risk in cell a8), and so on down to Group 1 (see Table 7-1).

The order of importance set out in Table 7-1 is obtained by applying the process usually followed in strictly quantitative risk assessments (where risk is the product of probability values multiplied by severity values) to this matrix.

Once the first grouping has been performed, prioritization within each group is carried out in the following way:

1. The MELs in each group are ordered from highest to lowest priority, depending on the total number of risks each one has in the cell corresponding to the group.

2. Where two or more sites have the same number of risks in the first cell, the MEL

with the highest number of risks located in the cell immediately below will occupy the first position. For example, where there are two MELs present with an equal number of risks in cell a9, the one with the greater number of risks in the cell immediately below (cell a8) will have the higher priority.

3. Where the cell immediately below also has the same number of risks, the priority will be given to the site with the greater number of risks in the next cell below, in this case a7.

Table 7-1: Cell identification codes in the Risk Matrix

	SEVERITY OF CONSEQUENCES				
PROBABILITY INDEX	Negligible (A)	Low (B)	Moderate (C)	High (D)	Catastrophic (E)
High (4)	b7	a1	a4	a7	a9
Medium (3)	b4	b8	a2	a5	a8
Low (2)	b2	b5	b9	a3	a6
Negligible (1)	b1	b3	b6	b10	b11

Once this process is complete, the result of the classification will be a list containing all MELs ordered from highest to lowest risk.

Notwithstanding the methodology offered here, it should be noted that decisions about future remediation of MEL sites may be based on other criteria such as public health risks, impact on certain economic activities and/or social impact, etc.

The figure below (Figure 7-1) offers a sample record of Hazard Scenarios found in three hypothetical mine sites (Sites 1, 2 and 3), for which the respective risks were assessed.

Applying the criteria outlined above, the prioritization process will begin by identifying the group to which each of these risks belongs. Observing the table, it can be seen that Site 1 presents risks in cell a9 and therefore belongs to Group 9, while Sites 2 and 3 both belong to Group 8, as their highest risks are found in cell a8. As a result, Site 1 has a higher priority than the other two.

Now, both Sites 2 and 3 present one risk each and therefore are ‘tied’. To apply the method described, the number of risks in the cell immediately below (a7) should be taken into account. In the example, Site 3 has two risks at this level, while Site 2 has only one risk in that position. Therefore, Site 3 would have a higher priority than Site 2. The order of priority of the three sites,

from greatest to lowest risk, would therefore be: Site 1, Site 3 and Site 2.

Figure 7-1: Example of MEL prioritization.

Risks: MEL (Significant Risks)	Number of Hazard Scenarios Evaluated											
	Safety and Public Health			Environment			Economic Activity			TOTAL Scenarios		
	Site 1	Site 2	Site 3	Site 1	Site 2	Site 3	Site 1	Site 2	Site 3	Site 1	Site 2	Site 3
a 9							1			1	0	0
a 8		1				1				0	1	1
a 7					1	1			1	0	1	2
a 6		2		3	1					3	3	0
a 5			1		1	1				0	1	2
a 4			1	2	1			1		2	2	1
a 3		2				2	1			1	2	2
a 2			1						1	0	0	2
a 1										0	0	0
TOTAL	0	5	3	5	4	5	2	1	2	7	10	10

7.2.2 Prioritization of Class II SD/AMS (non-MEL)

Prioritization of SD/AMS that are not MELs follows the same criteria that were applied in the case of MELs, but in this case taking into account that none of the risks are significant. The process is as follows:

1. Initially the non-MEL SD/AMS are divided into 11 groups according to the cells with the highest number of non-significant risks. Group 11 will include sites that contain the highest risks in cell b11; Group 10 will include sites with the highest risks in cell b10 and so on, successively, until all sites have been classified into their corresponding group.

2. Sites in Group 11 will be considered to have the highest risk, and within this group sites will be ordered from highest to lowest priority based on the number of risks each has in cell b11.

3. Where two sites have the same number of risks, the site with more risks in the cell immediately below (b10) will have the higher priority. If the two sites continue to have the same number of risks, then the site with the most risks in the following cell takes priority, and so on until the order is resolved.

4. Group 10 risks follow on the list, and will be ordered by the number of risks each one has in cell b10. Ties are resolved in the same manner described above. The process

continues until all groups have been ordered.

Once the process is complete, the classification yields a prioritized list of all non-MEL sites.

7.3 Periodic review of Class II SD/AMS Risk Assessment

Risk assessments of SD/AMS classified as Class II (non-MEL) must be reviewed regularly in order to detect changes in the Hazard Scenarios that could change the original level of risk for people, the environment and/or economic activities. The frequency of these re-assessments for sites classified as non-MEL will be determined by MME according to its own criteria.

Changes in conditions at the site could include the introduction of new receptors (e.g. from urban expansion, crop planting, new roads that allow more people to access the site, etc.) or to the increased instability of works due to major natural events (seismic events, flooding, etc.).

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Applications of geochemical modeling and reactive transport modeling in the evaluation of environmental impact of mining: PHREEQC program input files

Instructor: Ondra Sracek

Johannesburg, South Africa, July 13-15, 2013

1. Modification of data base and speciation: example of arsenic

At the beginning, SOLUTION 1 is used to enter water chemistry data:

```
SOLUTION 1-1 Well PK-7-2004
      temp  12.3
      pH    7.03
      pe    1.24
      redox pe
      units mg/kgw
      Alkalinity  179.3 as HCO3
      etc.
```

Since arsenic is not available in phreeqc.dat database, we have to enter data for arsenic.

First of all, arsenic is defined in SOLUTION_MASTER_SPECIES:

```
SOLUTION_MASTER_SPECIES
As          H3AsO4  -1.0      74.9216           74.9216
As(+3)      H3AsO3   0.0      74.9216
As(+5)      H3AsO4  -1.0      74.9216
```

Then aqueous complexes are entered using SOLUTION_SPECIES:

```
SOLUTION_SPECIES 1 # Do not change this number it is used by the program!
H3AsO4 = H3AsO4
      log_k 0
      delta_h     0     kcal
H3AsO4 + 2e- + 2H+ = H3AsO3 + H2O
      log_k 19.444
      delta_h     -30.015     kcal
H3AsO3 = H2AsO3- + H+
      log_k -9.228
```

etc.

Each species is formed from solution master species using stoichiometrically balanced equation. Then equilibrium constant k is entered. The k value is typically for 25 °C, so delta_h (enthalpy) is used to change it to the temperature of interest using van't Hoff's equation. Finally, minerals are entered using PHASES:

```
PHASES
Scorodite
        FeAsO4:2H2O = Fe+3 + AsO4-3 + 2H2O
        log_k           -20.249
Arsenolite
        As4O6 + 6H2O = 4H3AsO3
        log_k           -2.801
        delta_h 14.330 kcal
```

etc.

Name of a mineral is followed by equation written as dissolution here. Then equilibrium constant as log_k is shown, followed by enthalpy. When enthalpy is not entered (like for

scorodite here), program will run, considering k as a constant at any temperature. On the other hand program will not run without k value. Note that when equations are written as precipitation instead of dissolution, the values of log_k will have opposite signs.

The complete input file:

```
SOLUTION 1-1 Well PK-7-2004
      temp  12.3
      pH    7.03
      pe    1.24
      redox pe
      units mg/kgw
      Alkalinity  179.3 as HCO3
      Cl    76
      S     3318 as SO4
      P     1.39 as HPO4
      Na    15.3
      K     36.2
      Mg    567
      Ca    607
      Fe    54.4
        Mn  1.61
      Al    0.03
        Si      5.46
        As(5)   70
        Zn      0.03
SOLUTION_MASTER_SPECIES
As          H3AsO4  -1.0      74.9216           74.9216
As(+3)      H3AsO3   0.0      74.9216
As(+5)      H3AsO4  -1.0      74.9216
SOLUTION_SPECIES 1 # Do not change this number it is used by the program!
H3AsO4 = H3AsO4
      log_k 0
      delta_h     0     kcal
H3AsO4 + 2e- + 2H+ = H3AsO3 + H2O
      log_k 19.444
      delta_h     -30.015     kcal
H3AsO3 = H2AsO3- + H+
      log_k -9.228
      delta_h     6.56  kcal
H3AsO3 = HAsO3-2 + 2H+
      log_k -21.33
      delta_h     14.199      kcal
H3AsO3 = AsO3-3 + 3H+
      log_k -34.744
      delta_h     20.25 kcal
H3AsO3 + H+ = H4AsO3+
      log_k -0.305
      delta_h     0     kcal
H3AsO4 = H2AsO4- + H+
      log_k -2.243
      delta_h     -1.69 kcal
H3AsO4 = HAsO4-2 + 2H+
      log_k -9.001
      delta_h     -0.92 kcal
H3AsO4 = AsO4-3 + 3H+
```

```
      log_k -20.597
      delta_h     3.43  kcal
Ca+2 + H2AsO4- = CaH2AsO4+
      log_k 1.30
Ca+2 + HAsO4-2 = CaHAsO4
      log_k 2.66
Ca+2 + AsO4-3 = CaAsO4-
      log_k 4.36
Mg+2 + H2AsO4- = MgH2AsO4+
      log_k 1.52
Mg+2 + HAsO4-2 = MgHAsO4
       log_k 2.86
Mg+2 + AsO4-3 = MgAsO4-
       log_k 6.34
PHASES
Scorodite
        FeAsO4:2H2O = Fe+3 + AsO4-3 + 2H2O
        log_k           -20.249
Arsenolite
        As4O6 + 6H2O = 4H3AsO3
        log_k           -2.801
        delta_h 14.330 kcal
Claudetite
       As4O6 + 6H2O = 4H3AsO3
        log_k           -3.065
        delta_h 13.290 kcal
Orpiment
        As2S3 + 6H2O = 2H3AsO3 + 3HS- + 3H+
        log_k           -60.971
        delta_h 82.890 kcal
As2S3(am)
        As2S3 + 6H2O = 2H3AsO3 + 3HS- + 3H+
      log_k -44.9
      delta_h     244.2 kJ
Realgar
        AsS + 3H2O = H3AsO3 + HS- + 2H+ + e-
        log_k           -19.747
        delta_h 30.545 kcal
Pb3(AsO4)2
        Pb3(AsO4)2 = 3Pb+2 + 2AsO4-3
        log_k           -35.403
Ca4(OH)2(AsO4)2:4H2O
        Ca4(OH)2(AsO4)2:4H2O = 4Ca+2 + 2H3AsO4 + 6H2O - 8H+
        log_k 40.2
Ca5(AsO4)3(OH)
        Ca5(AsO4)3(OH) = 5Ca+2 + 3H3AsO4 + H2O - 10H+
        log_k 37.8
Ca3(AsO4)2:4H2O
        Ca3(AsO4)2:4H2O = 3Ca+2 + 2H3AsO4 + 4H2O - 6H+
        log_k 20.22
CaHAsO4:H2O
        CaHAsO4:H2O = Ca+2 + H3AsO4 + H2O - 2H+
        log_k 4.22
Ferrarisite
        Ca5(HAsO4)2(AsO4)2:9H2O = 5Ca+2 + 4H3AsO4 + 9H2O - 10H+
        log_k 27.75
Guerinite
```

```
Ca5(HAsO4)2(AsO4)2:9H2O = 5Ca+2 + 4H3AsO4 + 9H2O - 10H+
log_k 28.55
```

2. Inverse geochemical modeling of permeable reactive barrier (PRB) at Milovice, Czech Republic

In the example, based on paper by Jiricek et al. (2007), SOLUTION 1 represents water at the entry of permeable reactive barrier (PRB) and SOLUTION 2 represents water at the outflow of PRB. Water compositions are entered as in the case of speciation calculations. As in the case of the Guarani Aquifer modeling, principal module is called INVERSE_MODELING:

```
INVERSE_MODELING
-solutions 1 2
-uncertainty 0.149
-range
-balances
       pH   0.1
       Na
       Cl
-phases
      calcite precip
      siderite precip
      Fe dis
      N2(g)    precip
      H2(g)    precip
      Fe6(OH)12CO3  precip
```

In this module –solutions 1 2 indicate which solutions are used, -uncertainty 0.149 indicate that concentrations may vary 14.9 % around entered concentration values (e.g., this number may represent allowed analytical error), -balances indicate species, which are not included in –phases and thus must be included in mass balance. Phases are entered in –phases and they may be allowed to precipitate (here, for example, calcite) or dissolve (here Fe). If this is not specified, then both precipitation and dissolution are allowed.

Finally, mineral phases, which are not present in standard database of Phreeqc are entered under PHASES:

```
PHASES
   Fe
     Fe + 2.0H2O = 1.0Fe++ + 2.0OH- + H2
       -log_k 0
   Fe6(OH)12CO3
```

```
       Fe6(OH)12CO3 + 12.0H+ = 4.0Fe++ + 2.0Fe+++ + 1.0CO3-2 + 12.0H2O
 log_k -376
```

In inverse geochemical modeling, equations have to be stoichiometrically balanced, but log k values are meaningless because they are not used for calculations.

The complete input file:

```
TITLE PRB Milovice-inverse modeling 0-21 cm
SOLUTION 1 Entry
units mg/kgw
temp  13.2
pH 7.33
pe 5.427
Alkalinity  402.6 as HCO3
Ca  169
Na  18.4
Cl 55
Fe   1.2
N(5)  12
SOLUTION 2 Outflow
units mg/kgw
temp  12.4
pH 7.56
pe -2.797
Alkalinity 317.2 as HCO3
Ca  131
Na  18.2
Cl  53
Fe   42
N(5)  0.1
INVERSE_MODELING
-solutions 1 2
-uncertainty 0.149
-range
-balances
       pH   0.1
       Na
       Cl
-phases
      calcite precip
      siderite precip
      Fe dis
      N2(g)    precip
      H2(g)    precip
      Fe6(OH)12CO3  precip
PHASES
   Fe
     Fe + 2.0H2O = 1.0Fe++ + 2.0OH- + H2
       -log_k 0
   Fe6(OH)12CO3
       Fe6(OH)12CO3 + 12.0H+ = 4.0Fe++ + 2.0Fe+++ + 1.0CO3-2 + 12.0H2O
        log_k -376
END
```

3. Direct geochemical modeling of mine drainage mixing with river water at Smolnica site, Poland

This example is based on data from Smolnica site in Poland and is based on paper by Sracek et al. (in press). Water in the Bierawka River (SOLUTION 1) is mixing with mine drainage from coal waste pile (SOLUTION 2). Then there is a mixing of both waters in the ratio river water 9 : groundwater (mine drainage and background water) 1:

```
MIX 1
        1       0.90
        2       0.10
```

The mixing ratio was determined on the basis of hydrometric measurements of the river discharge on the profiles before and after waste pile. However, the groundwater input is a mixture of mine drainage from right, contaminated side, and left, uncontaminated side with background groundwater. The contribution from both sides of river was assumed to be 1 : 1.

After conservative mixing (i.e. without any geochemical reactions) resulting calculated river water was saved as SOLUTION 3:

```
SAVE solution 3
END
```

Then phases with which the river water resulting from mixing is equilibrated are entered in EQUILIBRIUM_PHASES module and water obtained by mixing is called in module USE:

```
EQUILIBRIUM_PHASES
        Calcite         0  0
        Dolomite        0  0
        Fe(OH)3         0  0
        Goethite        0  0
        Manganite       0  0
        Barite          0  0
        O2(g)          -0.68   10
        CO2(g)         -3.5    10
USE solution 3
END
```

In this case, first number after name of mineral is saturation index, second number is its initial amount in mol in contact with 1 liter of water. For example, for calcite it is

```
Calcite         0  0
```

This means that water after mixing will be pushed to the equilibrium with calcite and initial calcite amount is zero, i.e., calcite may only precipitate, but cannot dissolve. Situation is different for gases, where first number after name of gas is its log of partial pressure in atm and second number is again its amount. For example, for oxygen it is

```
O2(g)          -0.68   10
```

This indicates partial pressure of oxygen $10^{-0.68}$ atm (atmospheric pressure) and 10 indicates large (“infinite”) amount.

The complete input file:

```
TITLE Smolnica-mixing in Bierawka River
SOLUTION 1  River water
   pH      7.48
   temp    16.5
   pe      6.0 O2(g) -0.68
   units     mg/l
   density   1
    Alkalinity  341.6 as HCO3
    Cl        6670.8
    S(6)      608.9 as SO4
    Ba        0.109
    Ca        138.6
    Fe        0.66
    Mg        135
    Na        2656
    Mn        0.254
    Sr        3.410
    N(-3)     2.375 as NH4
    N(5)      8.543   as NO3
SOLUTION 2  Groundwater
temp      13
    pH        6.7
    pe        4.0
    redox     pe
    units     mg/l
    density   1
    Alkalinity 232.3 as HCO3
    Cl        211.3
    S(6)      1145.6 as SO4
    Ba        0.066
    Ca        185.8
    Fe        21.15
    Mg        94.6
    Mn        3.33
    Na        501.4
    Sr        0.695
    N(-3)     0.783
    N(5)      0.08
MIX 1
        1      0.90
        2      0.10
SAVE solution 3
END
```

```
EQUILIBRIUM_PHASES
        Calcite         0  0
        Dolomite        0  0
        Fe(OH)3         0  0
        Goethite        0  0
        Manganite       0  0
        Barite          0  0
        O2(g)          -0.68   10
        CO2(g)         -3.5    10
USE solution 3
END
```

4. Titration of AMD water with calcite

In this case we enter initial acid water as SOLUTION 1. Then we add 0.5 mol of calcite in 10 reaction steps:

```
REACTION 1
calcite 1.0
0.5 in 10 steps
```

i.e. we titrate water with calcite. In module EQUILIBRIUM_PHASES minerals, which are allowed to precipitate, are indicated:

```
EQUILIBRIUM_PHASES
gibbsite 0 0
Fe(OH)3(a) 0 0
gypsum 0 0
```

The complete input file:

```
TITLE Titration with calcite
SOLUTION 1
pH 2.4
pe 14.8
temp 16
redox pe
-units mg/L
Na 389
K 60
Ca 310
Mg 1000
Cl 550 charge
C(4) 5
S(6) 16500
Fe(3) 1950
Al 1020
EQUILIBRIUM_PHASES
gibbsite 0 0
```

```
Fe(OH)3(a) 0 0
gypsum 0 0
REACTION 1
calcite 1.0
0.5 in 10 steps
USER_GRAPH
-headings  Step Fe(OH)3(a) gibbsite gypsum pH
-chart_title "AMD-titration"
-axis_titles "step" "mineral [mol/l]" "pH"
-axis_scale x_axis 0 10 1
-axis_scale y_axis 0 0.1
-axis_scale sy_axis 0 10 1
-initial_solutions false
-plot_concentration_vs time
-start
10 graph_x step_no
20 graph_y  equi("Fe(OH)3(a)"), equi("gibbsite"), equi("gypsum")/10
30 graph_sy -LA("H+")
END
```

5. Direct geochemical modeling of acid mine drainage neutralization by calcite

This example shows neutralization of acid mine drainage by calcite in a batch (closed recipient, e.g., a beaker). This means that there is no flow, just adding of calcite into solution. Composition of water is entered in SOLUTION 1. Then calcite is added and equilibration with several minerals is forced in EQUILIBRIUM_PHASES module:

```
EQUILIBRIUM_PHASES
Calcite 0 0.20
Gypsum 0 0
Siderite 0 0
Al(OH)3(a) 0 0
Fe(OH)3(a) 0 0
END
```

Just like in previous example, first number after the name of mineral is saturation index, and second number is its amount in contact with water. Initially, there is only calcite in contact with acid water, i.e. only calcite can dissolve. All other minerals including gypsum, siderite etc. are not present at the beginning of the batch calculation, which means that they can only precipitate.

The complete input file:

```
TITLE AMD-neutralization_graph
PRINT
SOLUTION 0 AMD
units mmol/kgw
```

```
temp 25.0
pH 2.4
Na 2
Al 2
Fe(2) 2
Fe(3) 1
S(6)  15
EQUILIBRIUM_PHASES
Calcite 0 0.25
Gypsum 0 0
Siderite 0 0
Al(OH)3(a) 0 0
Fe(OH)3(a) 0 0
END
```

6. Modeling of acid mine drainage in a column, breakthrough curve (concentration vs. PV)

As shown in previous example, when acid mine drainage enters an aquifer with carbonates like calcite in solid phase, several neutralization reactions take place: (1) dissolution of calcite, (2) dissolution of siderite, (3) dissolution of $Al(OH)_3$, and dissolution of $Fe(OH)_3$. Each reaction buffers pH at different region. Only calcite may be initially present in aquifer and all other minerals are formed in preceding steps of neutralization (for example, when calcite dissolves, pH is buffered around 6.0 and siderite, $Al(OH)_3$, and $Fe(OH)_3$ precipitate; when siderite dissolves, $Al(OH)_3$ is stable or may still precipitate and so on). Simulation is performed in a column mode and output is plotted as a function of pore volumes (PV) in the version of Phreeqc with graphical capabilities prepared by Vincent Post.

Initial solution in column entered in SOLUTION 1-20 is pure water. SOLUTION 0 is flushing solution with low pH and high concentrations of Al, Fe, and sulfate. An essential module is the input of minerals in solid phase:

```
EQUILIBRIUM_PHASES
Calcite 0 0.25
Gypsum 0 0
Siderite 0 0
Al(OH)3(a) 0 0
Fe(OH)3(a) 0 0
```

As in previous case, first number after name of a mineral is saturation index SI. Value of 0 indicates that water will be pushed to equilibrium with that mineral. Second number indicates the amount of the mineral in moles in contact with 1 L of water prior to the injection of SOLUTION 0. When concentration of the mineral in solid phase is known in wt %, its amount in moles/L is calculated as

$$\text{Amount[mol/L]} = [(\rho_b/n).(\text{wt \%}/100)]/\text{MW}$$

where ρ_b is bulk solid phase density (g/dm^3), n is porosity and MW is molecular weight of a mineral. When the amount indicated in input is 0 (for example, for siderite), this means that the mineral is not initially present in the column at the beginning of simulation and may only precipitate later. Thus, in the example above only calcite is present initially.
Transport parameters are defined in the module TRANSPORT:

```
TRANSPORT
-cells 20
-lengths 0.01
-shifts 100
-time_step 180
-flow_direction forward
-boundary_conditions flux  flux
-diffusion_coefficient 1.0e-9
-dispersivities 0.12
-correct_disp true
-punch_cells 20
```

Identifier –cells indicate 20 cells in column, -lengths indicate that each cell is 0.01 m long, e.g., total column length is 20 cm. Identifier -time step [s] indicates residence time in a cell, which is linked to advective velocity v as

$$v[\text{m/s}] = \text{lengths [m]}/\text{time step [s]}$$

Identifier –boundary_conditions indicates flux boundary conditions at both inlet and outlet ends of the column (3rd type). Identifier –punch cells indicates that results will be written only for cell 20, e.g., for the cell at the end of the column.
Module USER_GRAPH is used for plotting of results:

```
USER_GRAPH
-headings PV Al Fe pH
```

```
-chart_title "AMD-buffering"
-axis_titles "PORE VOLUME" "Concentration" "pH"
-axis_scale x_axis 0 6 1 0.1
-axis_scale y_axis 0 6 1 0.1
-axis_scale sy_axis 0 10 1
-initial_solutions false
-plot_concentration_vs time
-start
10 graph_x (step_no + 0.5)/20
20 graph_y tot("Al")*1000, tot("Fe")*1000
30 graph_sy -LA("H+")
-end
END
```

In identifier –axis scale first number and second number indicate minimum and maximum values on the axis of a graph, respectively, other numbers are auxiliary markers on axis. Line 10 graph_x (step_no + 0.5)/20 indicates that points on x-axis will be related to pore volumes, for example, for step number 10 the point on x-axis will indicate mid-point of the column, for step number 20 this is one pore volume (PV) etc. The 0.5 is added because concentrations are calculated for the middle point of a cell. Line 30 defines secondary y axis where $-\log[H^+]$, e.g., pH scale will be plotted.

The complete input file:

```
TITLE AMD-neutralization_graph
SOLUTION 0 AMD
units mmol/kgw
temp 25.0
pH 2.4
Na 2
Al 2
Fe(2) 2
Fe(3) 1
S(6)  15
END
SOLUTION 1-20 Initial water
units mmol/kgw
temp 25.0
pH 7.0 charge
EQUILIBRIUM_PHASES
Calcite 0 0.25
Gypsum 0 0
Siderite 0 0
Al(OH)3(a) 0 0
Fe(OH)3(a) 0 0
END
PRINT -reset false
TRANSPORT
-cells 20
-lengths 0.01
-shifts 100
-time_step 180
```

```
-flow_direction forward
-boundary_conditions flux  flux
-diffusion_coefficient 1.0e-9
-dispersivities 0.12
-correct_disp true
-punch_cells 20
USER_GRAPH
-headings PV Al Fe(2) Fe(3) pH
-chart_title "AMD-buffering"
-axis_titles "PORE VOLUME" "Al"
-axis_scale x_axis 0 6 1 0.1
-axis_scale y_axis 0 6 1 0.1
-axis_scale sy_axis 0 10 1
-initial_solutions false
-plot_concentration_vs time
-start
10 graph_x (step_no + 0.5)/20
20 graph_y tot ("Al")*1000, tot("Fe(2)")*1000, tot("Fe(3)")*1000
30 graph_sy -LA("H+")
END
```

7. Adsorption of zinc in a batch

This example shows modeling of zinc adsorption using surface complexation method (SCM). Initial solution is entered under SOLUTION 1. Note that the solution is balanced using Ca charge, which means that it becomes electrically neutral adjusting input Ca concentration to charge balance. Then SURFACE 1 is entered, which comprises two types of adsorption sites on the surface of hydrous ferric oxide (HFO) with molecular weight of 89 g: weak sites labeled as Hfo_wH with concentration of 0.2 mol sites/mol HFO and strong sites labeled as Hfo_sH with concentration of 0.005 mol sites/mol HFO :

```
SURFACE 1
Hfo_wH  0.2  600.0  190.0
Hfo_sH  0.005  600.0  190.0
END
```

In this module, first number after name of sites is amount of adsorption sites in mol per 1 liter of water, second number is specific surface of adsorbent in m^2/g, and third number is the amount of adsorbent in g/l. The second number is from literature (but note that with aging of a mineral the degree of crystallinity generally increases and the value of specific surface decreases, for example, 600 m^2/g applies for freshly precipitated $Fe(OH)_3(a)$, but value of about 100 m^2/g applies for goethite). Values of 0.005 and 0.2 at first place are

moles of strong and weak sites, respectively, per mole of HFO based on Dzombak and Morel's data. Adsorbent is hydrous ferric oxide (HFO) with composition of goethite (FeOOH) and molecular weight of 89.

The complete input file:

```
TITLE Zn adsorption-batch
SOLUTION 1
units mmol/kgw
temp 25.0
pH 6.3
Ca 1.2 charge
Alkalinity 133 as HCO3
Zn 0.001
SURFACE 1
Hfo_wH  0.2  600.0  190.0
Hfo_sH  0.005  600.0  190.0
END
```

8. Transport of cadmium in column with adsorption, breakthrough curve (concentration vs. PV)

In that case, meaning of most parameters is the same as in previous examples. In the additional module SURFACE initial water is equilibrated with adsorption sites,

```
SURFACE 1-20
-equilibrate surface with solution 1-20
Hfo_wH  0.2  600.0  115.0
Hfo_sH  0.005  600.0  115.0
```

Again, Hfo_sH indicate strong adsorption sites and Hfo_wH indicate weak adsorption sites on the surface of hydrous ferric oxide (HFO) adsorbent. As in the case of batch adsorption modeling, first number after names of sites is number of sites in moles of sites/L of water, second number is specific surface of HFO adsorbent in m^2/g, and third number is the amount of HFO in contact with 1L of water. The output is in the form of concentration vs. pore volumes (e.g., breakthrough curve).

The complete input file:

```
TITLE Cd-PV_graph
PRINT
SOLUTION 0 CdCl2
units mmol/kgw
temp 25.0
```

```
pH 6.3
Cd 0.45
Cl 1.3
Pb 0.2
END
SOLUTION 1-10 Pure water
units mmol/kgw
temp 25.0
pH 7.0
SURFACE 1-10
-equilibrate surface with solution 1-10
Hfo_wH  0.2  600.0  115.0
Hfo_sH  0.005  600.0  115.0
END
PRINT -reset false
TRANSPORT
-cells 10
-lengths 0.01
-shifts 280
-time_step 180
-flow_direction forward
-boundary_conditions flux  flux
-diffusion_coefficient 1.0e-9
-dispersivities 0.12
-correct_disp true
-punch_cells 10
SELECTED_OUTPUT
-file  Cd-PV_graph
-reset false
-step  true
-pH  true
-totals Cd Cl
USER_GRAPH
-headings PV Cd Cl
-chart_title "Cd-transport"
-axis_titles "PORE VOLUME" "Concentration"
-axis_scale x_axis 0 28 1 0.1
-axis_scale y_axis 0 2 0.1
-initial_solutions false
-plot_concentration_vs time
-start
10 graph_x (step_no + 0.5)/10
20 graph_y tot("Cd")*1000, tot("Cl")*1000
END
```

9. Transport of cadmium in column with adsorption, concentration vs. distance curve

This differs from the previous case because fixed time is used to plot the graph of concentration vs. distance instead of breakthrough curve for fixed distance (end of column). First of all, adjustments in TRANSPORT module are made:

```
TRANSPORT
-cells 30
```

```
-lengths 30*0.01
-shifts 10
-time_step 2160
-flow_direction forward
-boundary_conditions constant  flux
-diffusion_coefficient 1.0e-9
-dispersivities 0.1
-correct_disp true
-punch_cells 1-30
-punch_frequency 10
-print_cells 1-30
-print_frequency 10
SELECTED_OUTPUT
-file  Cd-distance_graph
-reset false
-step  true
-pH  true
-totals Cd Cl
-distance true
```

In that case identifiers –punch cells and –print cells include all cells, e.g., cells 1-30. Identifiers –punch frequency and –print frequency are numbers, which are equal to the number of –shifts (here 10). This means that only concentrations after last shift (e.g., after complete simulation run) will be plotted. Then in SELECTED_OUTPUT –distance is set true:

```
SELECTED_OUTPUT
-file  Cd-distance_graph
-reset false
-step  true
-pH  true
-totals Cd Cl
-distance true
```

In USER_GRAPH headings and axis titles are changed accordingly and information about axis are included in Visual Basic commands on lines libeled 10 and 20:

```
USER_GRAPH
-headings distance(m) Cd(mmol/kgw) Cl(mmol/kgw)
-chart_title "Cd-transport"
-axis_titles "distance(m)" "mmol/kgw"
-axis_scale x_axis 0 0.3 0.02
-axis_scale y_axis 0 1 0.1
-initial_solutions false
-plot_concentration_vs x
-start
10 graph_x dist
20 graph_y tot("Cd")*1000, tot("Cl")*1000
END
```

The complete input file:

```
TITLE Cd-distance_graph
SOLUTION 0 CdCl2
units mmol/kgw
temp 25.0
pH 6.3
Cd 0.45
Cl 0.9
END
SOLUTION 1-30 Pure water
units mmol/kgw
temp 25.0
pH 7.0
SURFACE 1-30
-equilibrate surface with solution 1-30
Hfo_wH  0.2  600.0  115.0
Hfo_sH  0.005  600.0  115.0
END
PRINT -reset false
TRANSPORT
-cells 30
-lengths 30*0.01
-shifts 10
-time_step 2160
-flow_direction forward
-boundary_conditions constant  flux
-diffusion_coefficient 1.0e-9
-dispersivities 0.1
-correct_disp true
-punch_cells 1-30
-punch_frequency 10
-print_cells 1-30
-print_frequency 10
SELECTED_OUTPUT
-file  Cd-distance_graph
-reset false
-step  true
-pH  true
-totals Cd Cl
-distance true
USER_GRAPH
-headings distance(m) Cd(mmol/kgw) Cl(mmol/kgw)
-chart_title "Cd-transport"
-axis_titles "distance(m)" "mmol/kgw"
-axis_scale x_axis 0 0.3 0.02
-axis_scale y_axis 0 1 0.1
-initial_solutions false
-plot_concentration_vs x
-start
10 graph_x dist
20 graph_y tot("Cd")*1000, tot("Cl")*1000
END
```

10. Kinetic dissolution of quartz

This is an example of heterogeneous kinetic reaction, i.e. reaction between water and solid phase. This is different from homogeneous kinetic reactions taking place only in water like, for example, sulfate reduction. In the case of heterogeneous reactions there typically is an assumption about geometry of minerals (cube etc.) and about their specific surface and volume.

First of all, input solution is defined in SOLUTION 1. In this case it is pure water. Then rate of reaction is defined in the module RATES:

```
RATES
Quartz
-start
10 moles = parm(1)/parm(2) * (m/m0)^0.67 * 10^-13.7 * (1 - SR("Quartz"))
20 save moles * time
-end
```

At the beginning, name of mineral is indicated. This mineral has to be in database or has to be defined in PHASES. Then –start and –end indicate the beginning and end of the calculation. In line 10 there is a formula for the calculation of concentration change during reaction progress:

$dQuartz/dt = -k * (1 - \Omega_{Quartz})$ where Ω_{Quartz} is saturation ratio IAP/K_{sp} and k in this example is $k = 10^{-13.7}$ mol dm^{-3} s^{-1} at 25 °C. It is multiplied by ratio of parm(1)/parm(2) where parm(1) is surface area of mineral and parm(2) is water filled porosity in dm^3/kg of solid phase (see below). In ratio m/m_0 the m is the amount of remaining quartz from previous step of dissolution and m_0 is its initial amount.

In line 20, there is integration of gradual increase of concentration in solution. Values are positive when added to solution.

Then in the module KINETICS input parameters are entered:

```
KINETICS
Quartz
-formula SiO2
-m0 102.7
-parms 22.7 0.162
-step 1.58e8 in 10 steps
-tol 1e-8
```

There -m0 indicates initial mol of quartz, -parms are 22.7 (surface is in m^2/kg of solid phase) and 0.162 (water filled porosity dm^3/kg calculated from bulk density 2.65 kg/dm^3 and porosity 0.3). In –step simulation time is entered, here it is $1.58x10^8$ seconds or 5 years and in –tol integration tolerance 10^{-8} (default value) is entered.

`INCREMENTAL_REACTIONS true` indicates that cumulative amounts of dissolved quartz are added during integration. Graph is defined as in previous cases, but note total time divided by 3.1536 x 10^7 (seconds in year) to obtain years at x axis.

The complete input file

```
TITLE Quartz dissolution
SOLUTION 1
RATES
Quartz
-start
10 moles = parm(1)/parm(2) * (m/m0)^0.67 * 10^-13.7 * (1 - SR("Quartz"))
20 save moles * time
-end
KINETICS
Quartz
-formula SiO2
-m0 102.7
-parms 22.7 0.162
-step 1.58e8 in 10 steps
-tol 1e-8
INCREMENTAL_REACTIONS true
USER_GRAPH
-chart_title "Quartz disolution"
-headings time Si
-axis_titles years mmol/L
-axis_scale y_axis 0 0.12 0.02
-axis_scale x_axis 0 5
-start
10 graph_x total_time/3.1536e7
20 graph_y tot("Si")*1e3
-end
END
```

11. Acid injection into carbonate reservoir: equilibrium dissolution of calcite, kinetic dissolution of quartz

In this case, a column is divided into 20 cells, each is 1 m long. In the command –punch_cells all 20 cells are included. Then in –punch_frequency the number 14 indicates that results are calculated and plotted for 14 shifts as indicated by -shifts 14.

```
TRANSPORT
-cells 20
-lengths 1
-shifts 14
-time_step 500
-flow_direction forward
-boundary_conditions flux  flux
-diffusion_coefficient 1.0e-9
-dispersivities 0.12
-correct_disp true
-punch_cells 1-20
-punch_frequency 14
```

Dissolution of calcite is modeled as equilibrium process, which is a reasonable assumption. On the other hand, dissolution of quartz, being relatively slow is modeled as a kinetic process. Just like in the example of quartz dissolution in batch, there are modules RATES and KINETICS, but they are applied to all 20 cells, i.e. cells 1-20. The difference here is in initial amount of quartz in contact with 1L of water, -m0 15.

In USER_GRAPH concentrations of Ca and Si are multiplied by 100 and 10000 to plot these species together with Cl:

```
20 graph_y tot("Cl"), tot("Ca")*100, tot("Si")*10000
```

The complete input file:

```
TITLE Injection-acid plus quartz kinetic
SOLUTION 0 Acid
pH 2
pe 15
temp 16
Cl   0.01 charge
END
SOLUTION 1-20 Initial sea water
pH 8.22
pe 8.451
temp 16
redox pe
-units mg/L
Na 10768
K 399.1
Ca 412.3
Mg 1291.8
Cl 19353
Alkalinity 141.682 as HCO3
S(6) 2712 as SO4
Fe 0.002
Mn 0.0002
Si 1.301
EQUILIBRIUM_PHASES 1-20
Calcite 0 10
#Quartz 0 10
RATES 1-20
```

```
 Quartz
 -start
  1 A0 = parm(1)
  2 V = parm(2)
  10 rate = (A0 / V) * (m/m0)^0.67 * 10^-13.7 * (1 -  SR("Quartz"))
  20 save rate * time
 -end
KINETICS 1-20
Quartz
 -m0  15                       # moles of quartz
 -parms 23.13  0.16
INCREMENTAL_REACTIONS true
END
PRINT -reset false
TRANSPORT
-cells 20
-lengths 1
-shifts 14
-time_step 500
-flow_direction forward
-boundary_conditions flux  flux
-diffusion_coefficient 1.0e-9
-dispersivities 0.12
-correct_disp true
-punch_cells 1-20
-punch_frequency 14
USER_GRAPH
-headings    distance(m) Cl Ca Si pH
-chart_title "Acid-injection"
-axis_titles "x (m)" "Concentration (mol/l)" "pH"
-axis_scale x_axis 0 20 1
-axis_scale y_axis 0 5 1 0.1
-axis_scale sy_axis 0 10 1
-initial_solutions false
-plot_concentration_vs x
-start
10 graph_x dist
20 graph_y tot("Cl"), tot("Ca")*100, tot("Si")*10000
30 graph_sy -LA("H+")
END
```

12. Modeling of diffusion in a column

For modeling of diffusion both initial water, here SOLUTION 1-20, and water with diffusing species (water itself is immobile), SOLUTION 0, are entered just like in the case of advective transport modeling. Principal differences compared to advective transport are in TRANSPORT module:

```
TRANSPORT
        -cells  20
        -shifts 20
        -time_step 5e5   # in seconds, this is total time of diffusion
                         # not residence time in a cell!
        -flow_direction diffusion_only
        -boundary_conditions constant
        -lengths 0.05
        -diffusion_coefficient 2.59e-9    # in m2/s
        -punch_cells 1-20
        -punch_frequency 20
        -print_cells 1-20
        -print_frequency 20
```

In this case, the identifier –time_step indicates total time of diffusion simulation and not residence time in a cell like in the case of advective transport modeling. Diffusion coefficient in m^2/s is entered under command –diffusion coefficient. When diffusing species is adsorbed, diffusion coefficient is divided by retardation coefficient R. As in previous cases, -punch_frequency and –print frequency are equal to the number of –shifts to obtain final concentration vs. distance profile.

The complete input file:

```
TITLE Diffusion-conservative case
SOLUTION 0  NaCl
        units   mmol/kgw
        pH      7.0     charge
        temp    25.0
        Na      1.0
        Cl      1.0
SOLUTION 1-20  Initial solution for column
        units   mmol/kgw
        pH      7.0     charge
        temp    25.0
TRANSPORT
        -cells  20
        -shifts 20
        -time_step 5e5   # in seconds, this is total time of diffusion
                          # not residence time in a cell!
        -flow_direction diffusion_only
        -boundary_conditions constant
```

```
        -lengths 0.05
        -diffusion_coefficient 2.59e-9    # in m2/s
        -punch_cells 1-20
        -punch_frequency 20
        -print_cells 1-20
        -print_frequency 20
PRINT
        -reset  false
SELECTED_OUTPUT
        -file Dif-conserv
        -totals Na Cl
USER_GRAPH
-headings distance(m) Na Cl
-chart_title "Diffusion"
-axis_titles "distance(m)" "mmol/kgw"
-axis_scale x_axis 0 1
-axis_scale y_axis 0 1
-initial_solutions false
-plot_concentration_vs x
-start
10 graph_x dist
20 graph_y tot("Na")*1000, tot("Cl")*1000
END
```

ANNEX A1

GUIDES FOR ESTIMATING EACH HAZARD SCENARIO SAFETY PROBABILITY INDEX

ANNEX A1: Guide for Estimating each Hazard Scenario Safety Index

Component	Installations Deposits Works	Code	Safety Hazard Scenarios	Cause	PI Estimation Guide
MINE	Underground workings	SHS 1	Development of major cracks, dolines or sink holes that could affect people, the environment or economic activities.	Seismic movements, underground mine structural instability, or water entry.	GUIDE 1
		SHS 3	Asphyxiation of people entering the mine due to the presence of toxic gases.	Open access to abandoned mine.	GUIDE 7
		SHS 4	Drowning in underground pools.	Open access to abandoned mine.	GUIDE 7
		SHS 12	Falling into underground workings (people, stock, game animals).	Open access to abandoned mine.	GUIDE 7
		SHS 13	Rocks, unsafe remnant structures or elements falling on people.	Open access to abandoned mine.	GUIDE 7
	Open pits, trenches and other surface workings	SHS 2	Collapse of the pit or surface works that could affect people, the environment and/or economic activities.	Seismic movements, water erosion, or surface faults.	GUIDE 2
		SHS 4	Drowning in pool at bottom of pit.	Open access to abandoned mine.	GUIDE 7
		SHS 12	Falling into open pit or trench (people, stock, game animals).	Open access to abandoned mine.	GUIDE 7
PLANTS	Processing Plants	SHS 4	Drowning in tanks and ponds.	Open access to abandoned plant site.	GUIDE 7
		SHS 12	Risk of falling from elevated unsafe structures.	Open access to abandoned plant buildings.	GUIDE 7
		SHS 13	Rocks, unsafe remnant structures or other elements falling on people.	Open access to abandoned plant buildings.	GUIDE 7

Component	Installations Deposits Works	Code	Safety Hazard Scenarios	Cause	PI Estimation Guide
LARGE SCALE MINING WASTE	Tailings Dams	SHS 5	Dam failure that could cause a sudden release of tailings slurry that could affect people, the environment and/or economic activities.	Poor construction, seismic movements, rise in water table, overflow of dam, erosion of side walls.	GUIDE 3
		SHS 12	Risk of falling into tailings pond or from dam walls.	Open access to abandoned tailings dam.	GUIDE 7
		SHS 4	Drowning in tailings pond.	Open access to abandoned tailings dam.	GUIDE 7
	Tailings deposits dry-stacked or in other form	SHS 7	Failure of slopes of dry stacked or other tailings deposit that could affect people, the environment and/or economic activities.	Seismic movements, water erosion, poor construction, undermining of toe	GUIDE 5
		SHS 12	Risk of falling down steep slopes.	Open access to tailings impoundment.	GUIDE 7
	Heap leach waste dump	SHS 8	Failure of heap leach waste dumps that could affect people, the environment and/or economic activities.	Seismic movements, water erosion, poor construction.	GUIDE 5
		SHS 12	Risk of falling down steep slopes.	Open access to abandoned heap leach facility.	GUIDE 7
	Dumps for waste rock, low grade ore	SHS 9	Failure of slopes of dumps containing waste rock or low grade ore that could impact people, the environment or economic activities.	Seismic movements, water erosion, undermining of toe	GUIDE 6

Component	Installations Deposits Works	Code	Safety Hazard Scenarios	Cause	PI Estimation Guide
LARGE SCALE MINING WASTE	Dumps for waste rock, low grade ore	SHS 12	Risk of falling down steep slopes.	Open access to abandoned mine site.	GUIDE 7
	Slag heap	SHS 12	Risk of falling down steep slopes.	Open access to abandoned mine site.	GUIDE 7
SMALL SCALE INDUSTRIAL WASTE	Industrial waste deposits	SHS 14	Physical contact with unsafe remnant structures or other elements that may cause injury or damage.	Open access to abandoned mine site.	GUIDE 7
ASSOCIATED INFRASTRUCTURE	Explosives magazine	SHS 10	Incorrect and/or unprotected storage of explosives which could result in an explosion causing injury.	Open access to explosives magazine.	GUIDE 7
	Offices, camps, workshops and storage areas	SHS 12	Risk of falling in unsafe areas.	Open access to abandoned mine site.	GUIDE 7
		SHS 13	Falling of unsafe remnant structures or other elements onto people.	Open access to abandoned mine site.	GUIDE 7
		SHS 14	Physical contact with unsafe remnant structures or other elements that may cause injury or damage.	Open access to abandoned mine site.	GUIDE 7
	Water systems and tanks	SHS 4	Drowning in tanks.	Open access to abandoned mine site.	GUIDE 7

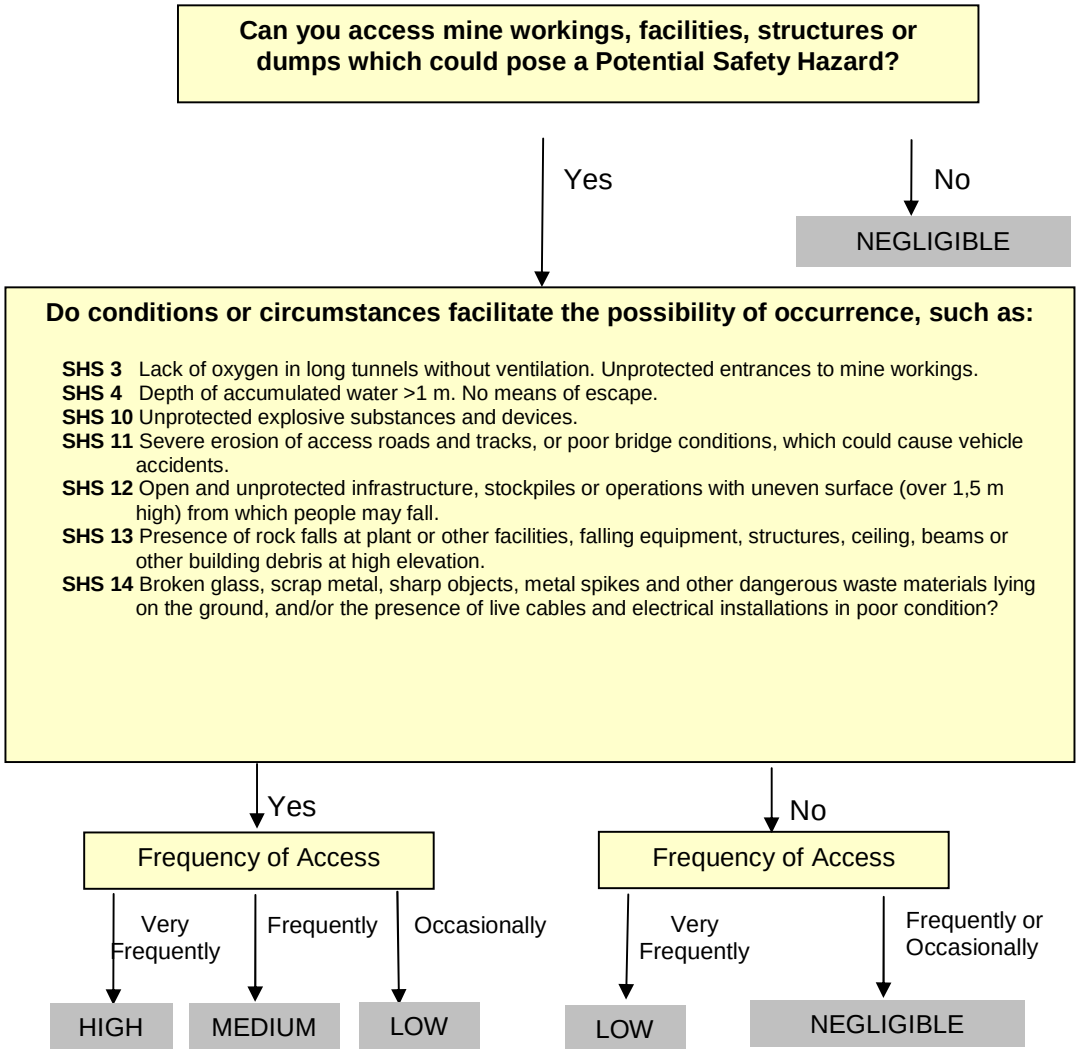
Component	Installations Deposits Works	Code	Safety Hazard Scenarios	Cause	PI Estimation Guide
ASSOCIATED INFRASTRUCTURE	Water systems and tanks	SHS 12	Risk of falling from elevated unsafe structures.	Open access to abandoned mine site.	GUIDE 7
		SHS 13	Falling of unsafe remnant structures and other elements onto people.	Open access to abandoned mine site.	GUIDE 7
	Power lines and substations	SHS 12	Risk of falling from elevated, unsafe structures.	Open access to abandoned mine site.	GUIDE 7
		SHS 14	Physical contact with high voltage cables and other electrical installations that may cause injury or electrocution.	Open access to abandoned mine site.	GUIDE 7
	Roads and bridges	SHS 11	Vehicle accidents due to roads and/or infrastructure (e.g. bridges) in poor condition.	Open access to abandoned mine site.	GUIDE 7
		SHS 12	Risk of falling from elevated unsafe structures.	Open access to abandoned mine site.	GUIDE 7

Note: there is no Guide 4 in the Namibian version of the Manual as this addresses Safety Hazard Scenario 6, which does not exist in the Namibia situation.

Guide to estimate Hazard Scenario Probability Index	General site safety	**GUIDE 7**

POTENTIAL SAFETY HAZARD :

SHS 3. Presence of toxic gases in the mine which could cause asphyxiation.
SHS 4. Drowning in ponds, dams, tanks, pools.
SHS 10. Unprotected explosive devices.
SHS 11. Vehicle accidents on old roads and tracks.
SHS 12. Risk of falling into underground workings or surface workings, down steep slopes, from unsafe elevated structures and due to uneven/unsafe surfaces.
SHS 13. Risk of falling rocks or parts of remnant structures onto people.
SHS 14. Physical contact with unsafe remnant structures and waste materials.



Notes:
Very Frequently: Site is visited on a daily basis (or at least 5 days every week)
Frequently: Site is visited on a few days per month (e.g. on weekends)
Occasionally: Site is visited once or twice a year.

Comments
Add comments on assumptions, data and criteria used to apply the guide.

Guide to estimate Hazard Scenario Probability Index	General site safety	**GUIDE 7**

Guide to estimate Safety Probability Index	Subsidence due to underground Mine	Guide 1

SAFETY HAZARD SCENARIO 1 (SHS1)

Development of major cracks, dolines or sink holes that could affect people, the environment or economic activities.

1. Surface strain

	Observation	*Partial Score*	*Choose Partial Score*
1.1 Evidence of ground caving	evidence	3	
	None	0	
1.2 Tension cracks	evidence	3	
	None	0	
1.3 Are buildings, facilities or structures neighbouring the mine area showing cracks and collapse associated with ground caving?	Yes	3	
	No	0	

2. Water balance

2.1 Weather

i) Annual Average Rainfall (mm/year)	> 500 mm/year	1	
	301 - 500 mm/year	0,75	
Value:	101 - 300 mm/year	0,5	
Source:	< 100 mm/year	0	

2.2 Surrounding drainage towards the underground workings (or subsidence potential)

i) Site geomorphology and drainage	Leads water towards potential subsidence area	1	
	Leads water away from the subsidence area	0	

3. Mining Method

Mining method	By caving	4	
	operations and/or stope < 50 m deep	3	
	operations and/or stopes> 50 m deep	1,5	

Guide to estimate Safety Probability Index	Subsidence due to underground Mine	Guide 1

SAFETY HAZARD SCENARIO 1 (SHS1)

Development of major cracks, dolines or sink holes that could affect people, the environment or economic activities.

Hazard scenario score (add from partial scores)	

Score Range	Hazard Scenario Probability Index
> 11.5	High
7.1 - 11.5	Medium
2 - 7	Low
< 2	Negligible

Choose the correct Score Range and enter the SAFETY HAZARD SCENARIO probability index

Comments Add comments on assumptions, data and criteria used in applying the Guide.

Guide to estimate Safety Probability Index	Open Pit	Guide 2

SAFETY HAZARD SCENARIO 2 (SHS2)

Collapse of the pit or surface works that could affect people, the environment and/or economic activities.

		Observation	*Partial Score*	*Choose Partial Score*
1. Earthquake				
1.1 Seismic Zone		Zone 3	3	
		Zone 2	1,5	
		Zone 1	0	
1.2 Overall (global) slope		>52°	2	
		<52°	0	
Measurement: Estimate:				
1.3 Slope height (or pit depth)		>50 m	1	
		< 50 m	0	
Measurement: Estimate:				
1.4 Evidence of partial sloughing/failures/rock fall		with evidence	1	
		None	0	
1.5 Tensile cracks in and around the pit		with evidence	3	
		None	0	
1.6 Cracks on the pit slope (failure)		Deep	3	
		Some evidence	1,5	
		None	0	
1.7 Underground water table		On the pit's slope wall	1,5	
		At the pit's footwall	0,75	
		None	0	
1.8 Erosion Gullies		Deep	0,5	
		some evidence	0,25	
		None	0	
Hazard scenario score (add from partial scores)				

Score Range	Hazard Scenario Probability Index
> 11.5	High
7.1 - 11.5	Medium
2 - 7	Low
< 2	Negligible

Choose the correct Score Range and enter the SAFETY HAZARD SCENARIO probability index

Guide to estimate Safety Probability Index	Open Pit	Guide 2

SAFETY HAZARD SCENARIO 2 (SHS2)

Collapse of the pit or surface works that could affect people, the environment and/or economic activities.

Comments

Add comments on assumptions, data and criteria used in applying the Guide.

Guide to estimate Safety Probability Index	Tailings Dams	Guide 3

SAFETY HAZARD SCENARIO 5 (SHS5)

Dam failure that could cause a sudden release of tailings slurry that could affect people, the environment and/or economic activities

1. Tailings dam (free standing)

	Observation	*Partial Score*	*Choose partial Score*
Construction method			
1.1 Dam construction method (Refer Annex A-2)	Upstream method	1,2	
	Central line	0,6	
	Downstream	0	
1.2 Coarse-Fines separation	None	1	
	Natural separation	0,5	
	Cyclone	0	
1.3 Toe drainage systems	None	0,7	
	Toe drainage	0	
1.4 Starter wall	None	0,8	
	Has fine material	0,4	
	Available	0	
Structural Behaviour			
1.5 Period where no relevant failure has taken place	Less than 10 years	0,6	
	Between 10 and 50 years	0,2	
	Over 50 years	0	
Data: Estimate:			
Source:			
1.6 Wall cracks	Over 2 longitudinal cracks various meters long and deep	0,3	
	1 to 2 longitudinal cracks various meters long	0,15	
	None	0	
1.7 Buttress cracks	Buttress cracks various meters long and deep	0,3	
	Some evidence	0,15	
	None	0	
1.8 Erosion gullies	Erosion gullies that weaken the wall	0,2	
	Some evidence	0,1	
	None	0	

Guide to estimate Safety Probability Index	Tailings Dams	Guide 3

SAFETY HAZARD SCENARIO 5 (SHS5)

Dam failure that could cause a sudden release of tailings slurry that could affect people, the environment and/or economic activities

Moisture content	***Observation***	***Partial Score***	***Choose partial Score***
1.9 Vegetation on tailings, or other means of stabilisation e.g. Rock cladding	Dense vegetation coverage or complete rock cover	1	
	Partial vegetation coverage or rock windrows and crest protection	0,5	
	None	0	
1.10 Phreatic surface within tailings related to slope height (1)	Water within the deposit with a phreatic level elevation over half the slope's height	1	
	Water within the deposit with phreatic level elevation less than half the slope's height	0,5	
	None	0	

Slope geometry

1.11 Slope design	Convex or various forms	0,4	
	Straight between berms or lifts	0,2	
	Concave between berms or lifts	0	
1.12 Overall (global) slope	>15°	2	
	5° - 15°	1	
	< 5°	0	
Measurement: Estimate:			
1.13 Slope angle downstream	> 18°	1	
	18° - 14°	0,5	
	< 14°	0	
Measurement: Estimate:			
1.14 Slope height	> 50 m	2	
	25m - 50m	1	
	< 25m	0	
Measurement: Estimate:			

1	**Seismic scenario score (add Partial Score 1.1 to 1.14)**	

Guide to estimate Safety Probability Index	Tailings Dams	Guide 3

SAFETY HAZARD SCENARIO 5 (SHS5)

Dam failure that could cause a sudden release of tailings slurry that could affect people, the environment and/or economic activities

2. Tailings Dam (valley contained)	*Observation*	*Partial Score*	*Choose partial Score*
Spillway			
2.1 Operational Spillways	None	4.5	
	Over the wall or penstock-related	3	
	Available and excavated in the ground	1.5	
	Available and excavated from the rock	0	
Surrounding Drainage towards the dam			
2.2 Perimeter rainwater collection systems	None	1.5	
	Present but poorly maintained/eroded	0.5	
(contour channel)	Adequate and in good standing	0	
2.3 Average annual rainfall (mm/year)	> 500 mm/year	1.2	
	301 - 500 mm/year	0.8	
	101 - 300 mm/year	0.4	
Data:	< 100 mm/year	0	
Source:			
2.4 Percentage of the total surface area of the tailings dam covered by a pond	> 60%	1.5	
	41% - 60%	1	
	21% - 40%	0.5	
	< 20%	0	
Measurement: Estimate:			
2.5 Maximum rainfall in 24 hour period (mm/24 hours) (return period 10 years)	> 80 mm	1.8	
	30 - 80 mm	1.2	
	10 - 30 mm	0.6	
	<10 mm	0	
Data:			
Source:			
2.6 Materials used in downstream embankment construction	Tailings	1.5	
	Rock with core of fine granular material	1	
	Rock with core of coarse granular material	0.5	
	Rockfill wall	0	
2.7 Materials used to clad upstream side of dam wall	None (tailings)	3	
	Fine granular material	2	
	Coarse granular material	1	
	Rock (riprap)	0	
2	**Tailings dam scenario score (add Partial Scores 2.1 to 2.7)**		

Guide to estimate Safety Probability Index	Tailings Dams	Guide 3

SAFETY HAZARD SCENARIO 5 (SHS5)

Dam failure that could cause a sudden release of tailings slurry that could affect people, the environment and/or economic activities

3. Phreatic level increase	*Observation*	*Partial Score*	*Choose partial Score*
Drainage			
3.1 Drainage systems (verify if water drainage intakes are available)	None in operation/blocked	3	
	Penstock present but not maintained	2	
	Penstock operational and toe drains working	0	
3.2 Vegetation on tailings	Dense vegetation coverage or complete rock cover		
	Partially vegetated or rock windrows with crest capping	0.5	
	Patchy and/or poor vegetation coverage with some small areas stabilised	0.25	
	None	0	
3.3 Phreatic surface within tailings related to slope height (1)	Water within the deposit with a phreatic level elevation over half the slope´s height	4.5	
	Water within the deposit with phreatic level elevation less than half the slope´s height	2,5	
	None	0	
Cracks and Erosion Gullies			
3.4 Wall cracks	Over 2 parallel cracks (longitudinal or transversal) various metres long and at least 1 over 3 cm wide	0.9	
	Over 2 parallel cracks (longitudinal or transversal) various metres long **or** 1-2 longitudinal or transversal cracks over 3 cm wide	0.6	
	1 to 2 longitudinal or transversal continuous cracks various metres long	0.3	
	None	0	
3.5 Buttress cracks	Visible cracks over 10 meters distance Deep and parallel cracks.	0.9	
	Well developed multiple cracks, but are not visible over 10 m.	0.6	
	Certain isolated cracks or small size (less than a metre).	0.3	
	None	0	
3.6 Erosion gullies	Several large erosion gullies some deep and well developed	0.9	
	1 Deep and well developed erosion gully or small gullies distributed in various areas	0.6	
	Small gullies	0.3	
	None	0	

Guide to estimate Safety Probability Index	Tailings Dams	Guide 3

SAFETY HAZARD SCENARIO 5 (SHS5)

Dam failure that could cause a sudden release of tailings slurry that could affect people, the environment and/or economic activities

Natural drainage around the tailings dam	***Observation***	***Partial Score***	***Choose partial Score***
3.7 Perimeter rainwater collection systems	None	1.2	
	Available but poorly maintained/eroded	0.8	
(Contour channel)	Available but not maintained	0.4	
	Adequate and in good standing	0	
3.8 Average annual rainfall (mm/year)	> 500 mm/year	1.35	
	301 - 500 mm/year	0.9	
	101 - 300 mm/year	0.45	
	< 100 mm/year	0	
Data:			
Source:			
3.9 Percentage of total tailings dam surface covered by pond	> 60%	0.75	
	40% - 60%	0.5	
	20% - 40%	0.25	
	< 20%	0	
Measurement: Estimate:			
3.10 Maximum rainfall in 24 hour period (mm/24 hours) (return period 10 years)	> 80 mm	0.75	
	30 - 80 mm	0.5	
	10 - 30 mm	0.25	
	<10 mm	0	
Data:			
Source:			
3	**Scenario score on phreatic level increase** ***(add Partial scores 3.1 to 3.10)***		

Choose the highest attained score (from the partial figures of 1, 2, and 3)

Score Range	**Hazard Scenario Probability Index**
> 11.5	High
7.1 - 11.5	Medium
2 - 7	Low
< 2	Negligible

Choose the correct Score Range and enter the SAFETY HAZARD SCENARIO probability index on the Risk Registration Form

Guide to estimate Safety Probability Index	Tailings Dams	Guide 3

SAFETY HAZARD SCENARIO 5 (SHS5)

Dam failure that could cause a sudden release of tailings slurry that could affect people, the environment and/or economic activities

Comments

Add comments on assumptions, data and criteria used in applying the Guide.

Note:

(1) Evidence of water levels may be found in different ways. The most reliable measurement is registered through piezometers. If piezometers are not available, the water level can be inferred from other evidence such as the obvious presence of seepage areas. The vegetation may sometimes also indicate the presence of moisture inside the deposit.

Guide to estimate Safety Probability Index	Tailings Impoundments (dry stacked) and Heap Leach Residue Dumps	Guide 5

Safety Hazard Scenario 7 (SHS7)

Failure of slopes of dry stacked or other tailings deposit that could affect people, the environment and/or economic activities.

Safety Hazard Scenario 8 (SHS8)

Failure of heap leach waste dump that could affect people, the environment and/or economic activities.

1. Earthquake

Dump geometry	Observation	Partial Score	Choose partial Score
1.1 General slope angle	> 30°	1,2	
	30° - 21°	0,6	
	< 21°	0	
1.2 Do slopes have berms?	No	0,8	
	Yes, but badly eroded	0,4	
	Yes	0	
1.3 Maximum dump height	> 50 m	1	
	25m - 50m	0.5	
	< 25m	0	
Measurement: Estimate:			
1.4 Gradient of original ground level	>10%	0,8	
	5 - 10 %	0,4	
	< 5%	0	

Structural behaviour

1.5 Period in which no significant failures have occurred	Less than 10 years	1,5	
	Between 10 and 50 years	0,75	
	Over 50 years	0	
Estimate:			
1.6 Landslide occurrence	Several landslides visible	2	
	A few landslides have occurred	1	
	None	0	
1.7 Cracks and gully erosion	Deep or well developed cracks or gully erosion	1,2	
	Some evidence of crack and gully erosion	0,6	
	None	0	

Moisture content

1.8 Presence of water within dumps or leached ore	Presence of water within the deposit with elevation of the phreatic surface more than half way up the footwall slope	4	
	Presence of water within the deposit with elevation of the phreatic surface about midway up the footwall slope	2	
	No evidence of phreatic surface in footwall slope	0	

1	**Dump stability scenario score (add partial scores 1.1 to 1.8)**	

Guide to estimate Safety Probability Index	Tailings Impoundments (dry stacked) and Heap Leach Residue Dumps	Guide 5

Safety Hazard Scenario 7 (SHS7)

Failure of slopes of dry stacked or other tailings deposit that could affect people, the environment and/or economic activities.

Safety Hazard Scenario 8 (SHS8)

Failure of heap leach waste dump that could affect people, the environment and/or economic activities.

2. Natural drainage and stormwater control

Surrounding drainage towards the dump	*Observation*	*Score Partial*	*Choose Score Partial*
2.1 Presence of stormwater drains around the dump	None	3	
	Yes but badly eroded	1	
	Adequate and in good standing	0	
2.2 Average yearly rainfall (mm/year)	> 500 mm/year	3.75	
	301 - 500 mm/year	2.5	
	101 - 300 mm/year	1.25	
	< 100 mm/year	0	
Data:			
Source:			
2.3 Percentage of total surface area of tailings dam covered by pond	> 60%	3.75	
	40% - 60%	2.5	
	20% - 40%	1.25	
	< 20%	0	
Estimate:			
2.4 Maximum rainfall in 24 hours (mm/24 hours) (10 year return period)	> 80 mm	4.5	
	30 - 80 mm	3	
	10 - 30 mm	1.5	
	<10 mm	0	
Data:			
Source:			

2	**Stormwater management scenario score** ***(add partial score 2.1 to 2.4)***	

Guide to estimate Safety Probability Index	Tailings Impoundments (dry stacked) and Heap Leach Residue Dumps	Guide 5

Safety Hazard Scenario 7 (SHS7)

Failure of slopes of dry stacked or other tailings deposit that could affect people, the environment and/or economic activities.

Safety Hazard Scenario 8 (SHS8)

Failure of heap leach waste dump that could affect people, the environment and/or economic activities.

3. Phreatic surface	***Observation***	***Partial Score***	***Choose Partial Score***
Dump drainage			
3.1 Drainage systems (verifiy if there´s a serviceable water receiving drain)	None	4.5	
	Drain is visible, but not well maintained	1.5	
	Drain at the base	0	
3.2 Presence of water within tailings or heap leach waste dumps	Water within the deposit with a phreatic level elevation more than half way up the dump slope	4,5	
	Water within the deposit with phreatic level elevation less than half way up the dump slope	2,5	
	None	0	
3.3 Cracks or gully erosion	Completely eroded	1.5	
	Some gully erosion	1	
	Some evidence of erosion	0.5	
	None	0	
Drainage surrounding the dump			
3.4 Presence of stormwater drains around the dump	None	1.2	
	Yes, but eroded and poorly maintained	0.4	
	Adequate and in good condition	0	
3.5 Average yearly rainfall (mm/year)	> 500 mm/year	1.2	
	301 - 500 mm/year	0.8	
	101 - 300 mm/year	0.4	
	< 100 mm/year	0	
Data:			
Source:			
3.6 Percentage of total surface area of tailings dam covered by pond	> 60%	1.2	
	40% - 60%	0.8	
	20% - 40%	0.4	
	< 20%	0	
Estimate:			

Guide to estimate Safety Probability Index	Tailings Impoundments (dry stacked) and Heap Leach Residue Dumps	Guide 5

Safety Hazard Scenario 7 (SHS7)

Failure of slopes of dry stacked or other tailings deposit that could affect people, the environment and/or economic activities.

Safety Hazard Scenario 8 (SHS8)

Failure of heap leach waste dump that could affect people, the environment and/or economic activities.

3.7 Maximum rainfall in 24 hours (mm/24 hours) (10 year return period)	> 80 mm	0.9	
	30 - 80 mm	0.6	
	10 - 30 mm	0.3	
	<10 mm	0	
Data:			
Source:			

3	**Phreatic level increase scenario score** ***(add partial scores 3.1 to 3.7)***	

Choose the highest attained score (from the partial figures of 1, 2, and 3)	

Score Range	Hazard Scenario Probability Index
> 11.5	High
7.1 - 11.5	Medium
2 - 7	Low
< 2	Negligible

Choose the right Score Range and enter the Hazard Scenario Probability Index on the mine site risk register (Annex E)

Comments

Add comments on assumptions, data and criteria used in applying the Guide.

Note:

(1) Evidence of water levels may be found in different ways. The most reliable measurement is registered through piezometers. If piezometers are not available, the water level can be inferred from other evidence such as the obvious presence of seepage areas. The vegetation may sometimes also indicate the presence of moisture inside the deposit.

Guide to estimate Safety Probability Index	Overburden/Waste Rock/ Low Grade Ore	Guide 6

SAFETY HAZARD SCENARIO 9 (SHS9)

Failure of slopes of dumps containing waste rock or low grade ore that could impact people, the environment **or economic activities.**

	Observation	*Partial Score*	*Choose Partial Score*
1. Dump stability			
General Characteristics			
1.1 Overall Slope angle	>37°	2,2	
	37° - 33°	1,1	
	< 33°	0	
Measurement: Estimate:			
1.2 Dump maximum height	> 50 m	2,4	
	25 - 50 m	1,2	
	< 25 m	0	
Measurement: Estimate:			
1.3 Component material (material type)	Fines	1,8	
	Coarse and fine mix	0,9	
	Coarse	0	
1.4 Water in deposit	Saturated deposit or unknown situation	2	
	Semi-saturated deposit	1	
	Dry deposit	0	
1.5 Gradient of the original ground under the dump	> 10%	0,8	
	5 - 10 %	0,4	
	< 5%	0	
Measurement: Estimate:			
Method of construction			
1.6 Is the dump lined with a geomembrane?	No	1,4	
	Yes	0	
1.7 Do slopes have berms?	No	1,4	
	Yes but badly eroded	0,7	
	Yes	0	
1	**Dump stability scenario score (add partial score from 1.1 to 1.7)**		

Guide to estimate Safety Probability Index	Overburden/Waste Rock/ Low Grade Ore	Guide 6

SAFETY HAZARD SCENARIO 9 (SHS9)

Failure of slopes of dumps containing waste rock or low grade ore that could impact people, the environment **or economic activities.**

2. Stormwater management	***Observation***	***Partial Score***	***Choose Partial Score***
Drainage surrounding the dump			
2.4 Maximum rainfall in 24 hours (mm/24 hours) (10 year return period)	> 80 mm	4,5	
	30 - 80 mm	2,25	
	10 - 30 mm	1	
	<10 mm	0	
Data:			
Source:			
2.2 Stormwater control systems around the base of the dump	None	3	
	Partial, but poorly maintained	1,5	
	Adequate and in good standing	0	
2.3 Natural drainage systems	Leads water towards the dump	3,5	
	Leads water away from the dump	0	
Cracks and gully erosion			
2.4 Cracks	Deep	0,8	
	Some evidence	0,4	
	None	0	
2.5 Gully erosion	Deep	0,8	
	Some evidence	0,4	
	None	0	
2.6 Drainage system: is it evident that the drainage system is working?	No	2,4	
	Yes	0	
2	**Score for stormwater management scenario** ***(add partial scores from 2.1 to 2.6)***		
Choose the highest score (from partial scores 1 and 2)			

Score range	**Category on Risk Matrix**
> 11.5	High
7.1 - 11.5	Moderate
2 - 7	Low
< 2	Negligible

Choose the right Score Range and enter the Hazard Scenario Probability Index on the site risk register (Annex E)

Guide to estimate Safety Probability Index	Overburden/Waste Rock/ Low Grade Ore	Guide 6

SAFETY HAZARD SCENARIO 9 (SHS9)

Failure of slopes of dumps containing waste rock or low grade ore that could impact people, the environment **or economic activities.**

Comments

Add comments on assumptions, data and criteria used in applying the Guide.

Phase-dependent phytoavailability of thallium – A synthetic soil experiment

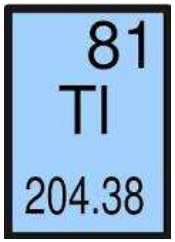
Aleš Vaněk

Department of Soil Science and Soil Protection
Czech University of Life Sciences Prague, CZECH REP.



INTRODUCTION

- **thallium (Tl) = trace metal**
  average concentration in the Earth crust → **≤1 ppm**



- **geochemical anomalies → specific sulfide deposits**
  (mainly Zn ores) or **K-rich magmatites** (substitution Tl^+ for K^+)





- **anthropogenic inputs → sulfide ore processing,**
  emissions from coal combustion or cement production

INTRODUCTION

- **extremely toxic** → similar to Hg or Cd
  LD_{50} **15 mg/kg**



- **Tl behavior in natural (eco)systems,**
  incl. soil–plant interface → limited information !

QUESTIONS

(I) **How are the Tl-bearing phases stable in the rhizosphere?**

(II) **Phytoavailability of Tl, if associated with different phases?**





METHODOLOGY

- **Synthetic (model) soils** → prepared to simulate mineral associations of Tl occuring in soils, **1 wt.%** of Tl-phase

↓

Fe(III) oxide – **ferrihydrite** or **goethite**
Mn(III,IV) oxide – **birnessite**
Ca carbonate – **calcite**
silicate – **illite**

mixed with Tl-free phases forming the "soil matrix"
→ SiO_2 sand (90 wt.%), perlite (4 wt.%), peat (5 wt.%)

METHODOLOGY

- **Phase composition of the model soils →**

Table 1
Phase composition of the model soils (wt.%) with corresponding thallium concentrations (mg kg^{-1} ± SD).

	Soil A		Soil B		Soil C		Soil D		Soil E	
	%	Tl	%	Tl	%	Tl	%	Tl	%	Tl
Ferrihydrite	1	9.64 ± 0	–	–	–	–	–		–	–
Goethite	–	–	1	6.35 ± 0.14	–	–	–	–	–	–
Birnessite	–	–	–	–	1	5.55 ± 0.13	–	–	–	–
Calcite	–	–	–	–	–	–	1	9.58 ± 0.12	–	–
Illite	–	–	–	–	–	–	–	–	1	9.89 ± 0.11
Perlite	4	0.03 ± 0	4	0.03 ± 0	4	0.03 ± 0	4	0.03 ± 0	4	0.03 ± 0
Peat	5	0.01 ± 0	5	0.01 ± 0	5	0.01 ± 0	5	0.01 ± 0	5	0.01 ± 0
Quartz	90	0.08 ± 0.02	90	0.08 ± 0.02	90	0.08 ± 0.02	90	0.08 ± 0.02	90	0.08 ± 0.02
∑		9.76		6.47		5.67		9.70		10.0



incubated using a **wet-dry cycle** for 2 months prior vegetation experiment to attain approx. **geochemical equilibrium**

METHODOLOGY

- **Plant uptake of Tl as affected by Tl-phase in soil**

  pot experiment with **white mustard** *(Sinapis alba L.)*
  → **Tl (hyper)accumulating plant**

  supplemented by nutrients (synthetic NPK)

  all plants harvested after **6 weeks** and analyzed
  for Tl and "structural" metals concentrations

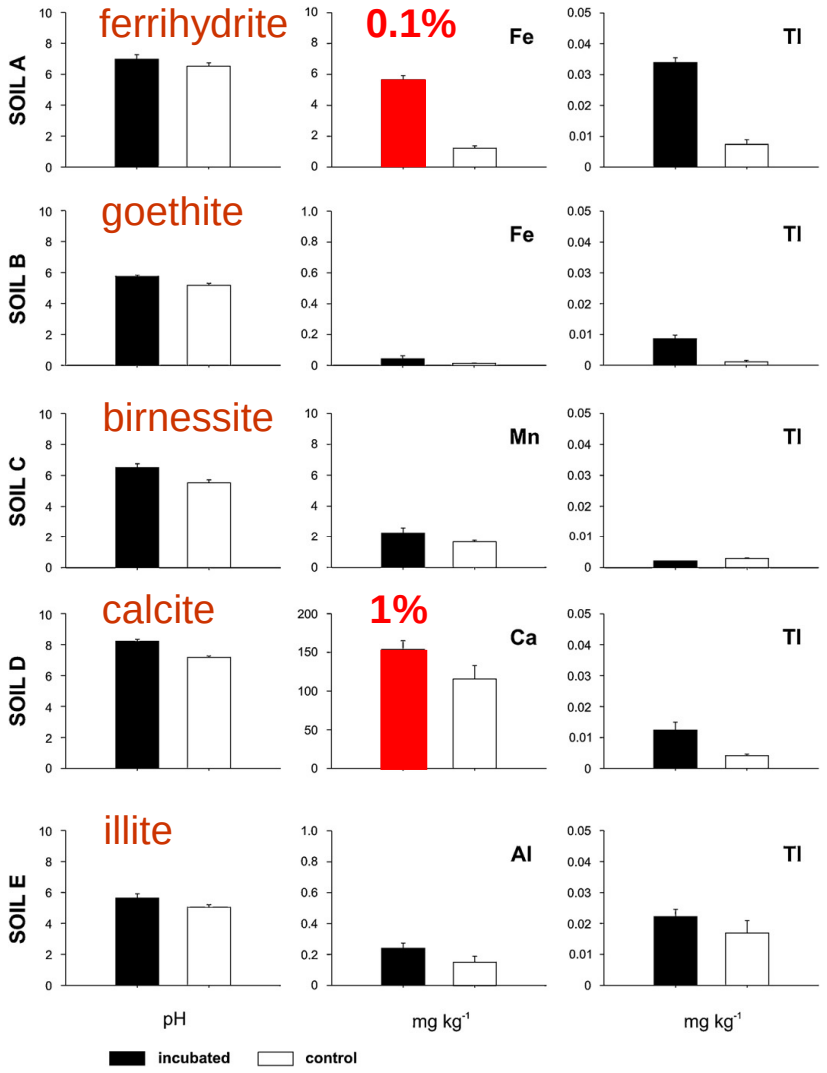
  Tl/metal fractionation in the rhizosphere soil
  → **role of Tl-phase in plant uptake** (BCR SE)



RESULTS

- **Stability of Tl-phases in the soil matrix** (without vegetation)

Me and Tl solubility in H_2O before and after incubation →



RESULTS

- **Plant uptake of Tl**

Table 2
Thallium and metal concentrations (mg kg^{-1}) in different parts of white mustard grown on the model soils.

	Tl	Fe	Mn mg kg^{-1}	Ca	Al
Soil A					
Root	19.5 ± 2.0	1280 ± 249	20.3 ± 2.6	14,400 ± 1000	189 ± 3
Stem	35.4 ± 2.6	407 ± 134	13.5 ± 0.6	3650 ± 40	17.2 ± 1.8
Leaf	28.1 ± 1.9	188 ± 12	40.7 ± 4.1	3510 ± 260	11.2 ± 3.1
Soil B					
Root	5.78 ± 1.60	536 ± 40	22.0 ± 1.7	7770 ± 790	94.8 ± 11.6
Stem	18.5 ± 0.8	282 ± 20	12.4 ± 0.6	2450 ± 220	14.2 ± 1.5
Leaf	7.22 ± 0.77	91.1 ± 10.3	37.7 ± 0.5	3450 ± 200	16.6 ± 9.1
Soil C					
Root	1.13 ± 0.02	260 ± 18	6560 ± 1340	11,500 ± 700	90.3 ± 13.1
Stem	3.90 ± 0.18	118 ± 30	772 ± 109	4120 ± 80	13.1 ± 0
Leaf	3.14 ± 0.42	145 ± 28	423 ± 18	4050 ± 320	6.1 ± 1.0
Soil D					
Root	24.5 ± 2.4	253 ± 97	66.9 ± 4.4	23,000 ± 4300	64.5 ± 13.9
Stem	41.3 ± 0.6	75 ± 14	13.8 ± 3.2	7090 ± 290	10.6 ± 1.8
Leaf	32.6 ± 0.7	131 ± 11	46.4 ± 7.0	4950 ± 820	7.0 ± 2.1
Soil E					
Root	49.1 ± 6.5	201 ± 10	23.3 ± 2.7	8260 ± 730	142 ± 17
Stem	123 ± 9	75 ± 1	16.3 ± 0.7	2930 ± 180	14.1 ± 2.0
Leaf	77.1 ± 14.9	138 ± 10	41.8 ± 1.7	4500 ± 160	11.0 ± 0.9

Data shown are means ± SD (n = 4).

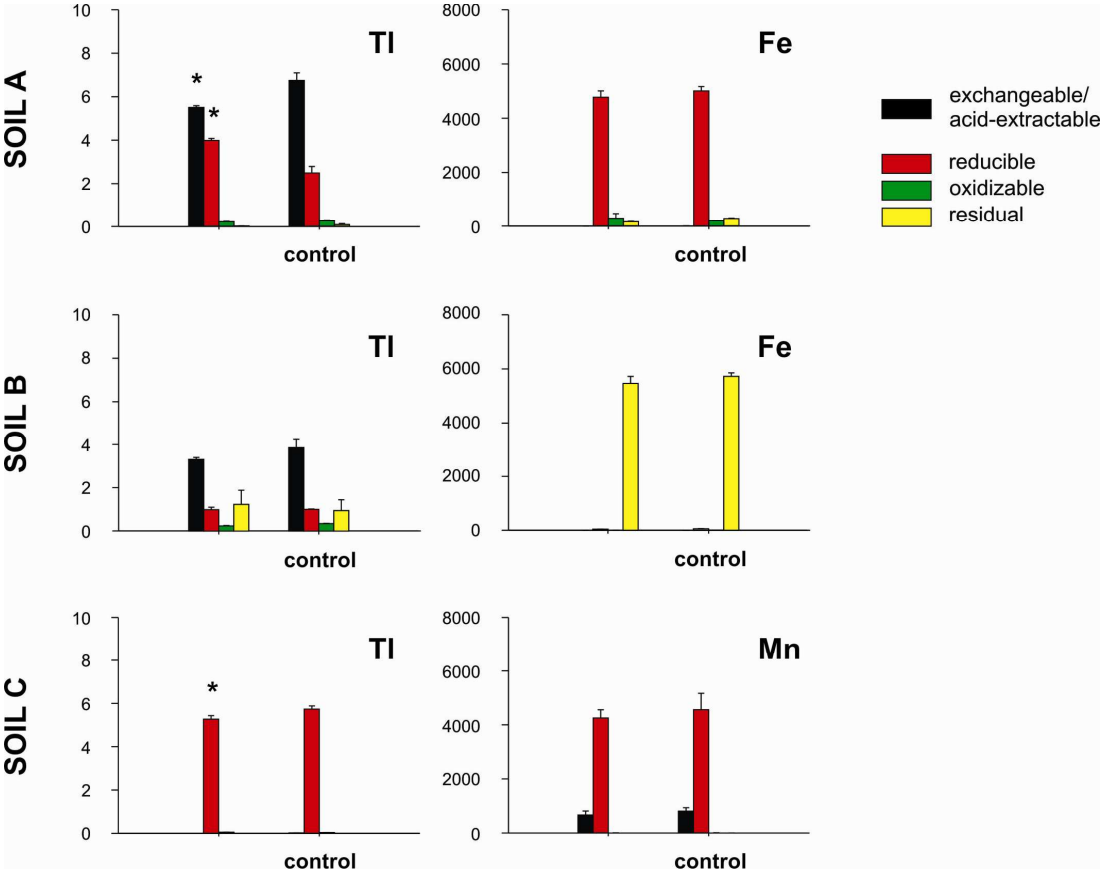
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soil–plant transfer of Tl (shoot:soil ratio) →

illite >> calcite ≥ ferrihydrite > goethite > birnessite

RESULTS

- **Tl dynamics in the rhizosphere**

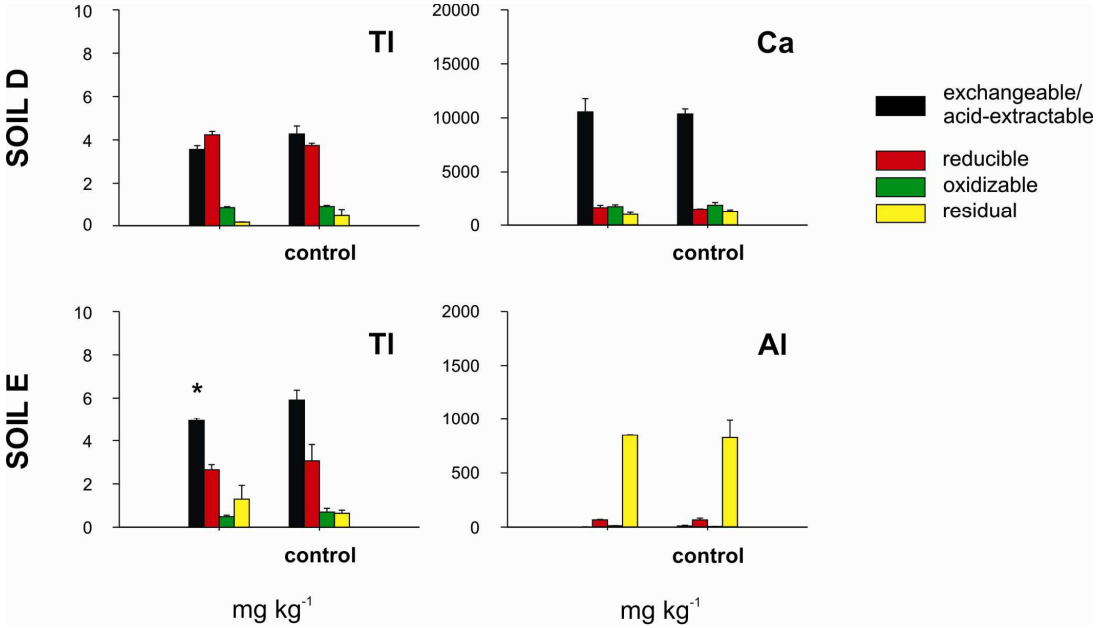






RESULTS

- **Tl dynamics in the rhizosphere**





CONCLUSIONS

- **soil mineralogy plays a key role in Tl phytoavailability**
- **soil enriched in Mn(III,IV) oxides can significantly reduce Tl uptake**
- **Tl of geochemical origin, frequently associated with silicates (illite), may be accumulated by plants to a great extent**
- **the mineralogical aspect must be taken into account prior to general environmental recommendations in areas affected by Tl**

- **THANK YOU FOR THE ATTENTION**

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Phase-dependent phytoavailability of thallium – A synthetic soil experiment

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ANNEX A2

SUPPORTING MATERIAL FOR THE SIMPLIFIED RISK ASSESSMENT FOR SAFETY

ANNEX A2

SUPPORTING MATERIAL FOR THE SIMPLIFIED RISK ASSESSMENT FOR SAFETY

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A.2.1 CONCEPTS ASSOCIATED WITH THE ASSESSMENT OF THE POTENTIAL HAZARD PROBABILITY INDEX

A.2.1.1. Underground mine works

Underground mining is the process of safely extracting economic mineral resources from below earth's surface. There are different kinds of underground mining methods of which long wall and room and pillar mining are examples. There are two kinds of Safety Hazards associated with underground mining i.e. rock fall and falling from elevated structures and general ground instability. General criteria for applying guidelines in order to calculate the Probability Index for Underground Mining include:

- Access to mine entry

Access is the means by which people can enter the mine either on foot or by vehicle using existing or new roads and pathways. Easy access to mine is obtained especially if the mine is partially or completely open.

The presence of security personnel, erection of fences, gates, rock barriers, caps and similar features can help in enforcing entry restriction to the old mine.

- Mine subsidence

Mine subsidence is the downward movement of a surface. The presence of dolines or uneven ground may be an indication of the development of subsidence. Knowledge (through research or interviews with local people) of the location of underground works, the geology (e.g. dolomite) and mining methods is important in determining areas that may be prone to subsidence.

- Tension cracks

Tension cracks are surface evidence of subsidence. They usually develop along the edges of the subsiding zone (Figure 1) and are produced by uneven settling of the land. Tension cracks appear when deformation occurs before sinking.

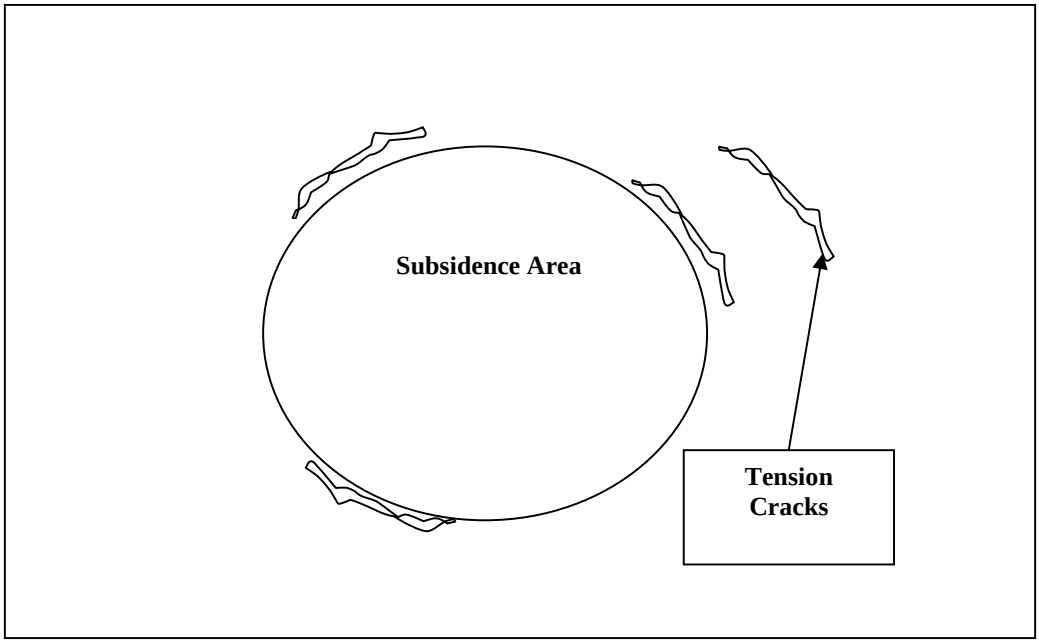


Figure 1: Location of tension cracks.

- Natural drainage.

Part of the underground mine inspection should be to verify whether the subsidence area or zones which may be susceptible to subsidence are located in areas of surface runoff. The location of mine water drainage paths is also important as they determine ways in which water enters the mine.

- Mining method

Certain mining methods create more extensive weak zones that affect the surrounding and overlying land to a greater or lesser degree, depending on the depth of the mine. Methods such as block caving or sublevel caving have a moderate influence, while mining in narrow veins has an almost negligible effect on the surface.

- Rock fall

Loose rocks, structures, or old mining equipment that are unstable could fall and harm persons. Such structures should be evaluated through observation of the condition of supporting structures. Records of previous rock falls including the presence of rock slabs on the ground, slide debris in mine tunnels and other indicators could point to possible future rock falls.

A.2.1.2. Surface mines (Open pits)

Open pit mining is the process of extracting resources from the earth by their removal from an open pit. Open pit mining like underground mining is associated with two main kinds of Potential Safety Hazard. The first is the potential of falling into the pit by people with unauthorized entry (and by livestock and game). The second safety hazard is as a result of ground instability of the abandoned works themselves. Where failures occur, the radius of influence is considered equal to one third of the maximum depth of the pit, and everything within that range from the edge of the pit could be affected by its collapse.

General criteria are provided below to facilitate the application of the Guides in Calculating the Probability Index for Open Pit Mines include:

- Unprotected open pit

Large open pits are generally easy to identify, due to their size and diameter which helps reduce the chances of anyone falling into them accidentally. Nevertheless, open pits which are not protected by some form of barrier can pose a serious hazard. Small pits and trenches on the other hand can be very difficult to see, especially if the area is overgrown, and can cause accidents to unsuspecting people, stock and game animals. Security measures including the presence of guards, fences and other barriers are important in reducing or preventing accidents from happening.

- Seismic Zone.

A seismic map showing seismic active zones and the location of the mine site in relation to the overall seismic active zones should be produced according to the available acceptable standards as required.

- Overall pit slopes

The overall pit slope refers to the inclination of the face of the pit wall or embankment. Different methods can be used to measure the slope including measurements from site plans, an inclinometer or estimation (see below). The overall slope angle is measured or estimated from the upper part of the pit edge to the foot of the pit (Figure 2).

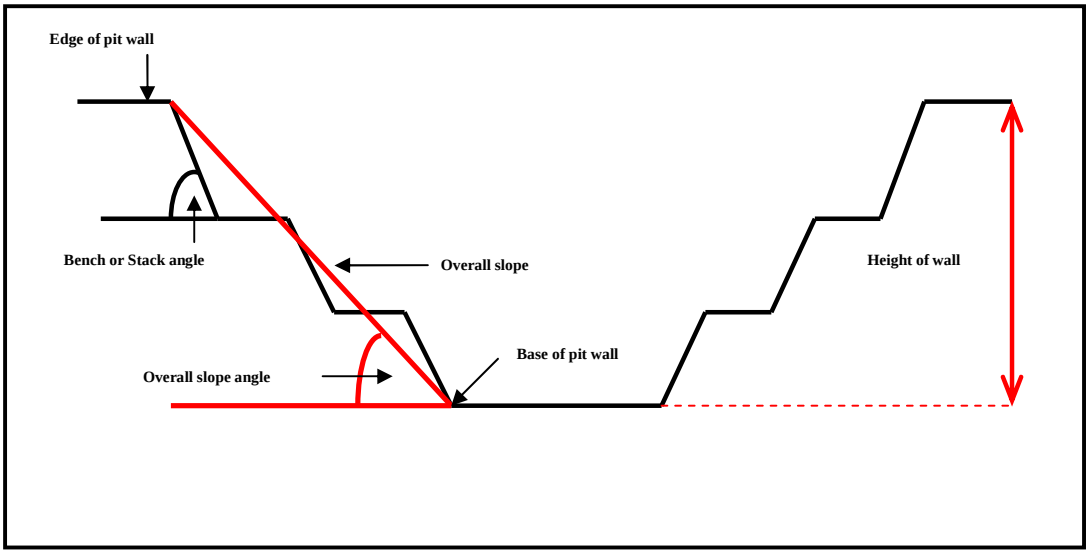


Figure 2: Overall Pit Slope

There are different methods that can be used to measure/determine the slope angle and height of a pit at a mine site.

Brunton compass or inclinometer.

1) Brunton compass with an inclinometer.

2) Ensure the compass is calibrated.

3) Once the instrument is calibrated, the edge of the compass should be projected over the inclined surface of the slope.

4) The inclinometer should be rotated until the tube bubble is centred between the lines of precision.

5) Measure the angle of inclination of the slope directly over the sights.

Procedure for measuring the height of the slope

The height of the pit wall is the difference in vertical elevation between the foot and the edge of the pit, as shown in Figure 2. This height can be measured using topographic methods or maps with contour lines, taking the estimated difference between the edge and foot of the structure. Survey methods can also be employed; either tachometric or a GPS can be used.

- Evidence of partial sloughing/failures/rock fall

Partial sloughing/failures or rock fall refer to the accumulation of rocks from wall failures or slides that occur between ramps or benches. When the slough/failure or rock fall affects more than one bench or the entire slope, then it is considered to be an overall slope failure. The presence of loose material at the foot of the slope is one indicator of its instability.

- Tensile cracks in and around the pit.

Tensile cracks form on the surface and within the pit, generally close to and parallel to the edge (Figure 3). In general they are evidence of deformations that precede failure. Their presence weakens the slope's rock structure by allowing water to penetrate; this deteriorates rock structures lower within the rock mass.

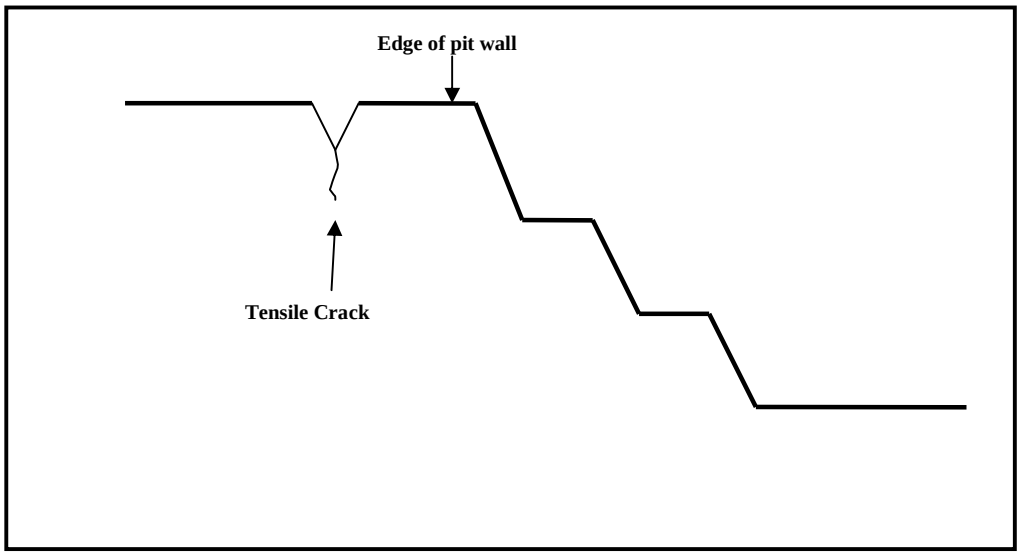


Figure 3: Tensile cracks near the pit edge.

- Presence of water table

In high precipitation zones or where the water table is naturally close to the surface, care should be taken in identifying upwelling of water in local slope walls or at the bottom of the pit (Figure 4).

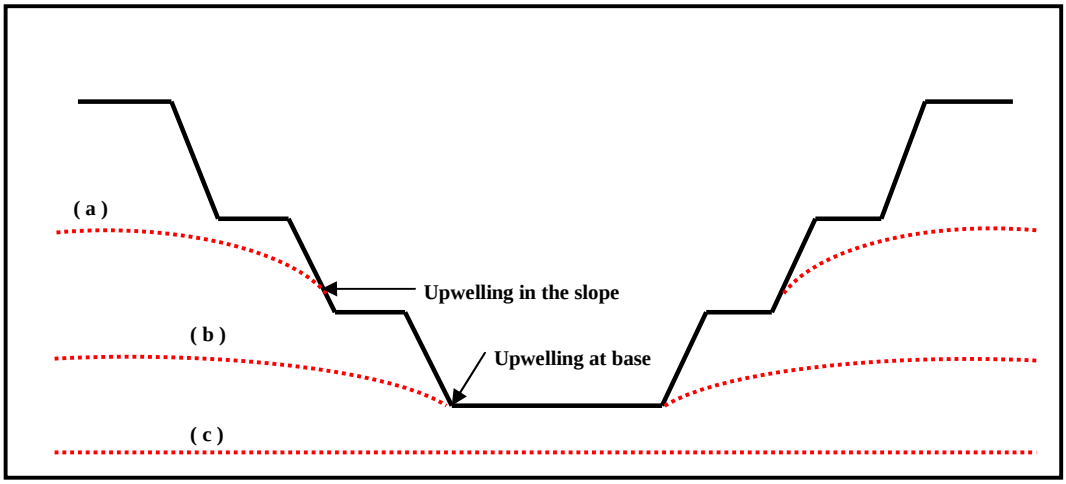


Figure 4: Location of water level in relation to the pit slope.

- Erosion ditches

Erosion ditches are discontinuities on the slope surface which results from the action of climatic agents such as rain and wind. They are considered evident when they are visible on a large portion of the exposed pit surface.

A.2.1.3. Processing plants

There are a number of safety risks that are associated with abandoned processing plants. The risks include falling of unstable structures that could cause serious injuries. Some of these risks are detailed below:

- High, unstable structures inside the plant that could easily fall and harm people

In assessing the integrity of an abandoned processing plant, the physical stability and structural characteristics must be analyzed through visual inspection in order to verify if any of the structures are in a state of disrepair and if any movement could exacerbate their collapse.

- Unsafe elements

Unsafe elements include floors with objects that could cause harm, openings that could lead to falls from elevation, broken stairs and ladders, unprotected walkways, open tanks with no escape routes, deep pools, places with little or no ventilation and all other elements that could seriously harm people.

A.2.1.4. Tailings deposits (dams and impoundments)

To characterize the safety status of a tailings deposit the Assessor should consider its construction and structural behaviour. The paragraphs below summarize some basic concepts related to these types of facilities.

- Wall building techniques

A tailings storage facility is usually constructed in stages, often using one of the following methods:

- Upstream Method;
- Centre Line Method;
- Downstream Method.

Upstream Method

The upstream method is the lowest initial cost and most popular design for a raised tailings embankment. One of the reasons for this is mainly due to the minimal amount of fill material required for initial construction and subsequent rising which normally consists entirely of the coarse fraction of the tailings.

The construction of an upstream designed embankment starts with a pervious (free draining) starter dyke foundation. The tailings are usually discharged from the top of the dam crest creating a beach that becomes the foundation for future embankment raises. Figure 5 shows a simplistic diagram of the stages of construction of an upstream raised embankment. Where the tailings properties are suitable, natural segregation of coarse material settles closest to the spigot and the fines furthest away. Cyclones can be used to accelerate this particle segregation for certain tailings characteristics to send the slime proportion to the centre of the impoundment and the sand fraction to the beach behind the crest. The conventional method of upstream raises relies on no compaction of the spigotted beach that forms the embankment shell. Today compaction by earthmoving equipment is common to increase the degree of safety of raised embankments. Generally the settled coarse fraction from the spigots/discharge point is used as the raise material for the embankments. For multiple spigot discharge a series of shallow pits are dug in front of the spigots (once the tailings have dried and consolidated) and tailings placed on the embankment crest, then they are compressed, the tailings lines lifted and reassembled then normal operation commences.

It is not surprising that the upstream method is the most common design to fail causing huge environmental consequences all over the world (ICOLD and UNEP 2001). Davies *et al.* (2000) note that there are reported to be just over 3,500 tailings dams worldwide of which 50% are of the upstream design. It was also noted that the key failure mode of upstream embankments is a static/transient load induced liquefaction flowslide event. This is not surprising considering the low relative density of the

tailings and the potential for water mismanagement to generate high saturation of the embankment and subsequently creating liquefaction induced flows of the tailings.

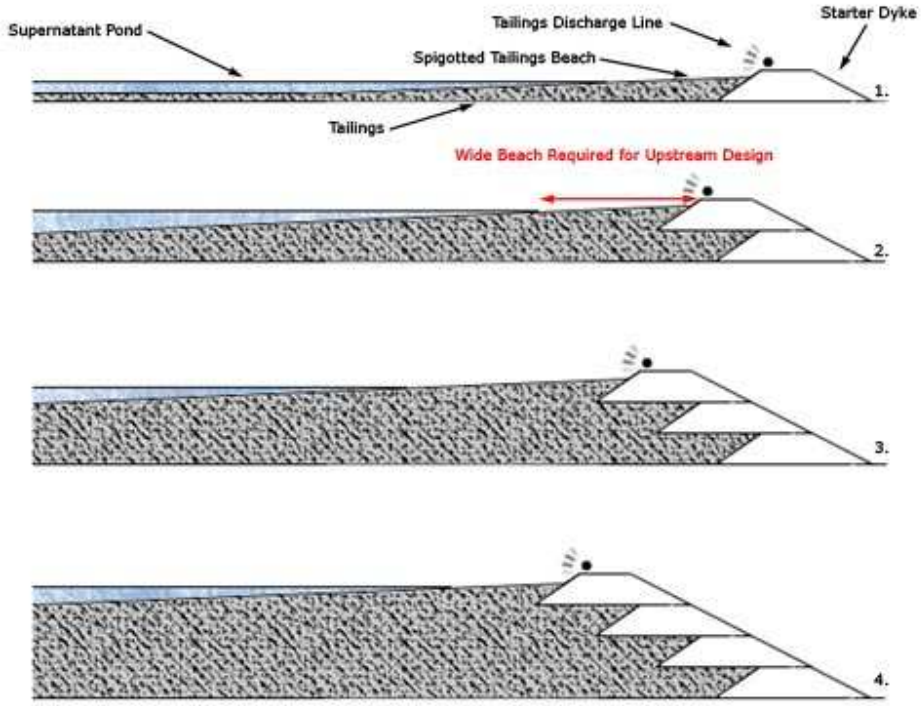


Figure 5: Upstream method of embankment construction

This coarse beach material is essential for upstream designed impoundments to aid drainage and prevent saturation of the embankments. This allows for a stronger and more permeable crest to develop which reduces the height of the phreatic surface as the embankment progressively rises. The best way to reduce the phreatic surface is to have a wide Beach Above Water (BAW) between the dam crest and the supernatant pond (free water) within the impoundment. The closer the supernatant pond is to the dam crest, the higher the phreatic surface of the embankment and thus the greater the risk of failure. The filter under-drain system of the embankments is a key component in reducing the phreatic surface of an upstream designed embankment (ICOLD and UNEP 2001).

Upstream embankments are suited to areas where the climate is arid, minimal amounts of water require storage in the impoundment and rapid water accumulation is improbable (e.g. upstream water inundation and flooding). This helps to promote wide beaches and prevent frequent water level deviations that can dramatically alter pond geometry, freeboard and the phreatic surface within the impoundment area. Upstream embankments are not suited to areas of seismic activity as the risk of liquefaction increases as a result of the potential for dynamic loading by earthquakes.

Rates of rise of upstream embankments have to be controlled to prevent increased pore pressures that can reduce the shear strength of the fill material. Excessive rates of rise have been a trigger for static liquefaction that has been the underlying cause for many upstream tailings impoundment failures.

Centre Line Method

The centre line method is really a compromise between both the upstream and downstream designs. It is more stable than the upstream method but does not require as much construction material as the downstream design. Like the upstream method the tailings are generally discharged by spigots from the embankment crest to form a beach behind the dam wall. When subsequent raising is required, material is placed on both the tailings and the existing embankment. The embankment crest is being raised vertically and does not move in relation to the upstream and downstream directions of subsequent raises, hence the term, centre line design (Figure 6).

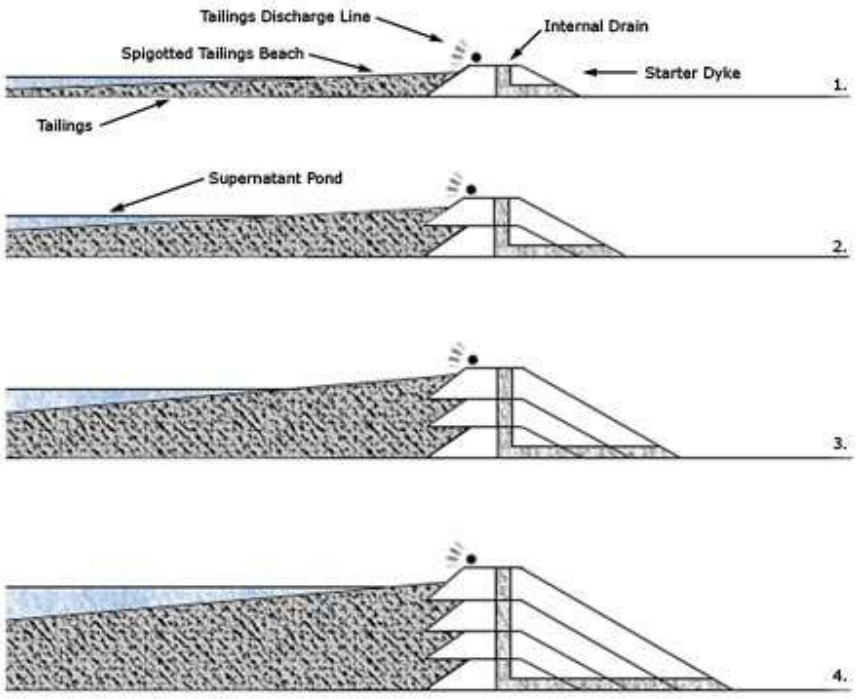


Figure 6: Centre line method of embankment construction

The design incorporates the internal drainage zones that are similarly found in the downstream method. Therefore, the free water can encroach closer to the dam crest than the upstream method without the worry of increasing the phreatic surface and causing a potential failure risk. However, a centre line dam cannot be used as a large water retention facility solely due to the subsequent raises being partially built

on consolidated tailings. A suitable decant system needs to be installed to prevent the free water submerging the beach around the dam crest.

In many cases the centre line design is a good compromise between the seismic risk and the costs associated with construction.

Downstream Method

The downstream design was developed to reduce the risks associated with the upstream design, particularly when subjected to dynamic loading as a result of earthquake shaking (ICOLD and UNEP 2001). The installation of impervious cores and drainage zones can also allow the impoundment to hold a substantial volume of water directly against the upstream face of the embankment without jeopardising stability.

The downstream embankment design starts with an impervious starter dyke unlike the upstream design that has a pervious starter dyke. The tailings are at first deposited behind the dyke and as the embankment is raised the new wall is constructed and supported on top of the downstream slope of the previous section (Figure 7). This shifts the centre line of the top of the dam downstream as the embankment stages are progressively raised (Vick 1990). An advantage to the downstream design is that the raised sections can be designed to be of variable porosity to tackle any problems with the phreatic surface of the embankment. This can be particularly useful where a processing plant has made changes to increase efficiency and as a result, the tailings characteristics may be altered. This may result in pumping more water to the tailings facility or alter the drainage characteristics of the newly deposited tailings.

The downstream design is very versatile for a range of site specific design parameters and behaves similarly to water retention dams. Their main advantage is that the downstream design can have unrestricted heights due to each raise being structurally independent of the tailings. The main disadvantage is the cost of raising the embankment as large volumes of fill are required which increases exponentially as embankment height increases, and subsequently a large area around the dam itself is required as the toe of the dam moves out as more raises are added. This can cause problems where limited space has been taken into consideration prior to building, or if property line and utilities are in close proximity. Although a downstream embankment can theoretically have no height limit, the dam's ultimate height is determined by the restriction of the advancing toe.

- Deposition methods

Spigots

Spigot disposal (normally sub-aerial) is used where the tailings are discharged generally around the perimeter of the tailings facility to create a beach between the embankment and the supernatant pond. This generally means the pond is completely surrounded by beached tailings (Figure 8). The spigots are

changed over as set out by the deposition plan to promote bleeding and drying prior to further layering and raising. It is essential that a deposition plan be established during the design stage and implemented and managed throughout the operational stage.

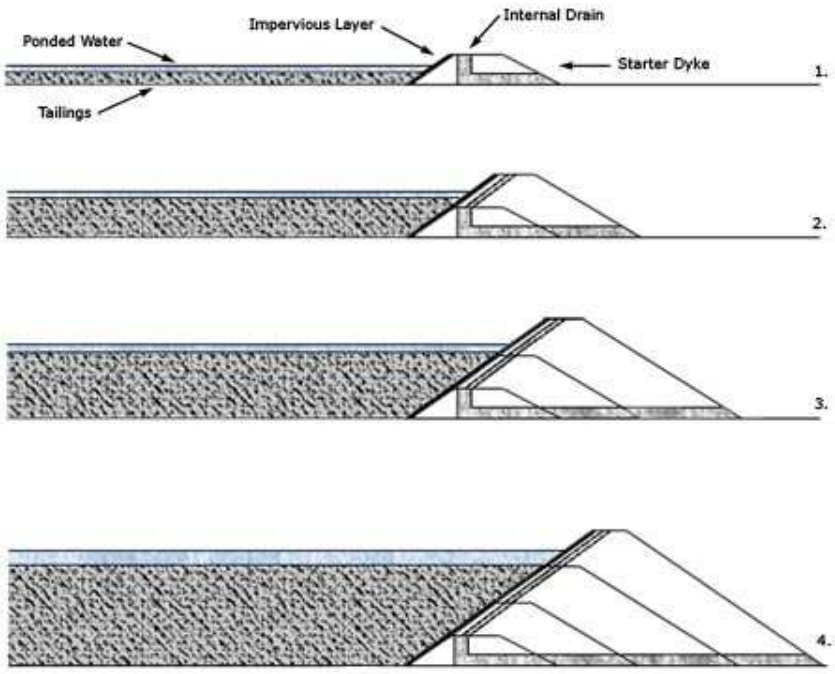


Figure 7: Downstream method of embankment construction

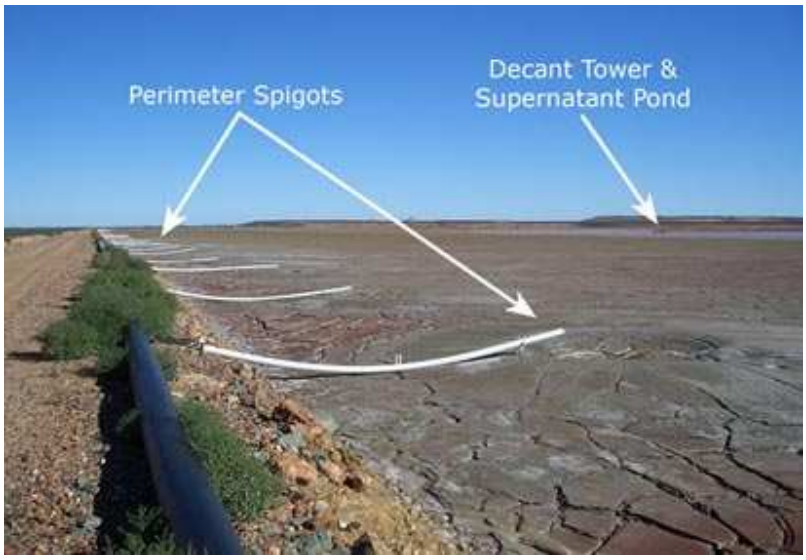


Figure 8: Multiple spigot discharge at the Jundee Gold Mine, NT, Australia

The ideal spigot spacing can be determined by deposition trials to establish likely beach slope angles and widths. Incorrect spacing can lead to undulating beaches between spigots that can ultimately reduce the efficiency of tailings deposition.

Multiple sighting creates pipework management challenges as blockages and ruptures can occur. Monitoring and maintenance schedules are also intensified to ensure that tailings are being delivered to the correct areas, for the correct time period and in the intended quantities. Normally multiple spigots are small diameter pipes that feed off ring main configurations (sometimes known as distribution lines) that then feed off the larger diameter main delivery lines from the plant. The pipeline size reduction ratios and incorrect flow velocities can lead to sanding and plugging of lines. Valve stations and flushing lines are also required for multiple spigots to allow lines to be flushed to prevent sanding after they have been shutdown.

Multiple spigotting helps to reduce the discharge velocity of the tailings being pumped to the storage facility compared to single point deposition. This helps to promote laminar rather than turbulent flow allowing the coarser particles to settle nearer the spigot creating a greater drainage potential. This will also promote a slightly steeper angled beach that will aid the removal of fluids from tailings deposited near the spigot.

Single point

Single point discharge requires irregular movement of the discharge lines. Vick (1990) reports that deltas are normally formed or a single beach deposit of tailings is created within the impoundment (Figure 9). This normally means that the supernatant pond is restrained to a certain area of the impoundment which may be against one of the embankment walls resulting in high and low ends of the impoundment. The lower end of the impoundment will collect the slimes increasing the possibility of seepage erosion. This type of deposition is not suitable where the pond and/or the slimes must be kept away from an embankment.



Figure 9: Single point discharge at Glebe Mines, Derbyshire, England

Single point deposition can place the tailings in fairly thick layers causing the tailings to remain saturated for years if not dried before new layers are deposited. This method of deposition is suited to valley type impoundments (downstream and some centre line embankment designs) where the supernatant pond can be forced to reside against a valley face (i.e. against the hillside away from the retaining embankments)

- Water balance and release

Establishing a stable water balance for a TSF during the design stage is one of the most important considerations to prevent water management problems occurring during operation and closure. Water plays a key role in the day to day responsibilities of a tailings operator and it is essential that a facility is designed to handle and control the required inflows and outflows as well as any unpredictable fluctuations (e.g. storms). Poor design of water management infrastructure and control methods can increase the risk of problematic situations occurring during the operating and closure stages (e.g. upstream inrushes, pipe bursts, low freeboard, seepage). During operation the plant will also demand a certain, and sometimes variable, flow of water that the surge capacity of the decant systems and reclaim/holding ponds have to cater for. Any water balance survey for a proposed tailings facility should take into account that higher volumes of water may require storage during the dry season to maintain plant production. Ice and snow melt, upstream inundation (valley impoundment) and severe storm reoccurrences (e.g. 1 in 100 year) should be considered when designing a TSF to prevent any loss of minimum freeboard levels.

When determining the water balance the various inputs and outputs of the proposed TSF will need to be considered. Wels et al. (2003) noted that determining the water balance of a tailings storage facility can be a difficult task if all the physical processes of water movements are to be considered. During the design stage a conceptual water balance of all inflows and outflows should be determined for a particular location and include all the worst case combination of risk factors (e.g. decant failure, storm, upstream snow/ice melt). A simple and accurate method to determine water balance of a TSF is to determine average annual water inflows and outflows as well as estimating seepage and evaporation rates. A more complex method is to use hydrogeological modelling methods. Estimating the phreatic surface will help to determine seepage plumes and groundwater movement. Figure 10 shows the various water gains and losses for a typical conventional TSF. The seepage and evaporation losses will be predictions and should be included in any design proposal.

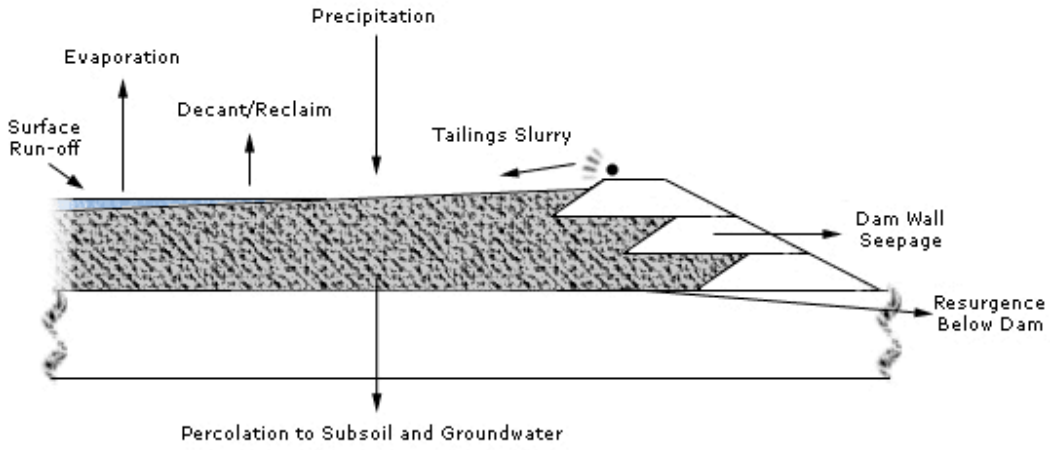


Figure 10: Water balance of a typical conventional tailings storage facility (Adapted from Vick, 1990)

Water stored in a tailings facility is either decanted to reclaim ponds or sent directly to the processing plant. If the plant requires none or only a small volume of the stored water then the remainder will need to be either sent to evaporation ponds or treated and discharged to the environment.

- Supernatant pond

The control of the supernatant pond is probably one of the most important procedures in managing a TSF. Inadequate pond control can result in overtopping, increase in pore pressures, reduction of freeboard, high seepage rates and embankment settlement. These few consequences can lead to instability and high risks of problematic situations occurring. For a conventional impoundment (particularly upstream and centreline designed) it is essential that the ponded water be kept to a minimum volume and the freeboard be sufficiently high all along the tailings embankment(s). Suitable monitoring and management of the supernatant pond is required to operate a TSF safely.

- Decant systems

The decant system(s) of a TSF should be designed to cope with the day-to-day management of the supernatant pond as well as storm condition surges. The design of the decant should allow for a high surge capacity of storm water to compensate for near future storm events. If the pond cannot drain fast enough (decant system or reclaim/evaporation pond ingress restriction), then the freeboard of the TSF may be lost if a near future storm reoccurs. As a guide the decant system should be able to remove storm water in 2 – 4 weeks, but this is highly dependent on climate conditions.

The two most common methods of water control within a tailings storage facility are a decant barge and a decant tower. A decant barge consists of a floating platform that houses the pumps used to reclaim water from the supernatant pond back to the processing plant or holding ponds. A decant tower is an intake structure consisting of a vertical hollow tower (riser) that is connected to a horizontal conduit or pipe that normally travels beneath the impoundment and through/under an embankment. The vertical riser is extended as the level of tailings in the impoundment rises. The decant tower skims off the clear water from the surface of the supernatant pond and carries it away by gravity through the underlying conduit.

- Decant tower

Decant towers (Figure 11) can be very effective at removing ponded water from a tailings facility but can be very problematic. Decant tower systems come under increasing stress as more tailings are disposed of in an impoundment. The ever increasing weight of the tailings can crack and damage a decant conduit that flows underneath and through an impoundment facility. Failures of decant conduits and towers can lead to water management problems that have caused impoundment failures in the past (ICOLD and UNEP 2001). It will not be immediately apparent to an operator that a decant system has failed until the decant outfall is showing signs of low flow or the presence of sediment (tailings). Water levels in the impoundment can rise rapidly and overtopping can occur if contingency plans are not implemented. The Stava disaster in Italy in 1985 was a good example of a decant conduit failure that created a rise in the phreatic surface of the embankment. A rotational slip occurred causing tailings from the upper impoundment to inundate the lower impoundment which eventually overtopped and failed. Tailings escaped down the hillside engulfing the town of Stava claiming the lives of 269 people. Stava remains as one of the world's worst tailings disasters in terms of loss of human life.



Figure 11: Decant tower with walkway (left), view inside the tower showing riser pipe and submerged decant collars (right).

One major disadvantage to a decant tower is that the water has to be continuously positioned around the tower as unlike a decant barge a tower cannot be relocated. If a decant tower becomes inoperative (beached tailings moving the pond away from the tower) then emergency pumping or spillways will need

to be implemented. Any tailings facility operating plan should have precise contingency plans documented in case a decant tower becomes inoperative either by isolation, blockage or failure.

Cracking of a decant conduit can cause internal erosion which will eventually lead to impoundment instability. Repairing the buried conduit is a near impossible task and far too expensive to carry out. The Aitik tailings dam failure in Sweden was triggered by a damaged concrete decant conduit. Cracks developed causing settled tailings to pipe through creating a sink hole. Figure 12 shows the extent of the breach and the cracks in the washed away conduit.



Figure 12: Aerial view of the embankment failure at Aitik (left) and the cracks in the decant conduit (right).

- Decant barge

Unlike decant towers that are gravity fed, a decant barge (Figure 13) requires power to operate the pumps that decant the water from the supernatant pond. This increases operating costs as a constant and reliable power source is required to ensure the pumps operate. If a power failure occurs then no water can be decanted. It is good practice to have standby pumps and diesel generators to use in emergency or when a decant barge cannot cope with rapid ingress (e.g. storm conditions or when process water is required in vaster quantities). Before power or equipment failures occur there should be emergency procedures and response plans to rapidly mitigate any decant problems that can be implemented in both normal and storm conditions.



Figure 13: Fixed decant barge (left) and a mobile barge (right).

The capacity of the barge(s) should be adequate enough to remove day-to-day decant demands as well as storm water accumulation. The barge should also be situated in an easily accessible location for maintenance and inspection purposes. Ideally this should be against the side of a valley wall (for a valley impoundment), or against the side of a jetty wall (either floatable walkway or purpose built) in an area of the impoundment where the ponded water is at its deepest. The water depth below the barge can influence the clarity of the decant water and prevents tailings being sucked up by the barge.

A decant barge or submersible pump can be moved as the decant pond location changes and/or the tailings volume increases. For valley impoundments or in-pit disposal the decant barge or pump is generally retracted to keep the equipment close to the valley or pit walls. This makes it easier to access and prevents the use of heavy anchoring to control varied movement which can be expected the further away the equipment is from surface anchoring points. Each time a barge is moved to other cells the plant water demand should be calculated to ensure the barge is capable of meeting the demand from the water in the new cell.

- Reclaim pond(s)

The reclaim pond(s) (or return pond(s)) store the water that is being decanted from the tailings dam. Reclaim ponds are sometimes referred to as decant ponds which in most parts of the world is another name for the supernatant pond. A reclaim pond is situated outside the confining walls of the tailings storage area a short distance away (

Figure **14**). The water in the reclaim pond is either sent to treatment/polishing ponds for discharge to the environment or pumped back to the plant for use in the processing operation. Some reclaim water can be sent to evaporation ponds or sprays if the climate is suitable.



Figure 14: Reclaim ponds at Kalgoorlie, Western Australia.

The reclaim ponds should be suitably sized to balance the water inflows from the TSF's supernatant pond with the normally variable outflows to the plant. For this reason the reclaim ponds can vary in volume and so an adequate depth is required to prevent overtopping and ensure the return pumps have sufficient head. The surge capacity should also be adequate to remove storm water flow rates from the TSF. This should be similar to the TSF's (2 – 4 weeks depending on climate conditions) to allow for reoccurring storms. This should be checked against the plant volume requirement and overspill/evaporation pond volumes.

The degree of design specification will be determined by the quality and quantity of the return water. The ponds will need to be suitably lined to prevent groundwater contamination (e.g. clay or normally HDPE/LLDPE lined). Prior to installation, the liner system should be checked to determine if the decant liquor will cause any chemical degradation. This is particularly true for HDPE where even UV radiation can degrade the liner (SANS 1998).

Reclaim ponds are particularly useful for tailings facilities that utilise the subaerial deposition technique as the supernatant pond can be drained into reclaim ponds increasing the beach exposure. This aids the drying and consolidating rates of the tailings in the TSF.

- Freeboard

Normally the minimum freeboard is determined by national/local legislation and/or company policies. It is essential in the design stage that water balance calculations take into account average and extreme conditions to prevent loss of freeboard during operation.

Freeboard is used to establish the elevation of the lowest point of the embankment crest relative to the normal or maximum operating levels of the supernatant pond (SANS 1998). Freeboard (Figure 15) management is a critical factor used to control water of a conventional tailings storage impoundment (DME 1998). To promote good drainage of the embankments, the supernatant pond has to be as far

away from the embankments as possible (maintain a high freeboard and wide beach). Ideally the pond should be of a small area, to reduce seepage, and be at a maximum depth at the decant facility to improve reclaim water clarity.



Figure 15: Loss of freeboard (left) and high freeboard (right). (Right picture courtesy of Anglo America)

The definition of freeboard varies in tailings guidance and legislation documents around the world. Confusion can arise where the freeboard is interpreted as the vertical height between the pond and the top of the beach OR the top of the embankment crest. This is further confused where the embankment crest is measured as the external rather than the internal height. The correct definitions of freeboard are (DME 1999):

Total Freeboard (freeboard) – The vertical height between the waterline and the top of the embankment crest (internal). Total freeboard (freeboard) = beach freeboard + operational freeboard 56

Beach Freeboard – The vertical height between the waterline and the beached tailings against the embankment crest.

Operational Freeboard – The vertical height between the beached tailings against the embankment crest and the crest itself.

The following (Figure 16) are diagrams explaining freeboard:

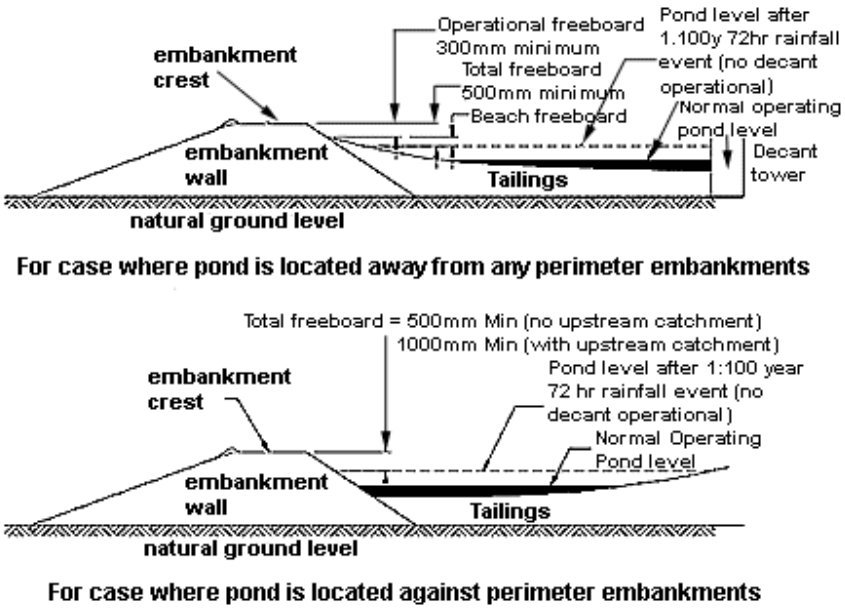


Figure 16: Freeboard of a tailings facility explained (Adapted from DME, 1999)

The freeboard limit for a TSF depends on the type of embankment raising, the method of deposition, geographical location, beach angles (if any beaching occurs), regulations, and the climate.

The use of wing walls around a decant tower can help to prevent the movement of a supernatant pond away from a tower and give more control over its location. This lowers the risk of a pond encroaching an embankment and subsequently lowering the freeboard. Wing walls are particularly suited to arid climates and TSF's that experience minimal water balance changes (e.g. no high inflow fluctuations).

- Storm considerations

The design of a TSF has to cater for storm events both during and after operation. The storm conditions vary depending on the climate, but as a guide the TSF's minimum freeboard should not be met even after a 1 in 100 year, 72 hour duration storm (DME 1998). Suitable storm condition mitigation measures should be in place if the minimum freeboard will be lost during a storm event. Typical mitigation measures are emergency spillways, overflow/storage ponds and emergency decant facilities (e.g. floating pumps).

The impacts of a storm on a TSF are not just specific to the impoundment area but also the surrounding environment. Suitable mitigation techniques will need to be in place to prevent storm water eroding and inundating a TSF. For a valley impoundment this is more difficult compared to the ring dyke facility. In this case, spillways and diversion channels will be required to prevent inundation and the risk of overtopping.

- Seepage control

Seepage flow through the tailings stored in a surface impoundment is inevitable. Vick (1990) notes that zero discharge of seepage from a tailings facility remains an elusive goal, even with complex liner systems. For this reason the control of seepage is an important water management requirement both during the operational and post-operational phases of a TSF (DME 1998). The design stage of a tailings storage facility should take into account seepage control methods to ensure the facility remains perpetually stable and that environmental regulations are not compromised, even after closure.

Seepage can be controlled by using either barrier or collection systems. Barrier systems retain or resist the flow of seepage outside the impoundment area whereas collection systems intercept and safely focus the seepage as it leaves the tailings storage facility. Barrier control methods consist of liners and embankment barriers to prevent or hinder seepage passing through the tailings containment area and into the surrounding environment. Collection methods create pathways for the seepage to accumulate then flow to controlled locations such as embankment and toe drains. Other types of collection systems intercept the seepage as it migrates into the environment by using extraction wells and ditch systems.

The monitoring of seepage is an essential part of any tailings management strategy to understanding how the facility is performing within. Visual inspections of a tailings facility can determine the superficial operations (e.g. pond control, discharge management, pipework integrity) but the internal performance of a TSF can only be identified by monitoring changes and anomalies of the seepage effluents. Understanding seepage can determine the consolidation of the tailings, high seepage pathways (e.g. caused by liner damage or internal erosion), and groundwater contamination and movements (e.g. plumes).

Lowering the water content of the delivery tailings can help to reduce seepage as the water handling and storage volumes of the TSF are reduced. One of the reasons for utilising thickened, paste and dry stack tailings storage is to reduce and even eliminate the water management requirements associated with conventional impoundment storage. Fourie (2003) notes that this lowers evaporation and seepage losses and reduces the potential for groundwater contamination, as there is less moisture present in the deposited tailings and no supernatant pond.

- Phreatic surface

The phreatic surface is essentially the water table in the tailings and is defined as the position between the zone of saturation and the zone of aeration. The exact level at where the phreatic surface resides is the point where the water rises have pressure equal to that of atmosphere.

The stability of a tailings embankment under static and seismic loads is influenced by the position of the phreatic surface. For long term stability, tailings embankments rely on the drawdown of the phreatic surface and therefore adequate internal and under drainage systems should exist. Essentially, the phreatic surface can be successfully controlled by using materials of differing permeability within the

embankment. Drainage zones and low permeable cores are common methods of controlling material saturation. Vick (1990) reports that the objective of prime importance is to keep the phreatic surface as low as possible in the vicinity of the embankment face. It is important that the properties of the materials used in the embankment zones are adequate and that low permeable cores will not crack and allow seepage through, and that drainage zones will not clog and become inoperative (ICOLD and UNEP 2001).

- Internal embankment zones

Blanket and chimney drains are the most common types of drainage zoning to use in tailings embankments. A chimney drain is a vertical or inclined zone that captures lateral seepage flows, and a blanket drain runs along the base of the embankment. Chimney drains are usually connected to the blanket drains to aid the flow of seepage migration. Finger drains are similar to blanket drains but are not continuous. They can be used in areas of high seepage (e.g. where water is designed to be against the upstream face).

Internal filters are required to prevent fines washing through into drainage zones and creating internal erosion. The Omai tailings impoundment failure of 1995 occurred as a result of inadequate internal filters. Synthetic materials such as geotextiles may be used if suitable filter material is not available locally or is too expensive to import. It is important to realise that the filter material should be adequate to prevent piping as well as drain the embankment, thus lowering the phreatic surface. If an unsuitable filter is chosen the filter may become clogged rendering the drain useless.

All drainage zones installed during tailings embankment construction need to be suited to the particular effluent and tailings characteristics. If for example seepage effluent has suspended particles then the drains may become blocked over time and render them useless. If coarse limestone is used for the drains and effluent of a low pH were to pass through, then erosion of the drains can cause instability of the dam wall, thus increasing the risk of catastrophic failure.

For downstream and centre line embankment design the use of low permeable cores can help to reduce the phreatic surface of the embankment. It is essential that the ratio of permeability be such that the embankment can drain easily compared to the seepage entering from the low permeable cores. Vick (1990) reports that cores are essential for embankments that are designed to have water against the upstream face.

- Collection systems

The two main methods used to collect seepage from a tailings impoundment are a collection ditch or a collection well (Figure 17). Ditches are the most common and cheapest method of entrapping seepage with the idea of eventually pumping the seepage back into the dam. A collection ditch is usually dug around the perimeter of a ring dyke impoundment, or at the toe of an embankment wall allowing the seepage to flow through the pervious strata material underneath the impoundment to the ditch. The

return system to the impoundment can simply be a submersible pump that steadily removes the seepage, and thus allowing more to import through the pervious layer into the ditch.



Figure 17: Seepage collection ditch (left) and a seepage well (right)

A collection well is basically the same as a dewatering system for a mine, in that a cone of depression is created when pumping starts. Several wells can be installed around the impoundment in the same vicinity as a collection ditch. The effectiveness of the well depends on the permeability of the soil, and the depth of extraction. Such wells are expensive to install and each well has to be pumped dry and so a ditch is preferred. Collection wells can be installed at the toe of a tailings embankment to reduce the phreatic surface. The well creates a drawdown through the dam wall and can help increase the strength of the embankment. This can be used as a remedial measure for an embankment with drainage problems, and/or where there is a risk of a liquefaction event occurring.

A.2.1.5. Heap Leach Waste

Estimating the Probability Index (PI) for Hazard Scenarios related to heap leach residue dumps is very similar to that of tailings storage facilities. As a result, the supporting information for calculating PI can be found in the sections above. Some aspects specific to heap leach residue dumps are discussed below.

- Presence of drainage systems (pipes, drains)

Most heap leach **residue dumps** are developed on a lined surface with sub-surface drainage systems to manage the phreatic surface within the heap and to ensure the stability of the heap leach pad.

The solution collection system consists of a redundant system that is comprised of a solution collection piping network placed directly on the geomembrane, and is within a free draining granular overliner material.

- The overliner for the HLP should be designed to account for the following:
    - Static Loading (maximum ore depth)

- Construction loading (dissipate construction loads and prevent construction equipment damage to the geomembrane during overliner placement)
- Dynamic Loading (ore loading from truck or track mounted ore stacking and reclaiming system)

- A key issue that impacts the performance of a HLP is the long term performance of the overliner material
- For an on-off HLP, the performance of the overliner is particularly sensitive to a low permeability boundary that can be created at the ore and overliner interface from one, or a combination of, the following:
  - Reclaim stacker compacts the surface
  - Breakdown of particles from the repeated trafficking of the track mounted stacking and reclaiming equipment
  - The migration of fines from the ore through the leaching process

In addition to increasing the solution recovery time, would increase the thickness of the saturated zone in the ore and stability

A.2.2 CONCEPTS ASSOCIATED WITH ASSESSING THE SEVERITY OF CONSEQUENCES

A.2.2.1. Open Pits

Slope failure in an open pit may cause harm to anybody or anything in its vicinity. To quantify the area that could be affected by a slope failure, the following general criteria should be applied:

Radius of influence of the pit (m) = Total depth (m) / 3

Where: 3 is a non dimensional term.

A.2.2.2. Tailings (ponds, dams and deposits)

To assess the consequences of a release of tailings it is necessary to estimate the area that would be affected by the released tailings and/or the distance they would travel. One way of calculating the hazard Distance (D) is as follows:

$$D = 2 \cdot 10^{-6} T \cdot i$$

Where:

I = the hydraulic slope expressed as a %

T = tons of material in the deposit, including fine and coarse tailings susceptible to liquefaction

An alternative formula that could be used to calculate the general area that could be affected by the sudden release of tailings is as follows:

Area covered by Tailings (m^2) = Volume Stored (m^3) / 1.5

In using the above formula to more precisely estimate the potential area affected by the sudden release of tailings, a number of factors that should be considered are outlined below:

- ***Volume of Tailings Stored:*** The volume of tailings stored is directly proportional to the surface area that would be covered if the entire deposit was released. It can be assumed that greater volumes of tailings can ultimately cover a larger area. This value should be estimated.

- ***Natural Slope:*** Places with a steeper slope or drop will result in faster movement of tailings. This implies that the tailings will travel a greater distance and have a higher carrying capacity and therefore destructive potential than when they are released on flat terrain. In addition, the area of impact of the released tailings would be limited to the area down slope of the dam, as the driving force would be gravity. In general, the route that released tailings follow is determined by the local drainage system. Estimating the direction in which the tailings will travel is crucial for determining which receptors could ultimately be affected by a release event.

- ***Geomorphology of the site:*** Topography can play a major role in determining the consequences of this kind of event. The movement of tailings stored in ponds located in narrow valleys is limited by the walls of the valley, and the area affected will be focused downstream. In contrast, tailings in ponds located in open areas could disperse laterally, thereby reducing the distance that the tailings are transported for the same volume of material released.

- ***Distance to Receptors:*** An important factor when assessing the consequences of potential hazard related to tailings deposits is the distance from receptors, especially the distance from local communities or populated areas.

A.2.2.3. Hazardous Waste

The consequences of Potential Hazard associated with hazardous waste is based on the toxicity of the substances stored, which is regulated by the draft Pollution Control and Waste Management Bill. This Bill lists all chemicals considered acutely toxic, flammable, corrosive or explosive; as well as waste catalogued as hazardous. Until such time that the Bill is enacted and Regulations are published, the information contained in the International Maritime Dangerous Goods Code can be used to determine the Severity of the Consequences in cases where people come into direct contact with the respective substances. Based on this rating, the public safety scale can then be applied.

IGCP/SIDA 594 Training course, University of the Witwatersrand, Johannesburg, July 13-15, 2013

Metals and arsenic in cassava: Indicators of contamination in the Zambian Copperbelt mining district

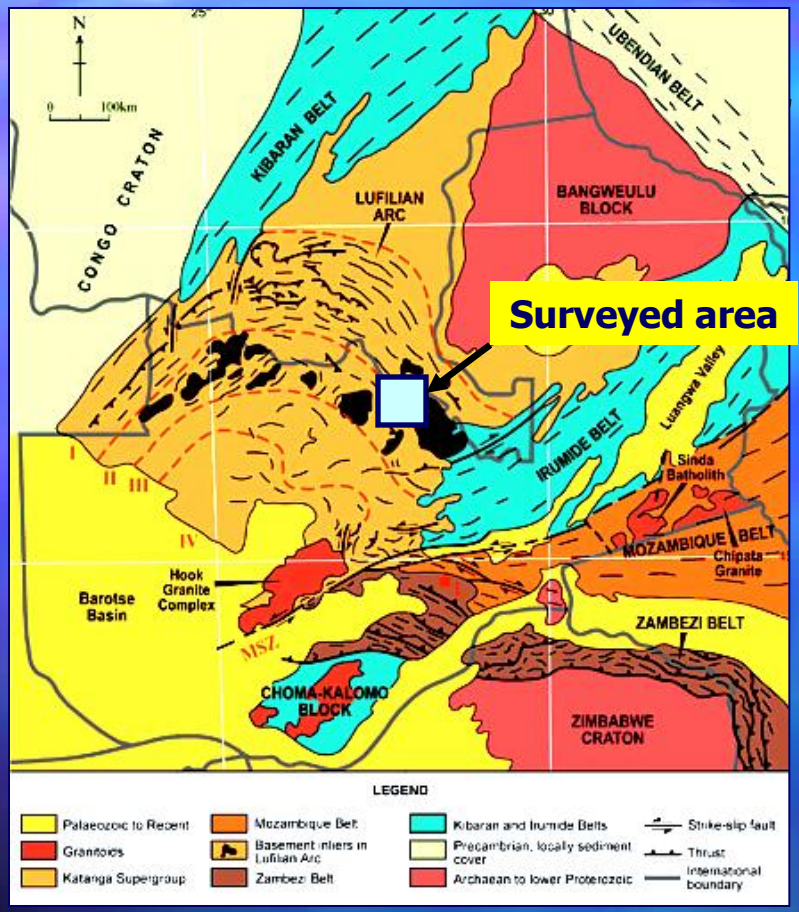
Bohdan Kříbek, Vladimír Majer and Ilja Knésl
Czech Geological Survey

Imasiku Nyambe
Department of Geology, School of Mines, University of Zambia

Martin Mihaljevič and Vojtěch Ettler
Institute of Geochemistry, Mineralogy and Mineral Resources, Faculty of Science, Charles University

Ondra Sracek
Department of Geology, Faculty of Science, Palacký University Olomouc, Czech Republic

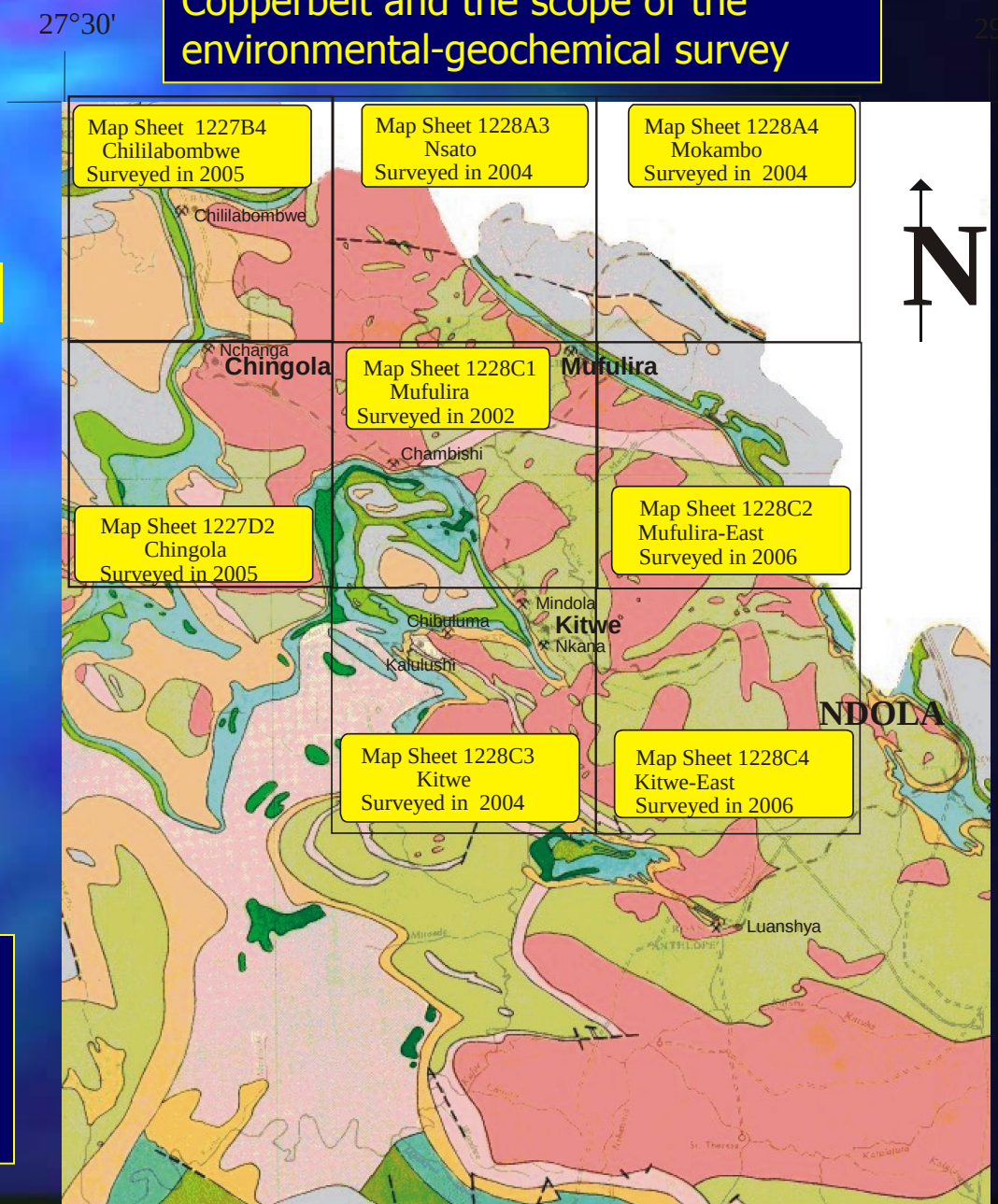
GEOLOGICAL MAP OF ZAMBIA



Total area: 4700 km^2

- 760 composite samples of surface soil
- 264 samples of subsurface soils
- 270 samples of stream sediments
- 120 samples of surface waters
- 60 special samples (slag, tailings, ochres)

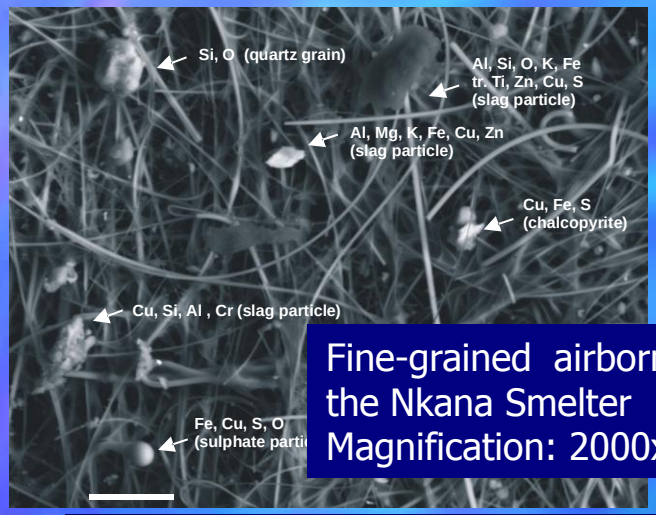
Geological sketch map of Zambian Copperbelt and the scope of the environmental-geochemical survey



SOURCES OF ANTHROPOGENIC CONTAMINATION OF SOILS AND PLANTS:

- Gaseous and solid emissions from smelters
- Dust from dry superfical parts of tailing ponds
- Dust from ore treatment plants and slag deposits
- Transport of concentrates and products

Airborne dust particles from smelters

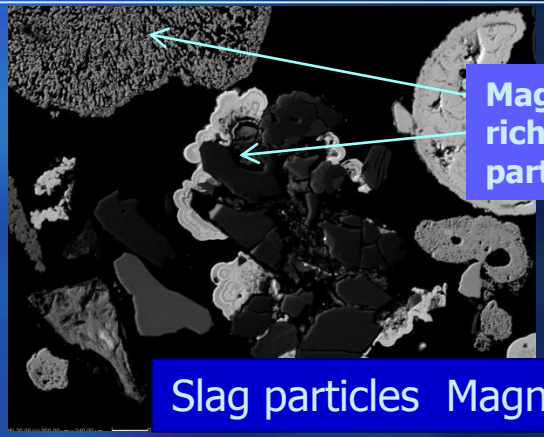


Fine-grained airborne particles from the Nkana Smelter
Magnification: 2000x



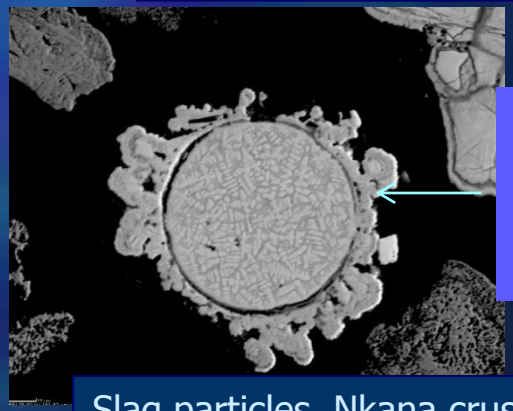
the Nkana Smelter

Dust particles contain:
As, Be, Co, Cr, Cu, Hg, Mo, Se, V a Zn



Magnetite-rich glass particles

Slag particles Magn. 800x



Cu-Fe-S intermediate solid solution particle (ISSN)

Slag particles, Nkana crushers
Magnification 600x

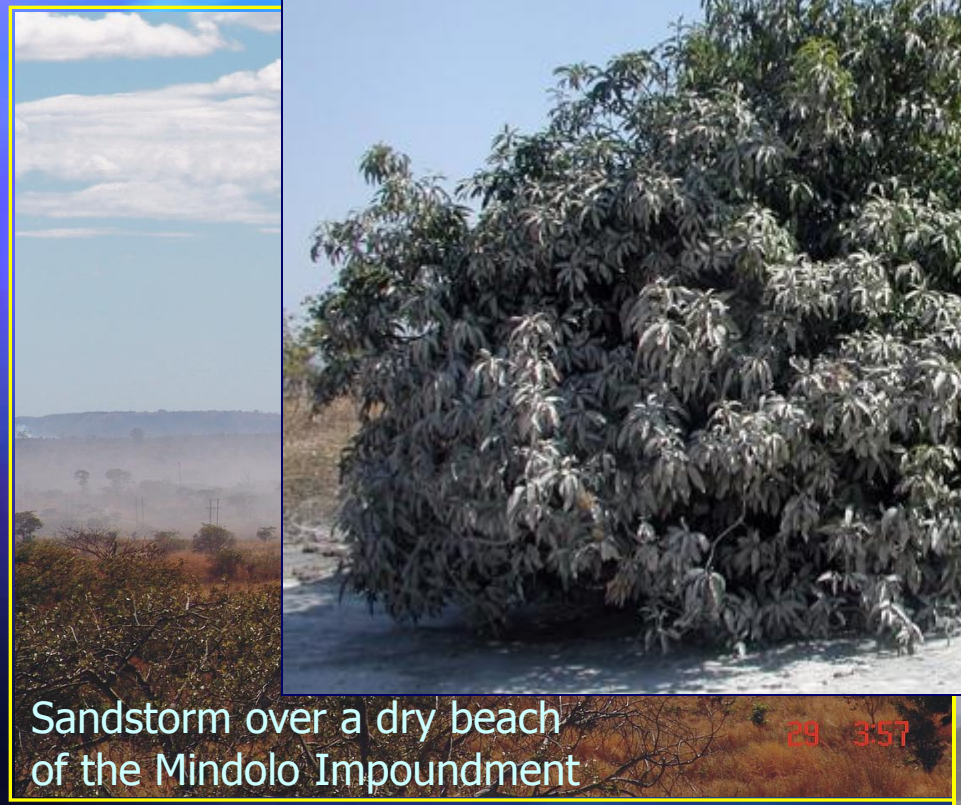
SOURCES OF ANTHROPOGENIC CONTAMINATION

Airborne particles from dry beaches of tailing i

Dust particles from the Mindolo Tailings

ntain up to:
0 ppm Co;
.02 ppm Hg;
ppm Ni;
pm Se and





Sandstorm over a dry beach of the Mindolo Impoundment



Sandstorm over the Mufulira Impoundment

METALS AND ARSENIC IN CROP PLANTS

The objectives of this study were:

(1) To assess contents of As, Cu, Co and Pb in crop plants (cassava, sweet potato, maize) in uncontaminated and contaminated areas

(2) To evaluate the plant-to-soil response

(3) To assess whether food prepared from crop plants grown in contaminated areas endangers the health of the local population

(4) To evaluate superfical contamination of leaves caused by dust fallout in the neighbourhood of smelters

Sampled plant/plant parts

Cassava/leaves, tubers (*n* = 55/49)
Sweet potato/leaves, tuber (*n* = 17/18)
Maize/grains (*n* = 32)





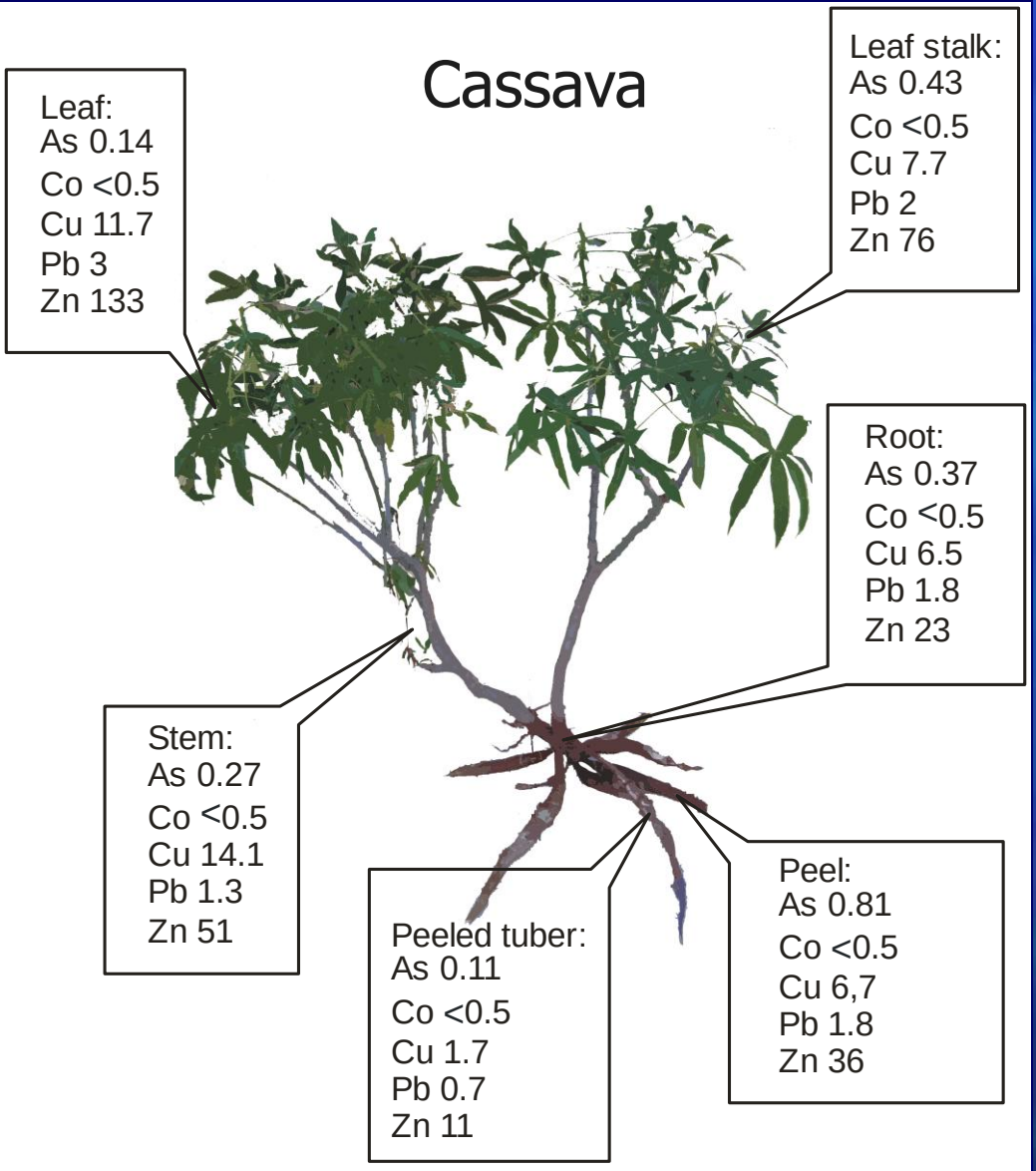
ANALYTICAL METHODS

The pseudo-total digests of soil samples were obtained by a standardized *aqua regia* extraction procedure (ISO 11466)

Bioavailable metals in soils:
- 0.01M solution of $CaCl_2$
- 0.1 M solution of ammonium fluoride and complexone III (Mehlich III)
- 0.025 M solution of Na_2EDTA
- 0.001M solution of DTPA

Approximately 1-g aliquots of the plant parts were burned down in a muffle oven. Temperature program: from 25 ^oC to 550 ^oC.

The Co, Cu, Fe, Pb and Zn were determined in ash leachate using Flame Atomic Absorption Spectroscopy (FAAS), arsenic was determined using Hydride-Generation Atomic Absorption Spectrometry (HGAAS)



Concentration in soil: As: 0.90, Co: 17, Cu: 48, Pb: 10,6, Zn: 55 mg kg^{-1}

RESULTS ACHIEVED

Distribution of metals and arsenic in plant parts (uncontaminated area, background data)

Cassava, accumulation factors

Leaf
As: 0.15
Cu: 0.24
Pb:0.28
Zn: 2.41

Tuber
As: 0.12
Cu: 0.04
Pb: 0.07
Zn: 0.23

Distribution of metals and arsenic in plant parts (uncontaminated area)

Sweet potato



Leaf:
As 0.16
Co <0.5
Cu 16.6
Pb 0.7
Zn 29

Leaf stalk:
As 0.2
Co <0.5
Cu 20.7
Pb 0.7
Zn 18

Root:
As 0.14
Co <0.5
Cu 15.7
Pb 0.5
Zn 19

Stem:
As 0.15
Co <0.5
Cu 17.6
Pb 0.5
Zn 11

Peeled tuber:
As 0.14
Co <0.5
Cu 7.1
Pb <0.5
Zn 10

Peel:
As 0.21
Co <0.5
Cu 8.8
Pb 0.7
Zn 28

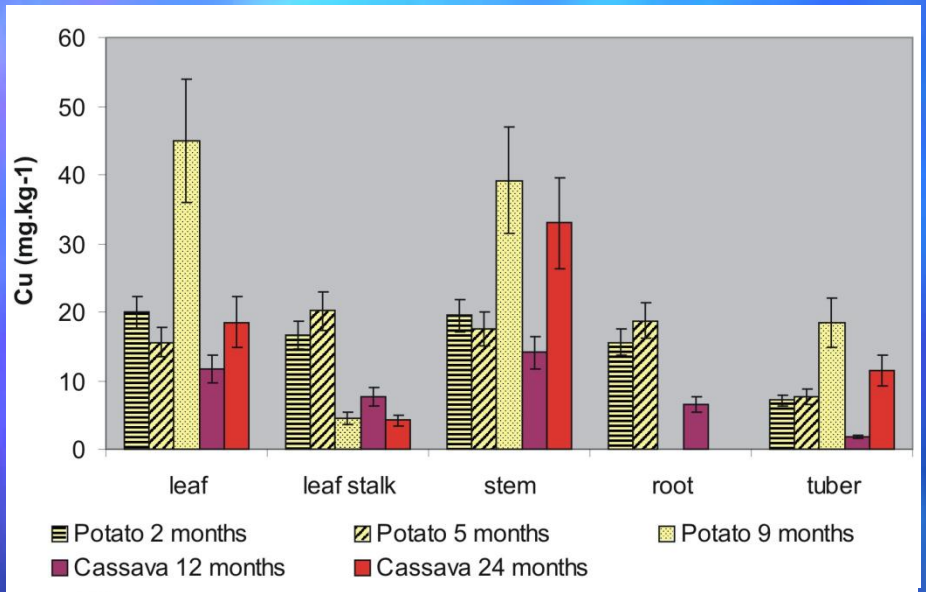
Concentration in soil: As: 0.90, Co: 17, Cu: 48, Pb: 10,6, Zn: 55 mg kg $^{-1}$

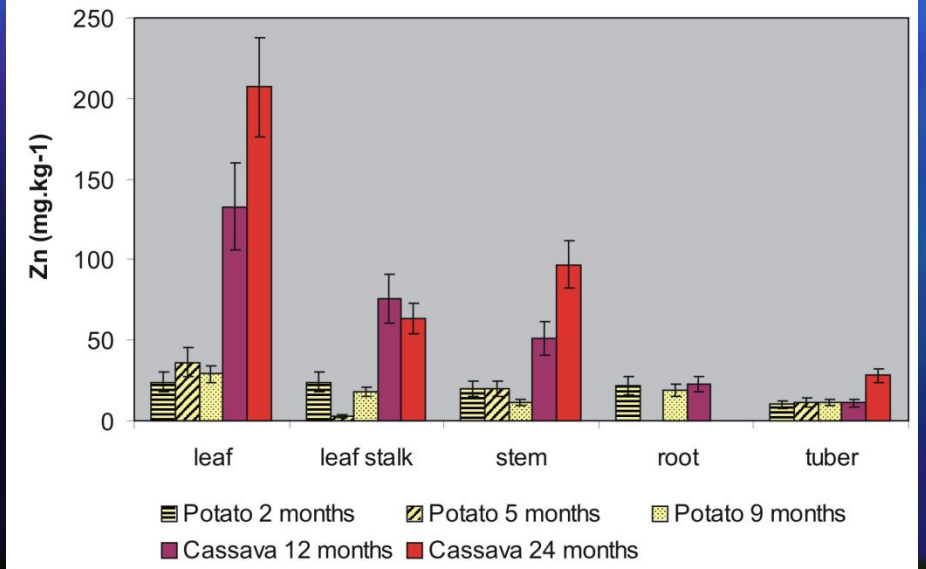
Sweet potato, accumulation factors

Leaf
As: 0.21
Cu: 0.36
Pb: 0.06
Zn: 0.52

Tuber
As: 0.15
Cu: 0.14
Pb: 0.03
Zn: 0.18

VARIATION IN CONCENTRATIONS



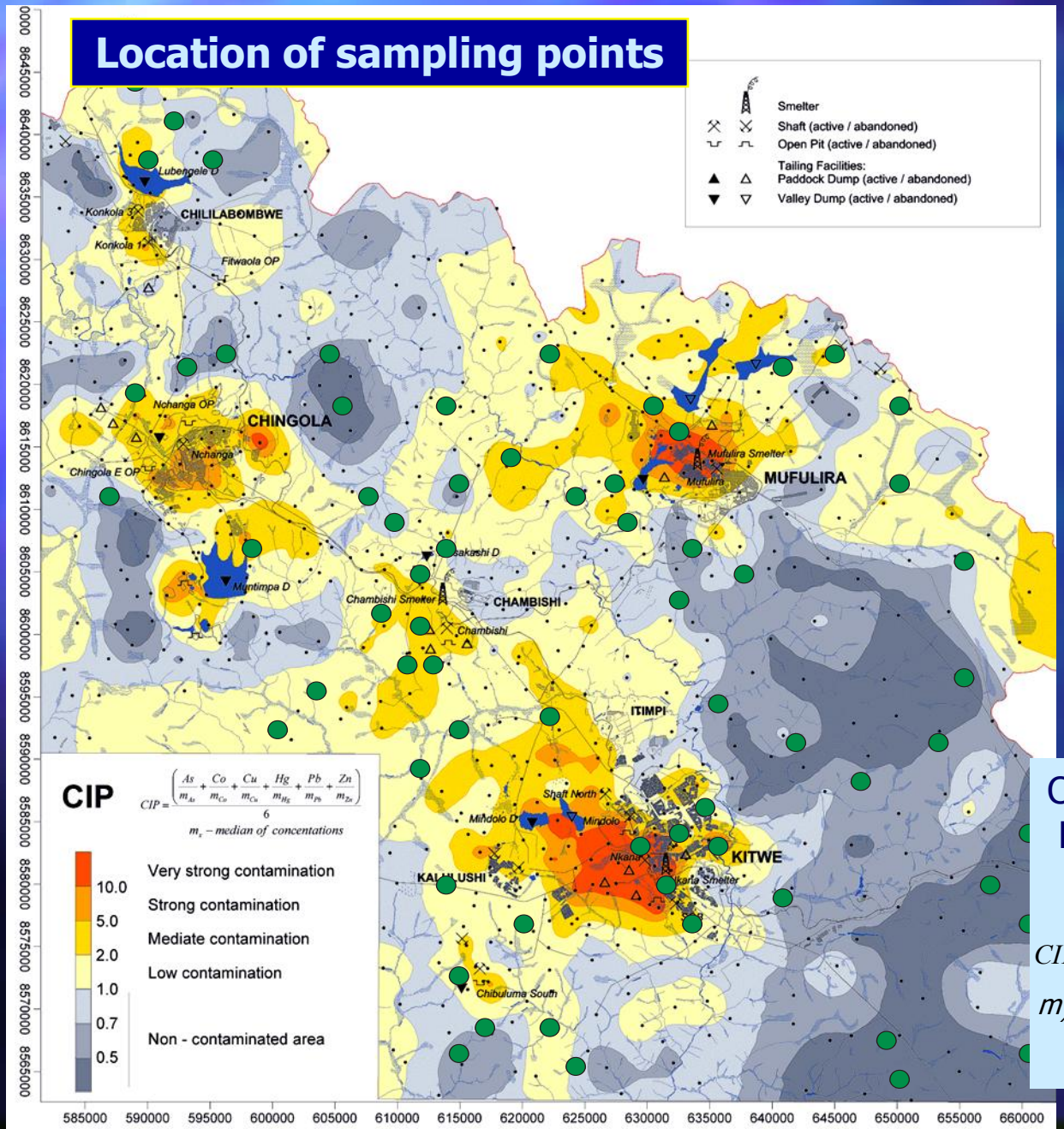


Contents of metals in plants are governed by a number of factors:

External factors:
- content of bioavailable metals in soil
- soil composition and pH
- vegetation period
- climatic conditions

Internal factors:
- age of plant
- bioessentiality of elements
- avoidance mechanisms
- antagonism of elements

Concentrations of copper and zinc in leaves and tubers of cassava and sweet potatoes in relation to the age of these crop plants



Metals and arsenic in uncontaminated and contaminated areas

Plant and soils were sampled in contaminated part of the Zambian Copperbelt (CIP > 1)

and,

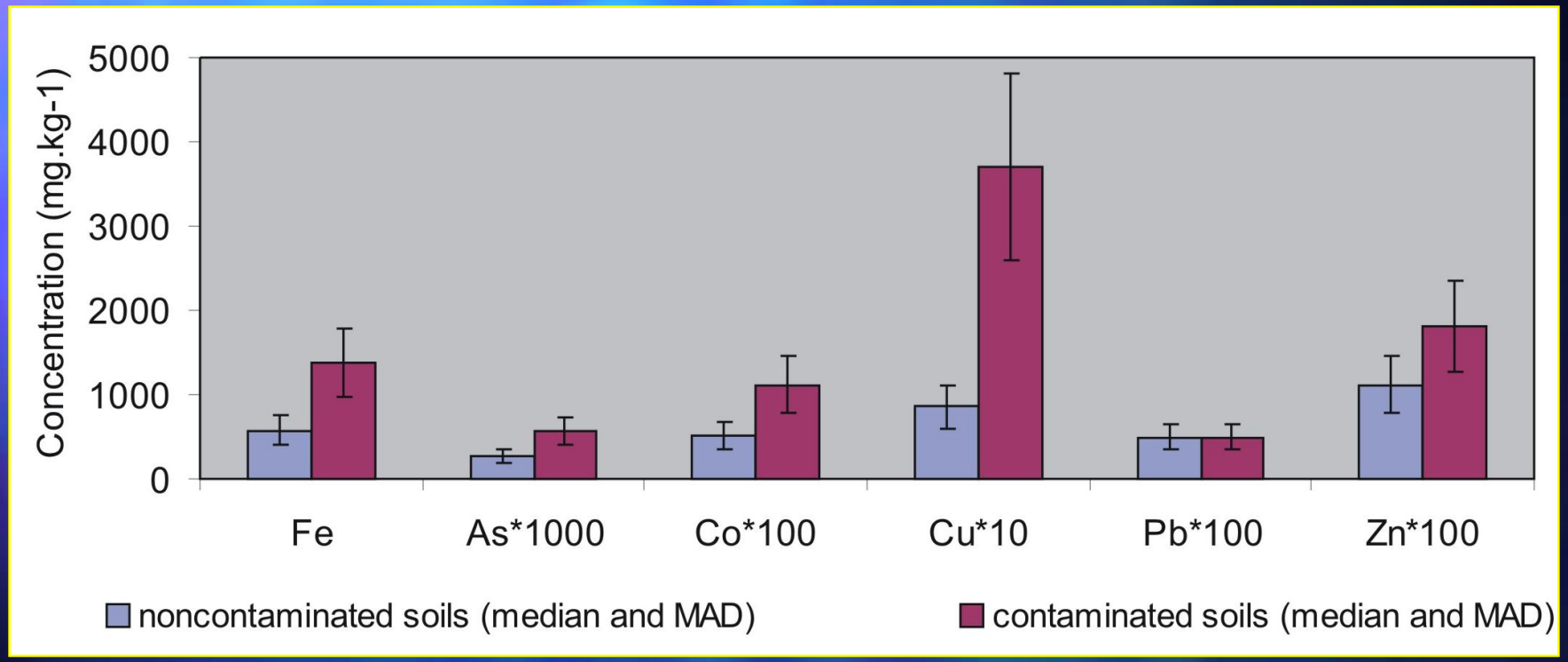
in the reference, uncontaminated part of the Zambian Copperbelt (CIP < 1)

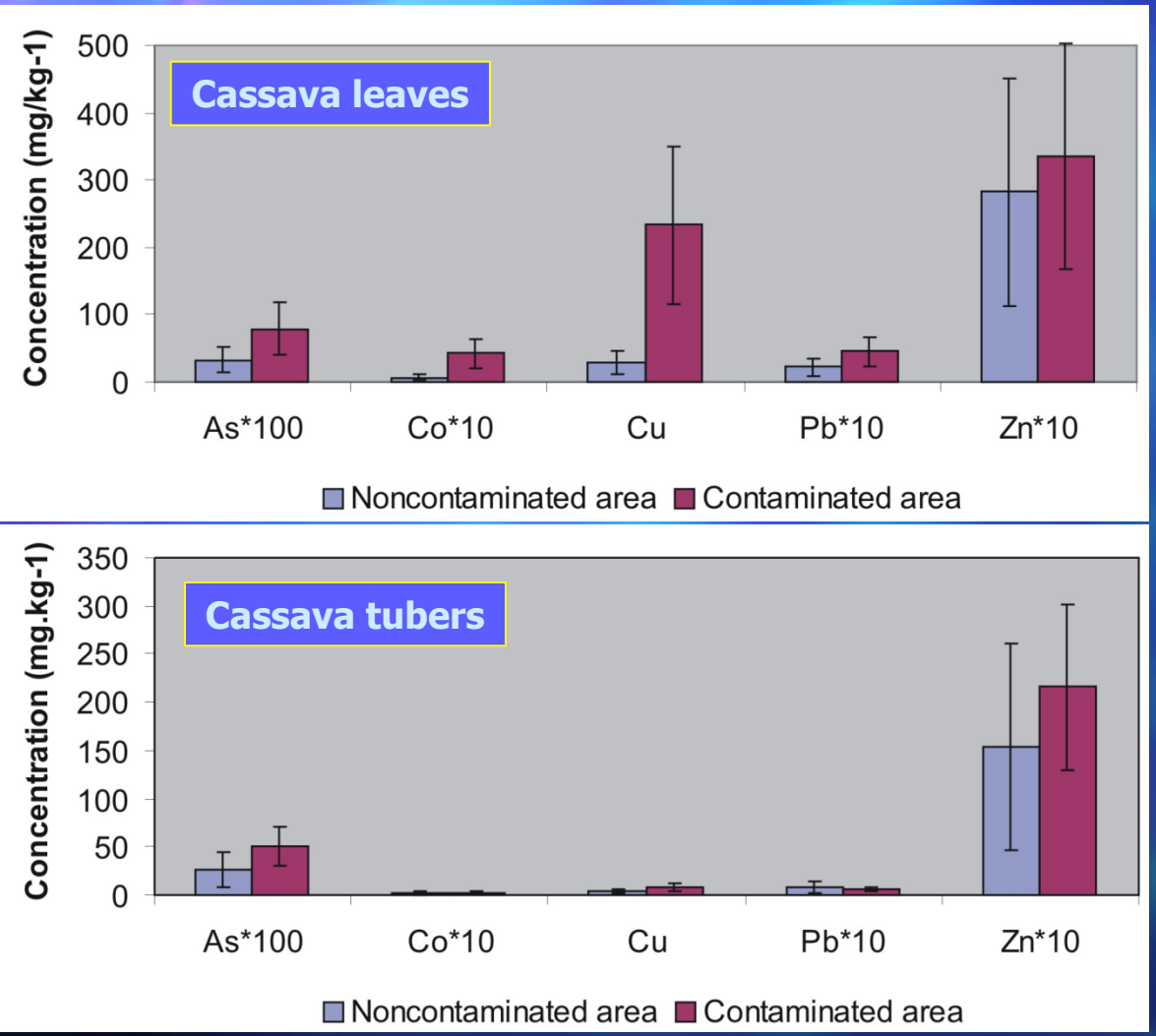
Coeficient of Industrial Pollution

$$CIP = \frac{\left(\frac{As}{m_{As}} + \frac{Co}{m_{Co}} + \frac{Cu}{m_{Cu}} + \frac{Hg}{m_{Hg}} + \frac{Pb}{m_{Pb}} + \frac{Zn}{m_{Zn}}\right)}{6}$$

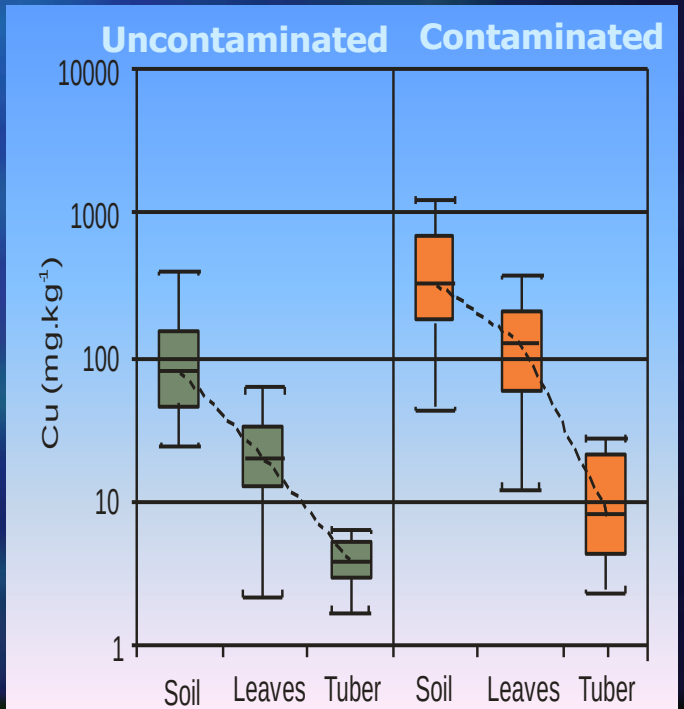
m_X – *value of the metal concentration*

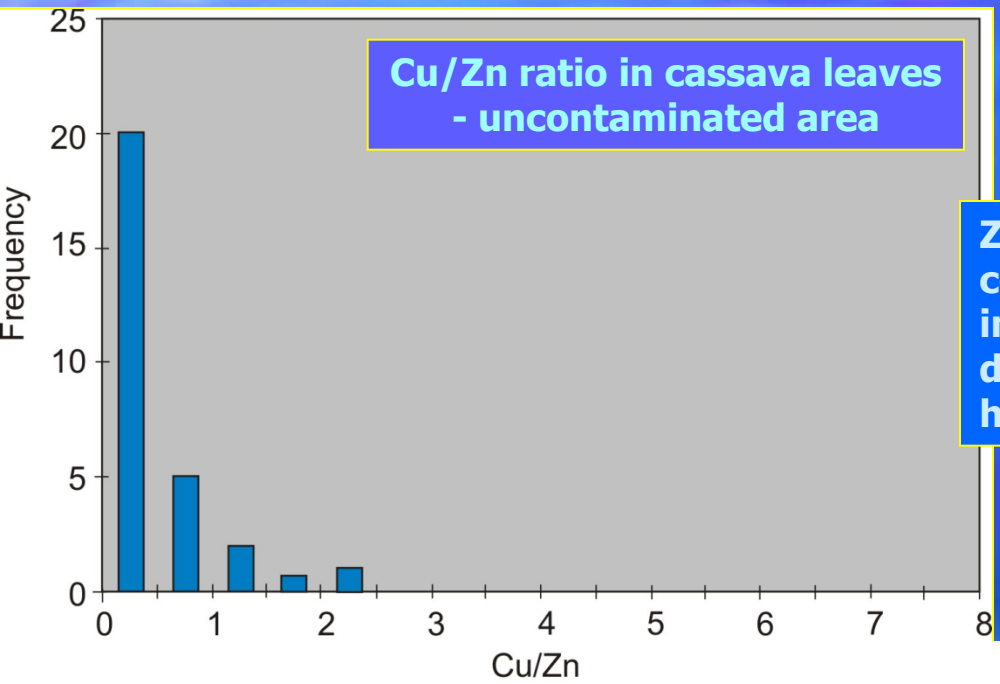
Contents of metals and arsenic in uncontaminated and contaminated soils of the Zambian Copperbelt





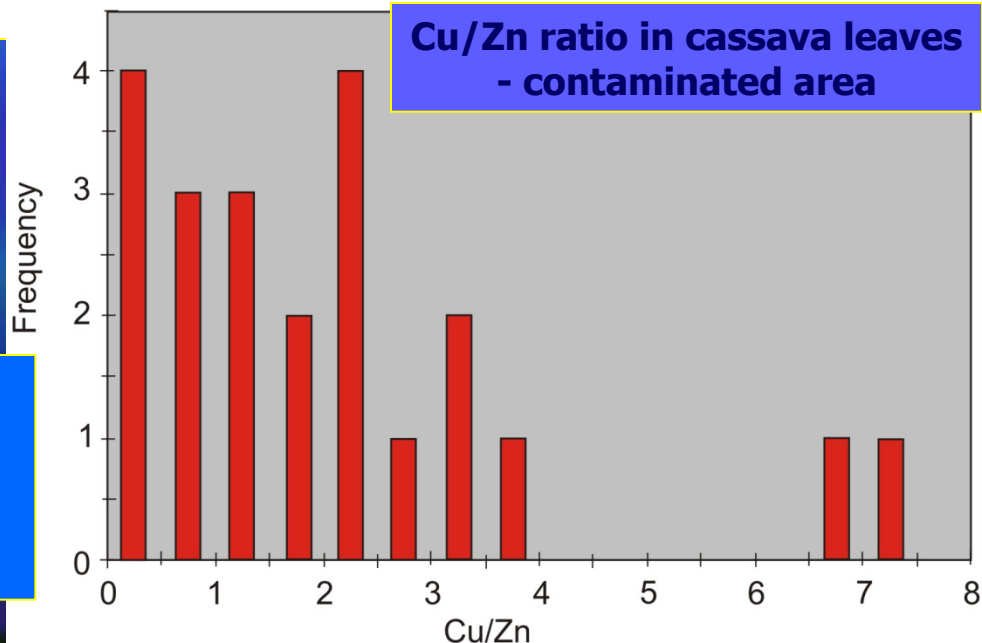
Content of metals and arsenic in cassava leaves and tubers (uncontaminated and contaminated area)





Zinc was found to prevail over copper in leaves of cassava growing in uncontaminated areas. The distribution of data is very homogeneous

In contrast, copper was mostly found to prevail over zinc in leaves of cassava growing in contaminated areas, but the distribution of data is rather very heterogeneous



Spearman correlation matrix

Soil-to-plant correlation

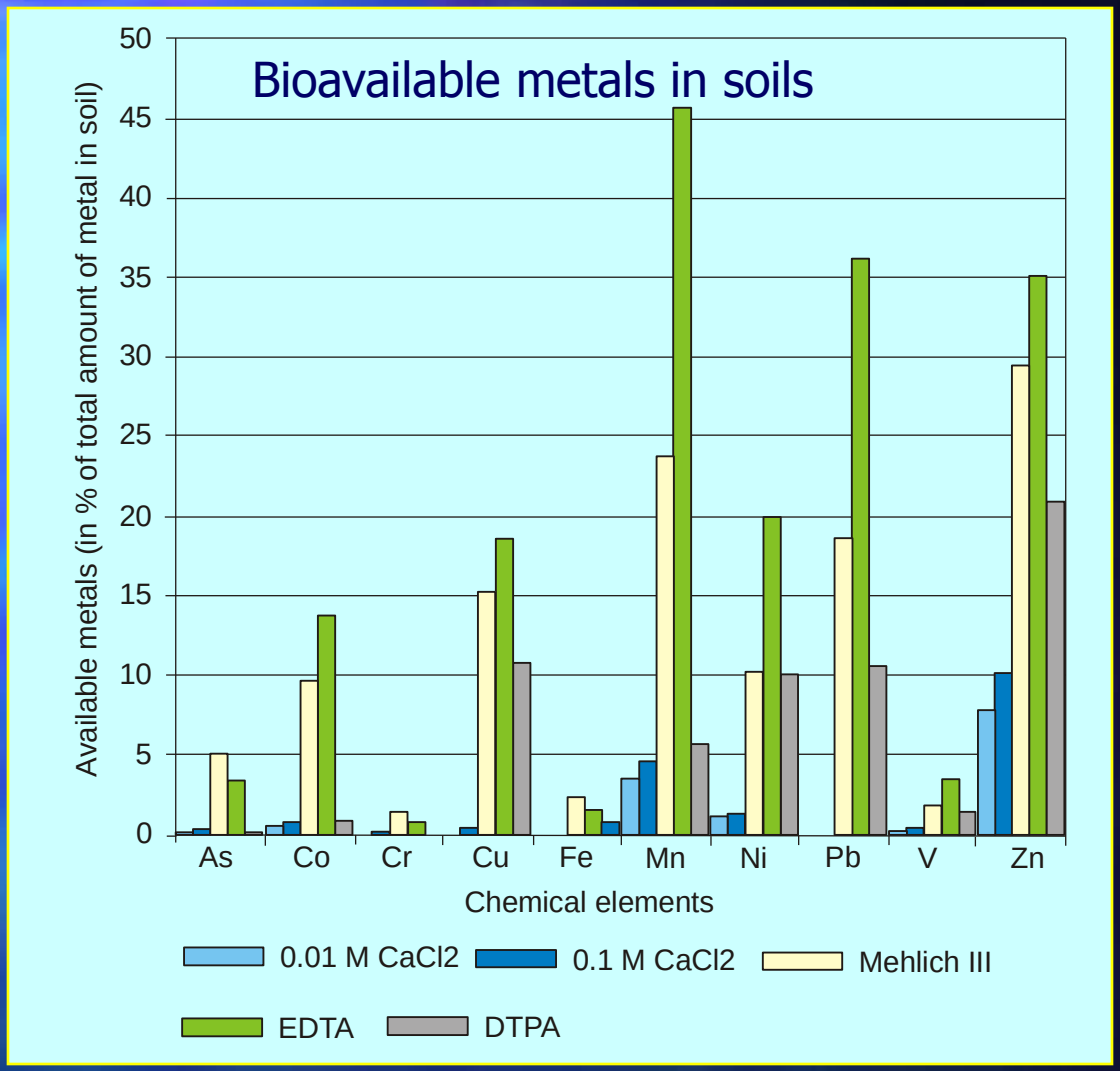
Significant correlation cassava-total metal in soil

	Root-Me$_{soil}$	Leaf-Me$_{soil}$
Cr		
Co		
Ni		
Cu	*0.5254*	
Zn		
Pb		
As		

Significant correlation cassava-biavailable metal in soil (EDTA)

	Root-Me$_{soil}$	Leaf-Me$_{soil}$
Cr		*-0.3301*
Co		**0.4868**
Ni		
Cu	**0.6134**	**0.5649**
Zn		**0.5262**
Pb		0.3701
As	0.3931	

values p < 0.05 values p < 0.01 **values p < 0.001**



Correlation between the contents of metals and arsenic in plants and soil is low obviously due to plowing or soil loosening during which the contaminated topsoil is mixed with deeper less contaminated layer of soil profile

COMPARISON WITH OTHER SITES

	Median Cu (mg.kg-1,dw)	Min-Max Cu (mg.kg-1, dw)	Reference
Cassava leaves, uncontaminated area, Nigeria	41.6	32.7-58.4	Chukwuma 1995
Cassava leaves, uncontaminated area, Copperbelt	20.1	2.1-252.4	This study
Cassava leaves, contaminated area, Copperbelt	**131.1**	**12.3-611.9**	This study
Cassava tubers, uncontaminated area, Nigeria	6.2	5.3-8.4	Nganje et al. 2000
Cassava tubers, uncontaminated area, Ghana	10.5	12.4-16.2	Boadi et al. 2009
Cassava tubers, uncontaminated area, Nigeria	12.4	10.7-18.9	Iyaka, 2007
Cassava tubers, uncontaminated area, Copperbelt	3.9	1.7-17.1	This study
Cassava tubers, contaminated area, Copperbelt	**8.4**	**2.3-92.9**	This study

The extremely high contents of copper in cassava leaves indicate that cassava is able to tolerate even extremely high contents of copper in soils in which it is grown.

Strategy adopted by plants to tolerate excess content of copper in soil:

- chelation of copper in the cytosol by peptides such as phytochelatins,
- repair of stress-damaged proteins,
- the compartmentation of metals in the vacuole by tonoplast-located transporters.

Dietary risk assessment

Highest tolerable intake limits for metals and metalloids
(after FAO/WHO Expert Committee on Food´s limits, JECFA, 2007)

Arsenic: weekly intake limit: 0.015 $mg.kg^{-1}$ of Human Body Weight (HBW)

Lead: weekly intake limit: 0.025 $mg.kg^{-1}$ HBW

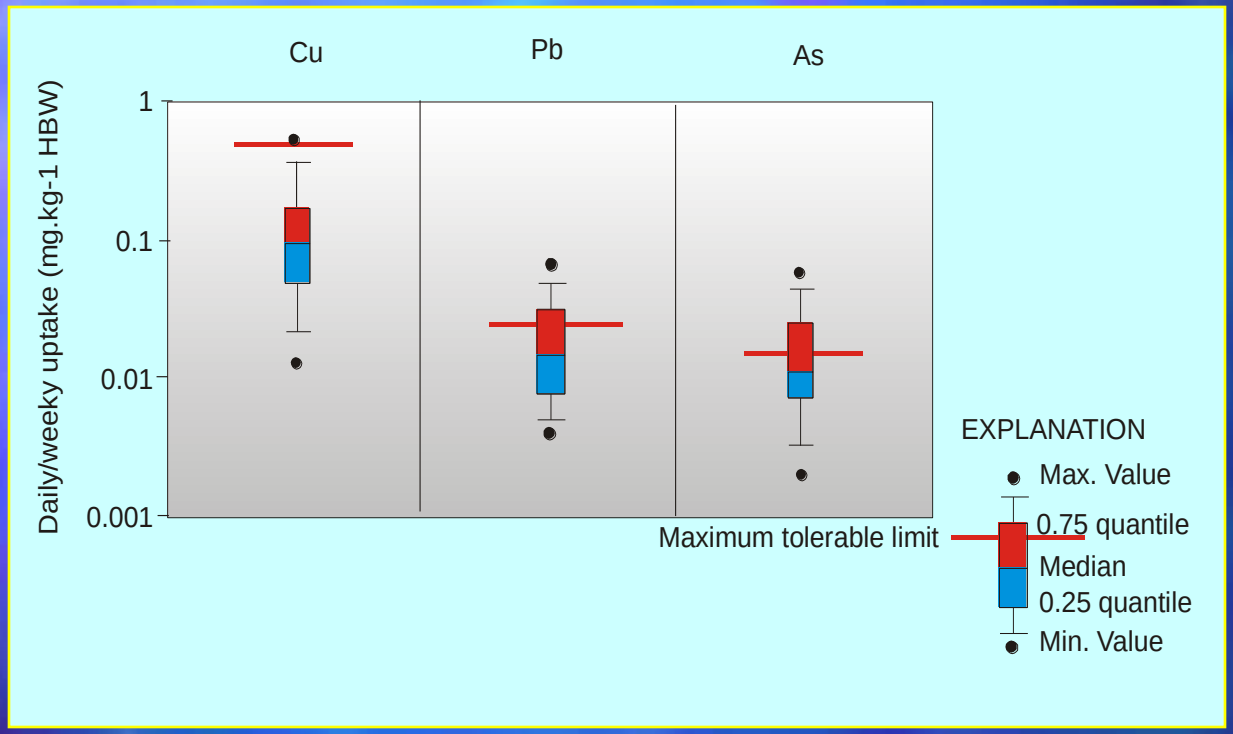
Copper: daily maximum tolerable limit: 0.5 $mg.kg^{-1}$ HBW

Estimation

Daily intake of cassava mush is estimated at 300 $g.d^{-1}$ (single meal)

The daily intake of cassava vegetable salad is estimated at 70 $g.d^{-1}$ (single meal).

The average weight (HBW) of Zambian rural population (adults) was estimated at 70 kg.

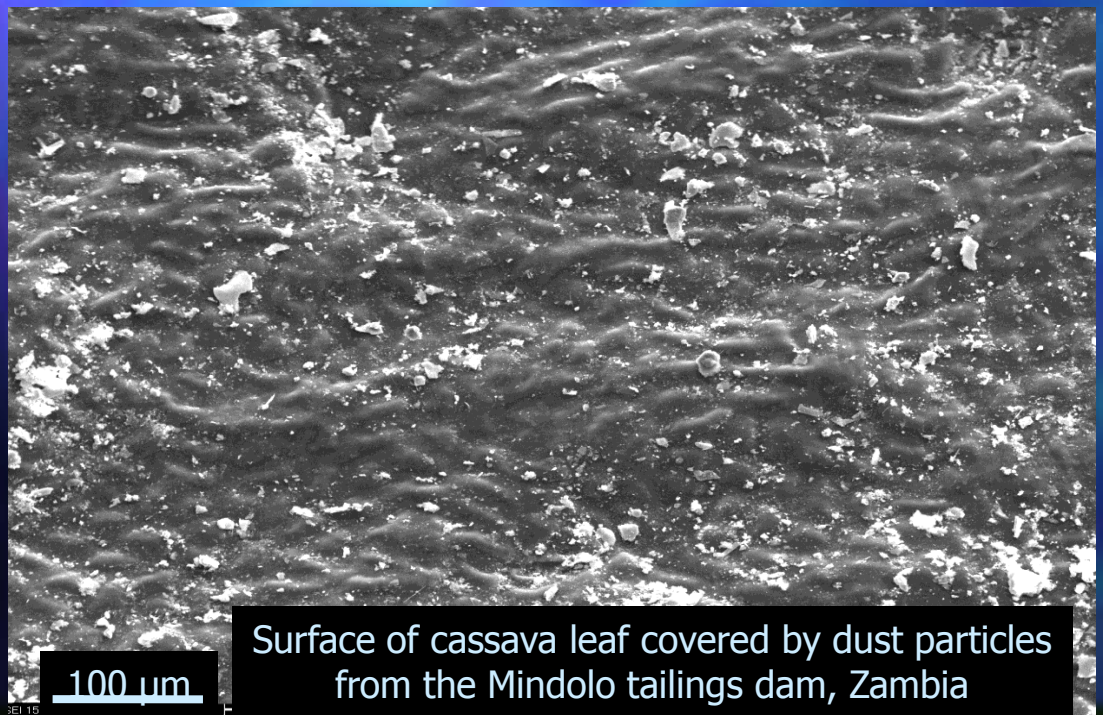


RESULTS OF THE DIETARY RISK ASSESSMENT (CASSAVA)

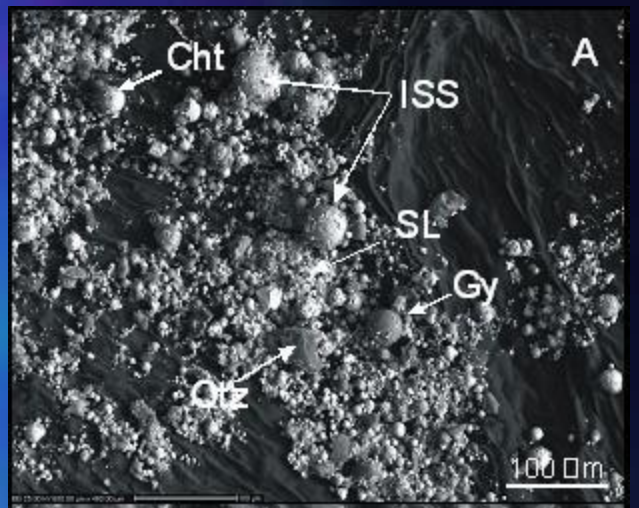
Cassava mush and cassava vegetable salad: Daily/weekly intake, Copperbelt	Cu (mg.kg-1 HBW, daily intake)	Pb (mg.kg-1 HBW, weekly intake)	As (mg.kg-1 HBW, weekly intake)
Minimum	0.013	0.005	0.002
Median	0.097	0.017	0.011
Maximum	0.592	0.063	0.062
MAX TOLERABLE INTAKE	**0.5**	**0.025**	**0.015**

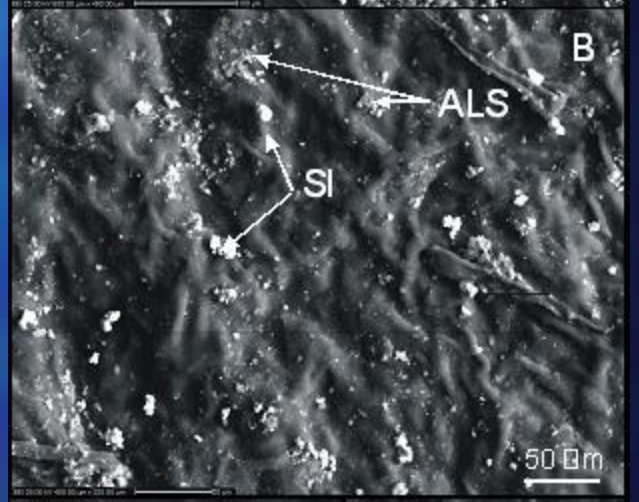
Surface contamination of the aboveground parts of vegetables by dust

The health risk linked with the intake of metals and arsenic from crop plants might be substantially higher when poorly washed leaves are used for preparation of salads.



Surface of cassava leaf covered by dust particles from the Mindolo tailings dam, Zambia





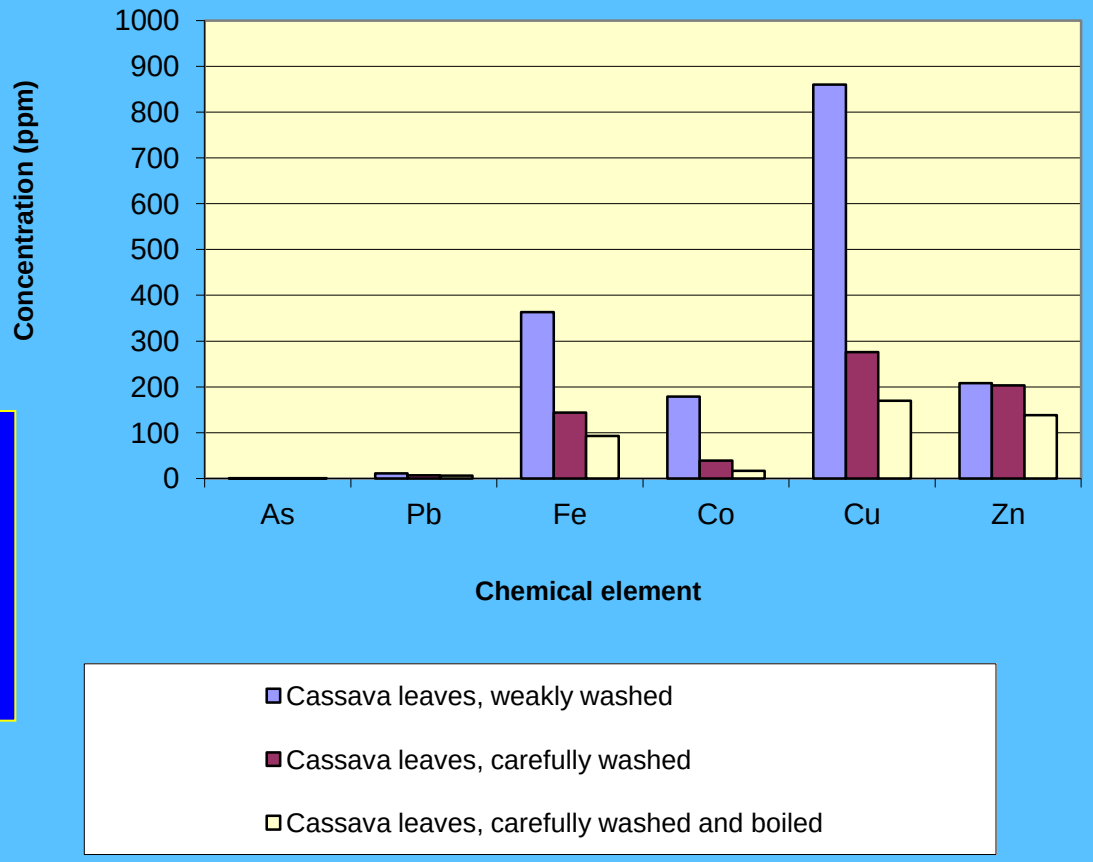




Chalcantite particle **Copper particle**

CONTAMINATION OF LEAVES BY DUST PARTICLES AND EFFECT OF WASHING

The amount of dust on surface of the leaves can be significantly reduced by their thorough washing when fresh vegetable salads are being prepared



CONCLUSIONS:

- **Because of strong contamination of some parts of the Zambian Copperbelt mining district caused by the extraction and processing of copper ores, the local soils and crop plants in contaminated areas contain high concentrations of copper.**

- **The leaves of both cassava and sweet potatoes in contaminated areas also contain higher contents of zinc, cobalt and arsenic, whereas the content of lead is low and more or less the same in plants from both contaminated and uncontaminated areas.**

- **The contents of metals in tubers of cassava and sweet potatoes are much lower than their contents in their leaves.**

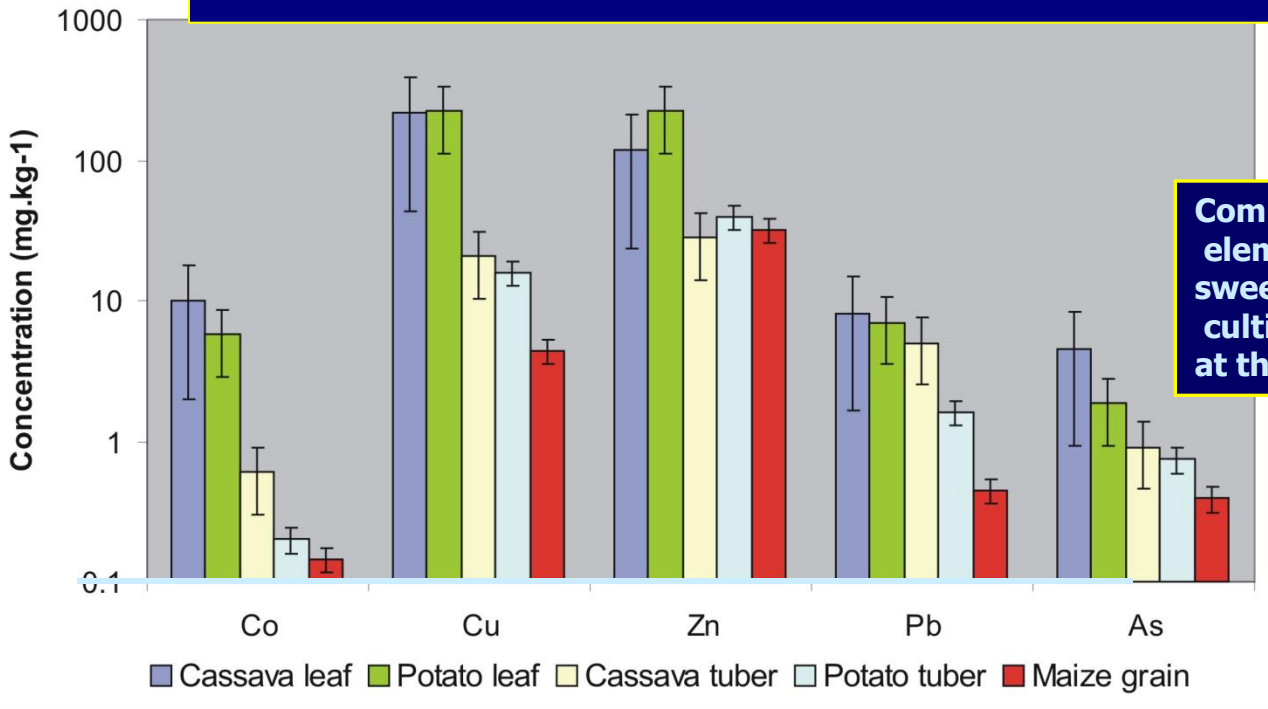
- **The values of correlation coefficients between individual metals and arsenic in soil and crop plants were found to be low at individual sampling sites. This is believed to be due to the mixing of strongly contaminated topsoil with the deeper horizons in the soil profile caused by hoeing.**

- **The dietary risk assessment has not indicated any excessive intake of copper, but excessive intake of Pb and As was occasionally recorded in contaminated areas of the Zambian Copperbelt.**

CONCLUSIONS:

- **The surfaces of cassava leaves are strongly contaminated by metalliferous dust particles in polluted areas and there is still a significant risk of ingesting dangerous levels of copper, lead and arsenic if dishes are prepared with poorly washed foliage.**

- **Compared with cassava tubers and particularly with cassava leaves, the grains of maize contain very low contents of metals and arsenic even in strongly contaminated areas. Therefore, planting of maize is recommended instead of growing cassava or sweet potato in areas strongly affected by contamination.**



Comparison of average contents of elements in leaves and tubers of cassava, sweet potatoes and in grains of maize cultivated near the Nkana smelter at the city of Kitwe, Zambia.



Thank you for your attention

ANNEX B1

GUIDES TO ESTIMATE THE PROBABILITY INDEX FOR EACH CONTAMINATION HAZARD SCENARIO

ANNEX B1
GUIDES TO ESTIMATE THE PROBABILITY INDEX FOR EACH CONTAMINATION HAZARD SCENARIO

Component	Installations Deposits Works	Code	Contamination Hazard Scenario	Medium Susceptible to Contamination	PI Estimation Guide
MINE	Underground Workings	CHS 1	Presence of drainage that has in the past, or could in future contaminate **surface water**, affecting people, the environment and/or economic activities.	Surface water	GUIDE 1
		CHS 2	Infiltration of drainage that has in the past, or could in future contaminate **groundwater**, affecting people, the environment and/or economic activities.	Groundwater	GUIDE 2
		CHS 3	Presence of contaminated water in underground mine workings that could be used for drinking water or other uses (irrigation, bathing, livestock).	Not applicable	GUIDE 3
	Open Pit	CHS 1	Presence of drainage that has in the past, or could in future contaminate **surface water**, affecting people, the environment and/or economic activities.	Surface water	GUIDE 1
		CHS 2	Infiltration of drainage that has in the past, or could in future contaminate **groundwater**, affecting people, the environment and/or economic activities.	Groundwater	GUIDE 2
		CHS 3	Presence of contaminated water the open pit that could be used for drinking water or other uses (irrigation, bathing, livestock).	Not applicable	GUIDE 3
PLANTS	Processing Plants	CHS 3	Presence of contaminated water in the plant area that could be used for drinking water or other uses (irrigation, bathing, livestock).	Not applicable	GUIDE 3
		CHS 4	Movement of remnant hazardous waste from contaminated structures, machinery or soil that has in the past, or could in future pollute **surface water**, affecting people, the environment and/or economic activities.	Surface water	GUIDE 4

Component	Installations Deposits Works	Code	Contamination Hazard Scenario	Medium Susceptible to Contamination	PI Estimation Guide
PLANTS	Processing Plants	CHS 5	Movement of remnant hazardous waste from contaminated structures, machinery or soil that has in the past, or could in future pollute **groundwater**, affecting people, the environment and/or economic activities.	Groundwater	GUIDE 5
		CHS 6	Movement of remnant hazardous waste from contaminated structures, machinery or soil that has in the past, or could in future pollute the **soil** and affect people (by ingestion or skin contact), the environment and/or economic activities.	Soil	GUIDE 6
		CHS 8	Movement of particulate matter by wind action that has in the past, or could in future affect people (by inhalation), the environment and/or economic activities.	Air	GUIDE 8
		CHS 9	Ingestion, inhalation or dermal contact with hazardous waste.	Not applicable	GUIDE 9
LARGE SCALE MINING WASTE	Tailings Dams and Impoundments Heap Leach Waste Dumps for Waste Rock, Low Grade Ore	CHS 1	Presence of drainage that has in the past, or could in future contaminate **surface water**, affecting people, the environment and/or economic activities.	Surface water	GUIDE 1
		CHS 2	Infiltration of drainage that has in the past, or could in future contaminate **groundwater**, affecting people, the environment and/or economic activities.	Groundwater	GUIDE 2
		CHS 3	Presence of contaminated water in tailings ponds, slurry dams etc., that could be used for drinking water or other uses (irrigation, bathing, livestock).	Not applicable	GUIDE 3
		CHS 7	Activities carried out on the surface of tailings deposits or contaminated soil that could affect people (through inhalation, accidental ingestion or skin contact), the environment and/or economic activities.	Soil	GUIDE 7

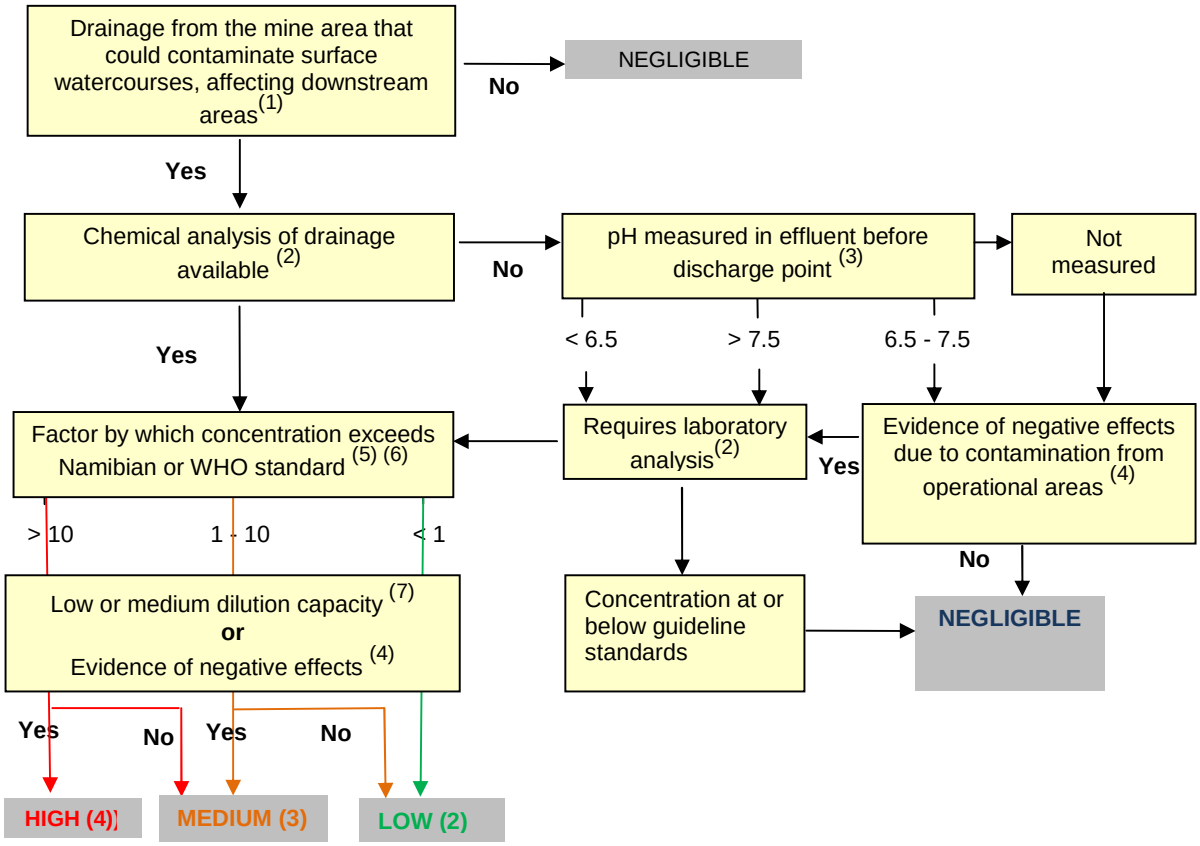
Component	Installations Deposits Works	Code	Contamination Hazard Scenario	Medium Susceptible to Contamination	PI Estimation Guide
		CHS 8	Movement of particulate matter by wind action that has in the past, or could in future affect people (from inhalation), the environment and/or economic activities.	Air	GUIDE 8
SMALL SCALE MINING WASTE AND INDUSTRIAL WASTE SMALL SCALE MINING WASTE AND INDUSTRIAL WASTE	Small scale mining waste dumps and Industrial Waste Dumps	CHS 1	Presence of drainage that has in the past, or could in future contaminate **surface water**, affecting people, the environment and/or economic activities.	Surface water	GUIDE 1
		CHS 2	Seepage that has in the past, or could in future contaminate **groundwater**, affecting people, the environment and/or economic activities.	Groundwater	GUIDE 2
		CHS 3	Presence of contaminated water in mine works that could be used for drinking water or other uses (irrigation, bathing, livestock).	Not applicable	GUIDE 3
		CHS 4	Movement of remnant hazardous waste from contaminated structures, machinery or soil that has in the past, or could in future pollute **surface water**, affecting people, the environment and/or economic activities.	Surface water	GUIDE 4
		CHS 5	Movement of remnant hazardous waste from contaminated structures, machinery or soil that has in the past, or could in future pollute **groundwater**, affecting people, the environment and/or economic activities	Groundwater	GUIDE 5
		CHS 6	Movement of remnant hazardous waste from contaminated structures, machinery or soil that has in the past, or could in future pollute the **soil** and affect people (by ingestion or skin contact), the environment and/or economic activities.	Soil	GUIDE 6
		CHS 7	Activities carried out on the surface of waste dumps or contaminated soil that could affect people (through inhalation, accidental ingestion or skin contact), the environment and/or economic activities.	Soil	GUIDE 7

Component	Installations Deposits Works	Code	Contamination Hazard Scenario	Medium Susceptible to Contamination	PI Estimation Guide
		CHS 8	Movement of particulate matter by wind action that could affect people (from inhalation), the environment and/or economic activities.	Air	GUIDE 8
		CHS 9	Ingestion, inhalation or dermal contact with hazardous waste.	Not applicable	GUIDE 9
ASSOCIATED INFRA-STRUCTURE	Workshops and Storehouses Power Lines and Substations	CHS 3	Presence of water in water storage structures that may be polluted, which could be used for drinking water or other uses (irrigation, bathing, livestock).	Not applicable	GUIDE 3
		CHS 4	Movement of remnant hazardous waste from contaminated structures, machinery or soil that has in the past, or could in future pollute **surface water**, affecting people, the environment and/or economic activities.	Surface water	GUIDE 4
	Workshops and Storehouses Power Lines and Substations	CHS 5	Movement of remnant hazardous waste from contaminated structures, machinery or soil that has in the past, or could in future pollute **groundwater**, affecting people, the environment and/or economic activities	Groundwater	GUIDE 5
		CHS 6	Movement of remnant hazardous waste from contaminated structures, machinery or soil that has in the past, or could in future pollute the **soil** and affect people (by ingestion or skin contact), the environment and/or economic activities.	Soil	GUIDE 6
		CHS 9	Ingestion, inhalation or dermal contact with hazardous waste.	Not applicable	GUIDE 9

GUIDE TO ESTIMATE CONTAMINATION PROBABILITY	Facilities/stockpiles/operational areas	GUIDE 1

HAZARD SCENARIO 1 (CHS1): Presence of drainage that could contaminate **surface water**, affecting people, the environment or economic activity (see Annex B2, section B.2.3).

ENVIRONMENTAL RESOURCE: SURFACE WATER



(1) Consideration must be given to any potentially contaminated water from the mine, tailings deposits, waste rock or mineral stockpiles or dumps, heap leach dumps, etc., that may drain beyond the limits of the operational area, due to the movement of contaminants by rain or surface runoff.

(2) It is necessary to know at least the concentrations of those chemicals of potential concern in the drainage that are associated with the type of mining operation.

(3) The measurement must be made at the point where the drainage exits the area of the facility, stockpile or operational area, and if this is not possible, at the closest feasible point to that point.

(4) A determination must be made as to whether there is evidence that contamination from the operational area negatively affects any recipient – e.g., stressed vegetation, dead fish, birds and animals, salt crusts, visible indications in soil or water, press reports, and reports and studies by public agencies or universities.

(5) The factor by which the contaminant's concentration in the effluent exceeds its guideline concentration must be established (see Annex C1).

(6) Compare concentrations to Namibian water quality standards, WHO guidelines values or other relevant standards.

(7) Dilution capacity is to be considered low to medium when the receiving water course's available flow is 1 to 100 times greater than the average monthly flow of the drainage.

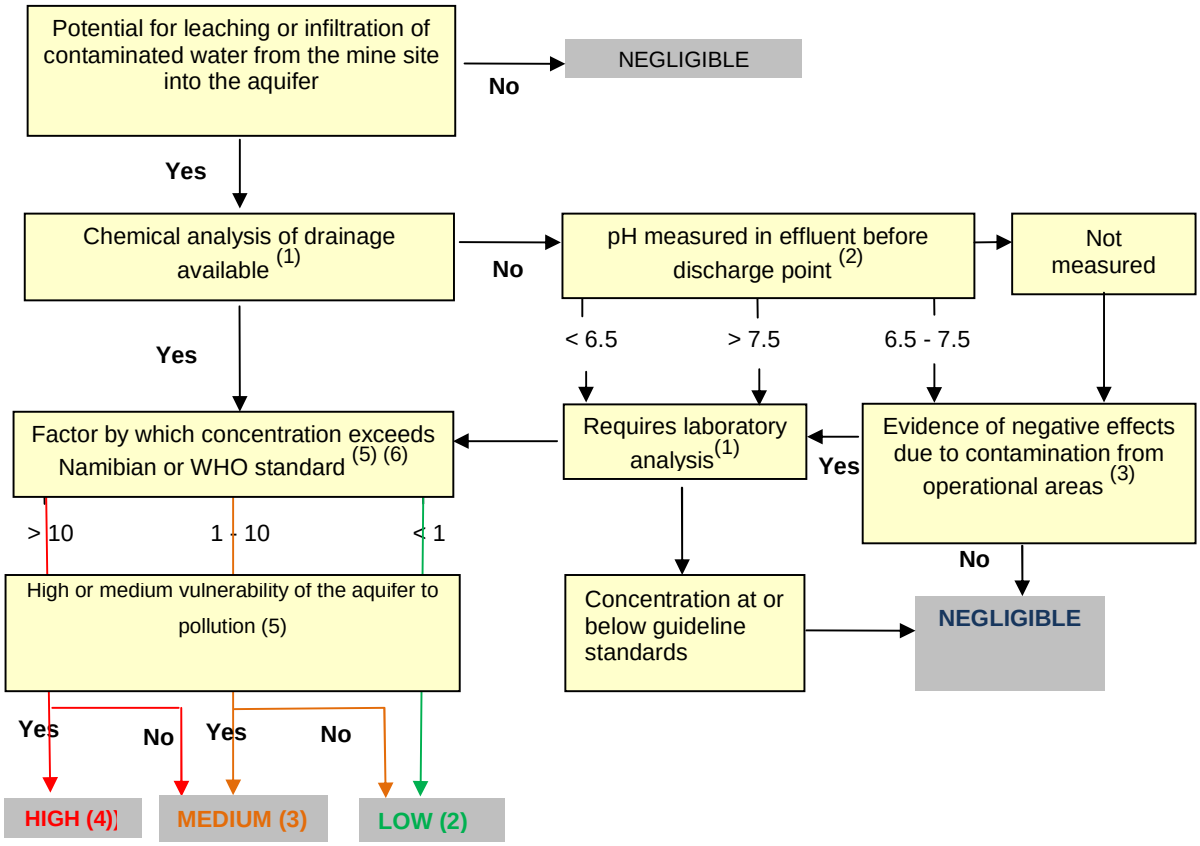
GUIDE TO ESTIMATE CONTAMINATION PROBABILITY	Facilities/stockpiles/operational areas	GUIDE 1

Comments Add comments on assumptions, data and criteria used in applying the Guide.

GUIDE FOR ESTIMATING INDEX OF PROBABILITY OF CONTAMINATION	Facility, stockpile, or operational area	GUIDE 2

HAZARD SCENARIO 2 (CHS2): Infiltration of drainage that could contaminate **groundwater**, affecting people, the environment or economic activity (see Annex B2, section B.2.3)

ENVIRONMENTAL RESOURCE: GROUNDWATER



(1) It is necessary to know at least the concentrations of those "chemicals of potential concern" in the drainage identified in Chapter 6, Table 6.2 and for which Namibian standards are available or other guidelines.

(2) The measurement must be made at a point that is representative of the drainage leaching into the groundwater.

(3) There is evidence that contamination from the operational area negatively effects recipients – e.g., stressed vegetation, visible indications in soil or water, press reports, and reports and studies by public agencies or universities.

(4) The factor by which the concentration exceeds the guideline is the ratio of the contaminant's concentration in the effluent to the guideline concentration.

(5) Consider factors such as the permeability of the subsoil, the geology and buffering capacity, the depth of the aquifer, the volume of the waste, the potential receptors, etc.

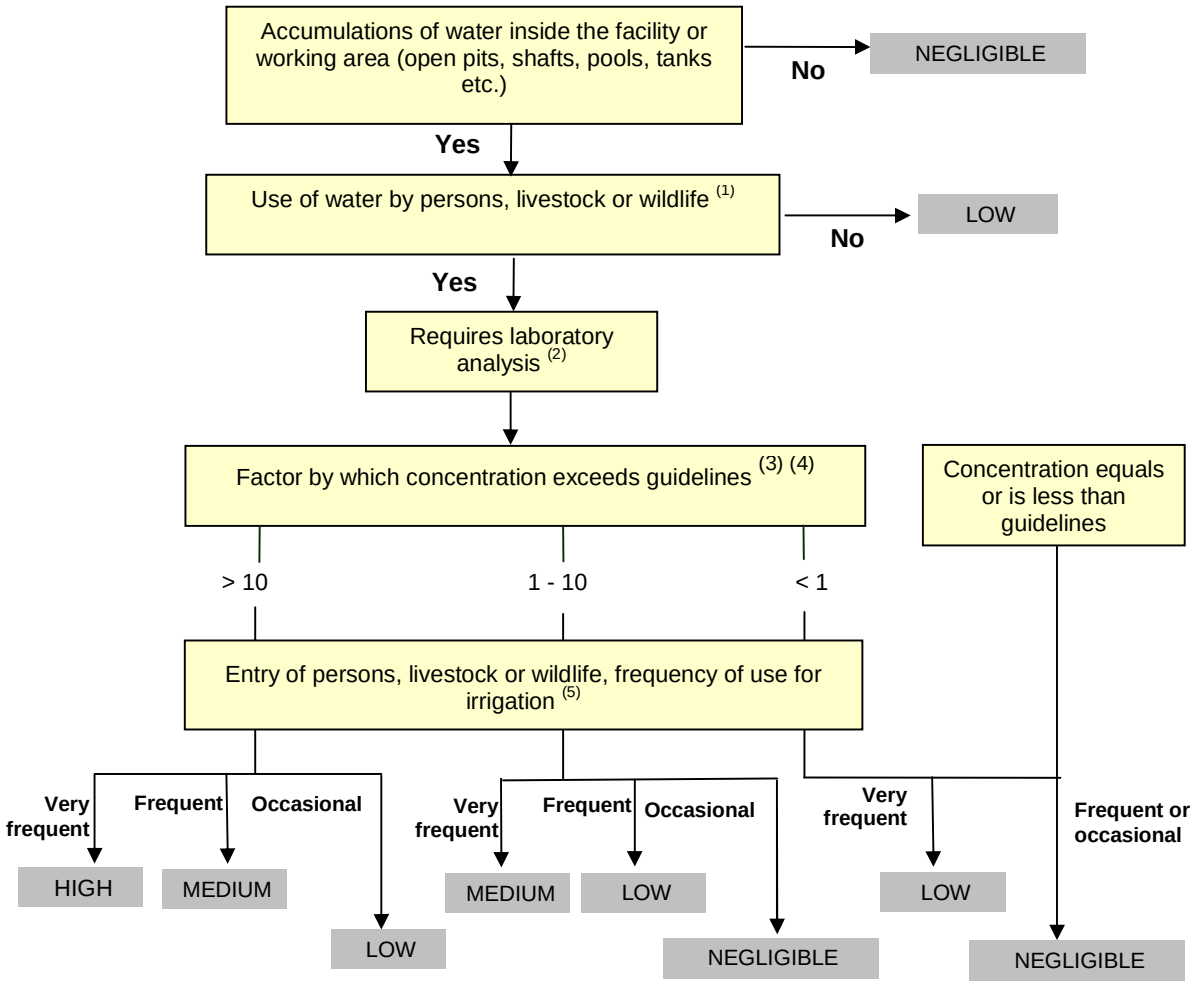
GUIDE FOR ESTIMATING INDEX OF PROBABILITY OF CONTAMINATION	Facility, stockpile, or operational area	GUIDE 2

Comments Add comments on assumptions, data and criteria used to apply the guide

GUIDE FOR ESTIMATING INDEX OF PROBABILITY OF CONTAMINATION	Facility, stockpile, or operational area	GUIDE 3

HAZARD SCENARIO 3 (CHS3): Presence of contaminated water on the mine site that could be used for drinking water or other uses (irrigation, bathing, drinking water for livestock and wildlife).

ENVIRONMENTAL RESOURCE: SURFACE WATER



(1) Persons use the accumulated water for drinking, bathing, irrigation or other uses. Wild animals or livestock enter to drink.

(2) It is necessary to know at least the concentrations of those chemicals of potential concern in the drainage that are associated with the mining activity.

(3) The factor by which the concentration exceeds the guideline is the ratio of the contaminant's concentration in the effluent to its guideline.

(4) If persons are recipients, consider the WHO Guideline Values, the Namibian Drinking Water Quality standards or any of the other guidelines presented in Annex C1). For aquatic fauna and terrestrial fauna, consult the South African Guidelines for aquatic ecosystems and livestock watering (Annex C1)

(5) **Very frequent**: Entry on a daily basis (or most days per week); year-round irrigation use
Frequent: Some days each month (e.g. on weekends); irrigation use only during the dry season
Occasional: Few or very few entries over the course of the year; only occasional use of water for irrigation.

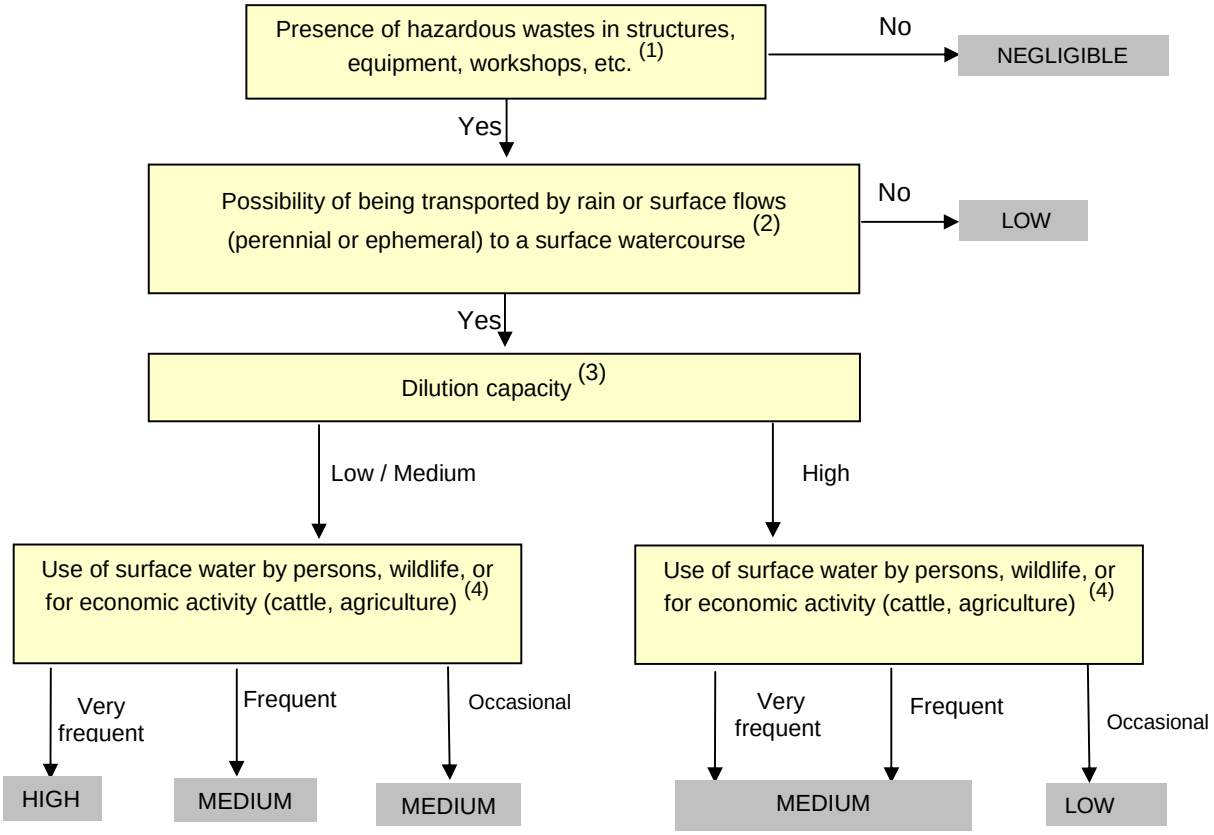
GUIDE FOR ESTIMATING INDEX OF PROBABILITY OF CONTAMINATION	Facility, stockpile, or operational area	**GUIDE 3**

Comments Add comments on assumptions, data and criteria used to apply the guide

GUIDE FOR ESTIMATING INDEX OF PROBABILITY OF CONTAMINATION	Facility, stockpile, or operational area	GUIDE 4

HAZARD SCENARIO 4 (CHS4): Flow of water over sources of contamination (e.g. hazardous wastes, hydrocarbon spills, contaminated structures, machinery or soil) that could pollute **surface water**, affecting people, the environment and/or economic activities (see Annex B2, section B.2.3).

ENVIRONMENTAL RESOURCE: SURFACE WATER



(1) The Assessor must indicate the presence of wastes that may be hazardous and assess the amount to judge the potential for contamination of nearby waterways. When there is doubt as to the hazardousness of the waste, it must be sampled for chemical analysis.

(2) The Assessor should determine the feasibility of hazardous wastes reaching surface waterways. The proximity of the latter should be evaluated, as well as slopes, absence of obstacles, the integrity and state of the container or dump, etc.

(3) An estimate must be made of the flow that is moving, or may eventually move, the hazardous constituents from the waste and this must be compared with the flow of the receiving waterway during the least favourable time of year. The dilution capacity is:

Low: when the receiving waterway's flow is 1 to 10 times greater than the flow moving the wastes.
Medium: when the receiving waterway's flow is 10 to 100 times greater than the flow moving the wastes.
High: when the receiving waterway's flow is 100 to 1000 times greater than the flow moving the wastes.

(4) Very frequent: Daily use of water
Frequent: Water used on several days each month e.g. on weekends
Occasional: Water only used on a few days per year.

Note: In the case of assessment of impacts on aquatic receptors, use "very frequent".

Comments

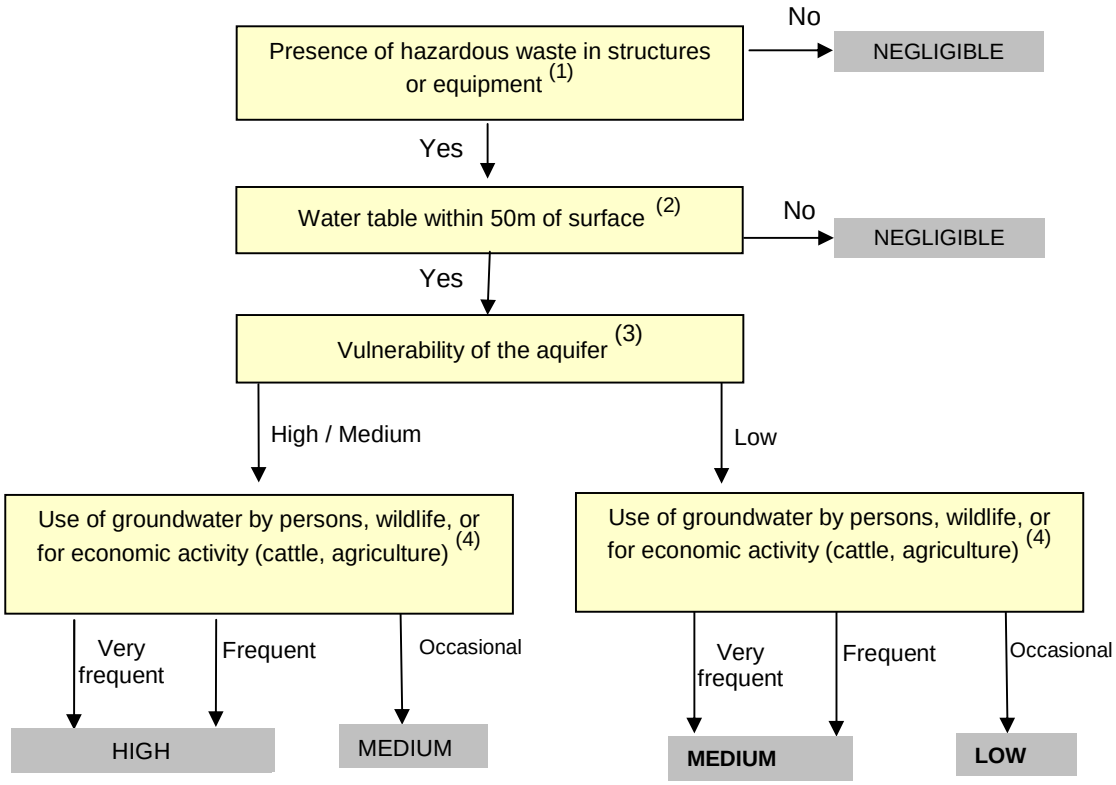
GUIDE FOR ESTIMATING INDEX OF PROBABILITY OF CONTAMINATION	Facility, stockpile, or operational area	**GUIDE 4**

Add comments on assumptions, data and criteria used to apply the guide

GUIDE FOR ESTIMATING INDEX OF PROBABILITY OF CONTAMINATION	Facility, stockpile, or operational area	GUIDE 5

HAZARD SCENARIO 5 (CHS5): Flow of water over sources of contamination (e.g. hazardous wastes, hydrocarbon spills, contaminated structures, machinery or soil) that could infiltrate the ground and pollute the **groundwater**, affecting people, the environment and/or economic activities (see Annex B2, section B.2.3).

ENVIRONMENTAL RESOURCE: GROUNDWATER



(1) The Assessor must indicate the presence of wastes that may be hazardous and assess the volume to judge the potential for contamination of groundwater. When there is doubt as to the hazardousness of the waste, it must be sampled for chemical analysis.

(2) Information can be obtained from nearby wells, hydrological maps, official information from the DWA, field interviews, proximity of bodies of water, etc.

(3) Considering factors such as the permeability of the subsoil, the geology, buffering capacity, the depth of the aquifer, the volume of the waste, presence of receptors etc.

(4) **Very frequent**: Daily use of water.
Frequent: Water used on several days per month.
Occasional: Water only used on a few days per year.

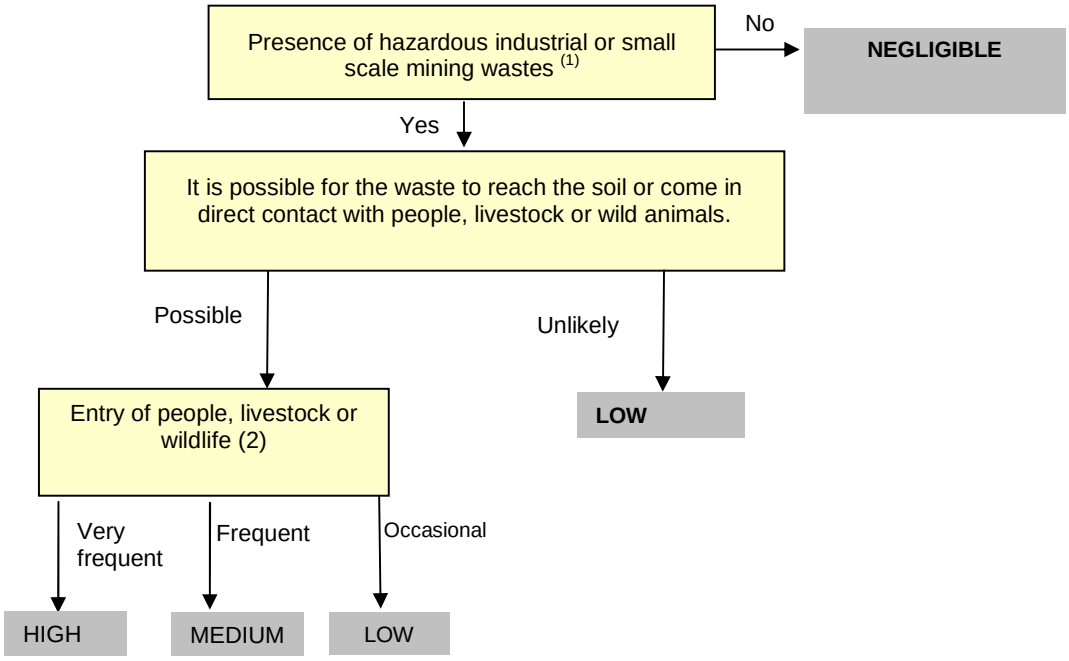
GUIDE FOR ESTIMATING INDEX OF PROBABILITY OF CONTAMINATION	Facility, stockpile, or operational area	**GUIDE 5**

Comments Add comments on assumptions, data and criteria used to apply the guide

GUIDE FOR ESTIMATING INDEX OF PROBABILITY OF CONTAMINATION	Facility, stockpile, or operational area	GUIDE 6

HAZARD SCENARIO 6 (CHS6): Flow of water over sources of contamination (e.g. hazardous wastes, hydrocarbon spills, contaminated structures, machinery or soil) that could infiltrate the ground and pollute the **soil**, affecting people, the environment and/or economic activities.

ENVIRONMENTAL RESOURCE: SOIL



(1) The classification of a waste as hazardous is provided in the draft Pollution and Waste Management Bill or as per the classification in the IMDG Code.

(2) **Very frequent**: Daily entries or most days per week.
Frequent: Some days each month.
Occasional: Few or very few entries over the course of the year.

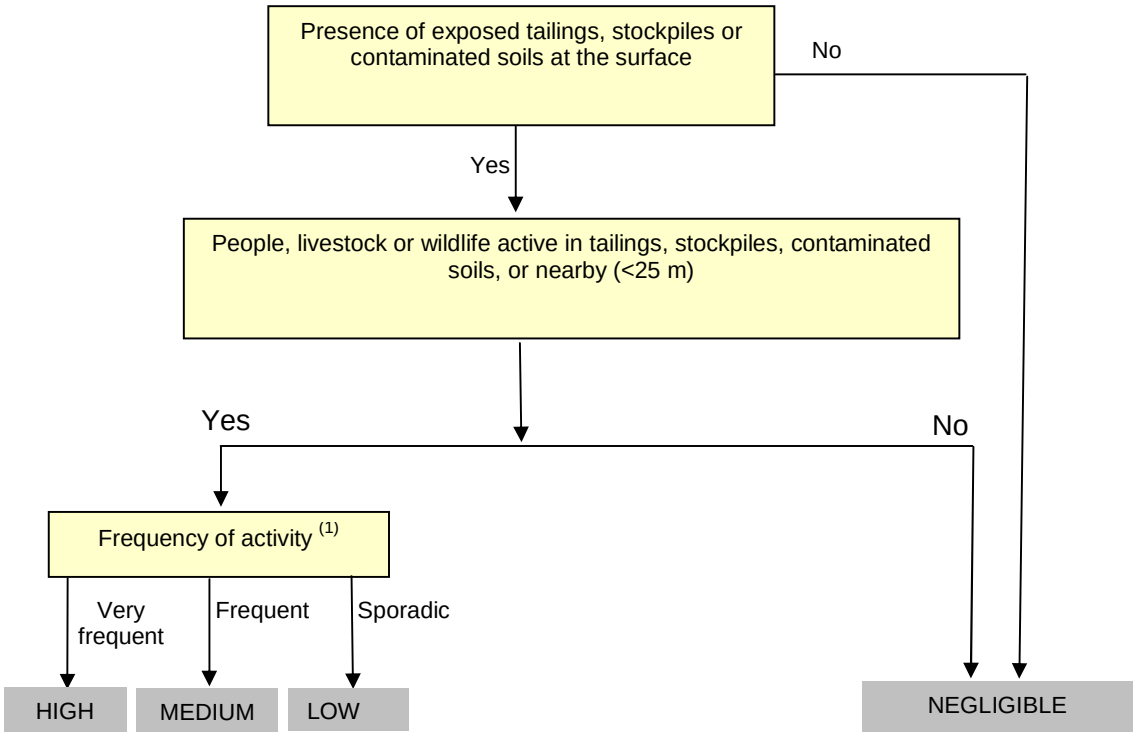
GUIDE FOR ESTIMATING INDEX OF PROBABILITY OF CONTAMINATION	Facility, stockpile, or operational area	**GUIDE 6**

Comments Add comments on assumptions, data and criteria used to apply the guide

GUIDE FOR ESTIMATING INDEX OF PROBABILITY OF CONTAMINATION	Tailings deposits	GUIDE 7

HAZARD SCENARIO 7 (CHS7): Activities carried out on the surface of tailings deposits or contaminated soil that could affect people (through inhalation, accidental ingestion or skin contact), the environment and/or economic activities.

ENVIRONMENTAL RESOURCE: SOIL



(1) **Very frequent:** Daily entries or most days per week.
Frequent: Some days each month e.g. on weekends.
Sporadic: Few or very few entries over the course of the year.

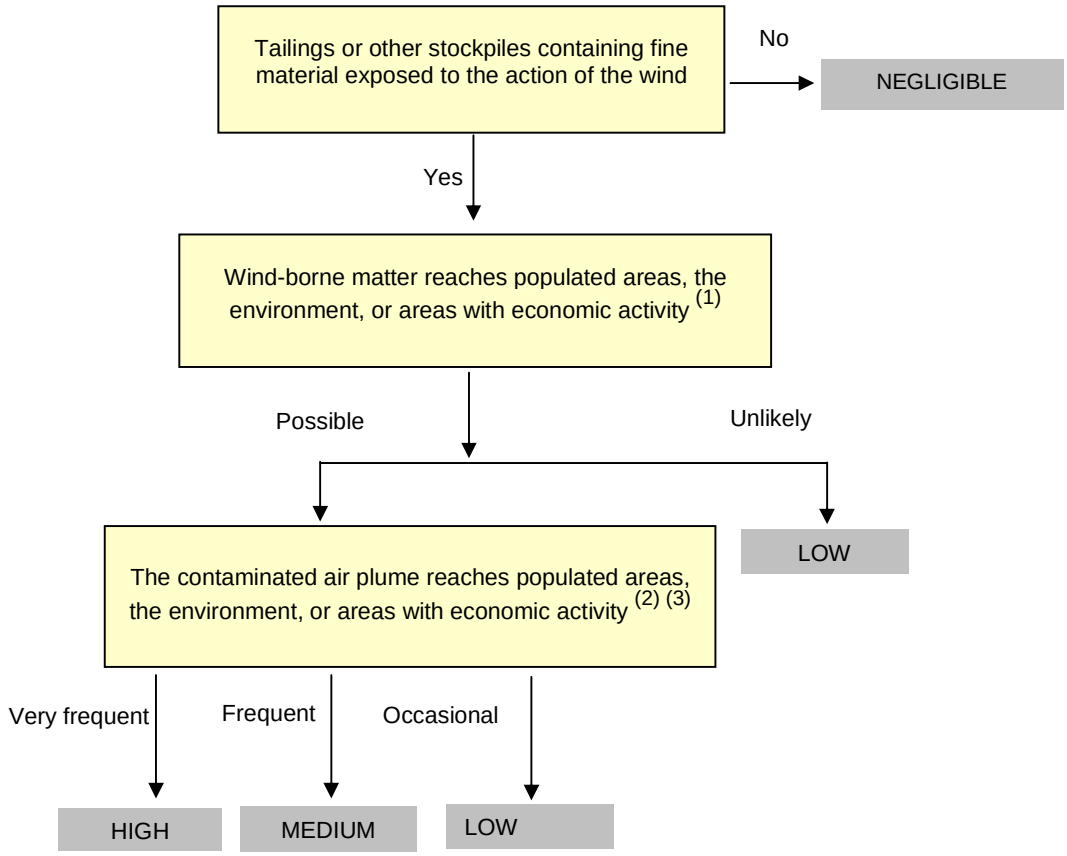
GUIDE FOR ESTIMATING INDEX OF PROBABILITY OF CONTAMINATION	Tailings deposits	GUIDE 7

Comments Add comments on assumptions, data and criteria used to apply the guide

GUIDE FOR ESTIMATING INDEX OF PROBABILITY OF CONTAMINATION	Facility, stockpile, or working area	GUIDE 8

HAZARD SCENARIO 8 (CHS8): Movement of particulate matter by wind action that could affect people (from inhalation), the environment and/or economic activities (see Annex B2, section B.2.4).

ENVIRONMENTAL RESOURCE: AIR



(1) The Assessor must determine the possibility that the particulate material may reach people, the environment, or affect economic activities. Factors to be considered include distance from recipients, volume of deposit, particle size, moisture content, the wind direction and velocity, etc.

(2) Examples of evidence are complaints by nearby inhabitants, accumulation of particulate matter on vegetation and/or crops, visible dust plumes, etc.

(3) **Very frequent**: Blowing dust is visible daily or most days per week.
Frequent: Blowing dust is visible on a few days each month.
Occasional: Blowing dust occurs on a few days per year.

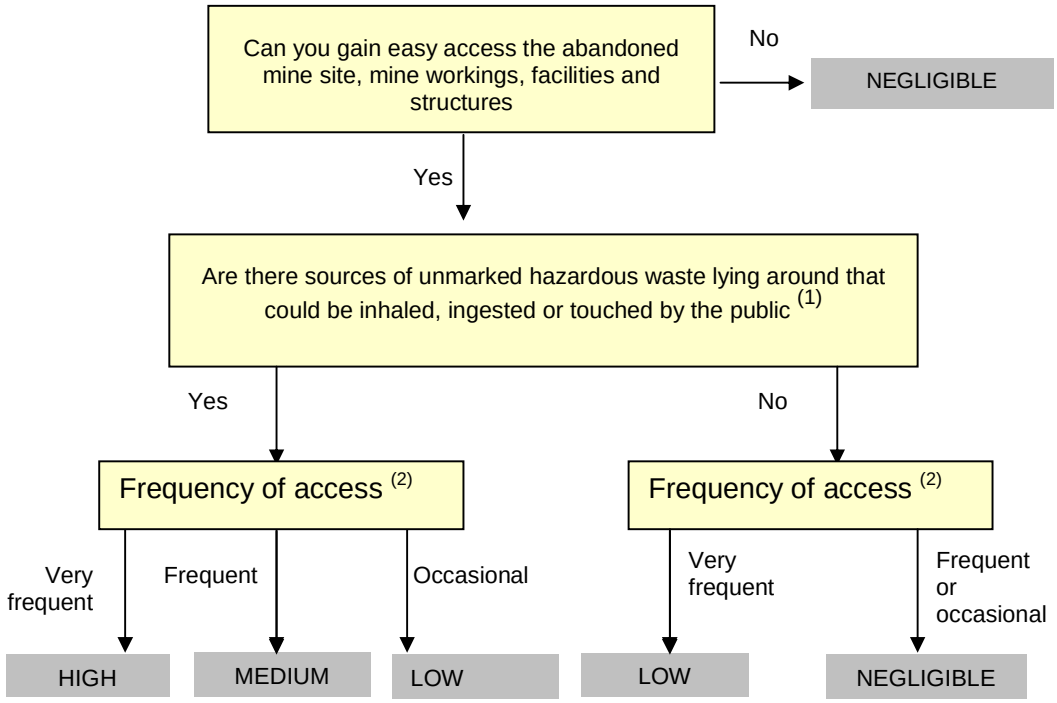
GUIDE FOR ESTIMATING INDEX OF PROBABILITY OF CONTAMINATION	Facility, stockpile, or working area	**GUIDE 8**

Comments Add comments on assumptions, data and criteria used to apply the guide

GUIDE FOR ESTIMATING INDEX OF PROBABILITY OF CONTAMINATION	Facility, stockpile, or working area	GUIDE 9

HAZARD SCENARIO 9 (CHS9): Ingestion, inhalation or dermal contact with hazardous waste.

PEOPLE



(1) The Assessor must determine the possibility that the public could come into contact with hazardous wastes. This is especially true for children who may use the site as a play area and may inhale, ingest and touch hazardous substances. It is also possible that scavengers may remove asbestos sheeting, contaminated equipment of otherwise remove hazardous substances without proper PPE or knowledge of the inherent health risks. See Annex B2, section B.2.2 for more information.

(2) **Very frequent**: Site is visited on a daily basis or on most days per week.
Frequent: Site is visited on a few days per month (e.g. on weekends).
Occasional: Site is visited only a few times per year.

ANNEX B2

SUPPORTING MATERIAL FOR THE SIMPLIFIED CONTAMINATION RISK ASSESSMENT

ANNEX B2

SUPPORTING MATERIAL FOR THE SIMPLIFIED CONTAMINATION RISK ASSESSMENT

B.2.1 Acidity and alkalinity

Acid Rock Drainage (ARD) is produced by chemical and biological oxidation of sulphide, creating a sulphate acid solution that has a significant impact on the environment. In acidic conditions (pH <5.5) metal ions and toxic salts are brought into solution, the activity of micro-organisms, the agents of breakdown and decay, is restricted, and shortages of available calcium and phosphate are induced in soils. In acidic water and soil, toxic concentrations of aluminium, iron and manganese are commonplace and other metals, such as Cu, Pb, Cd, may be present in toxic concentrations (Williamson, Johnson and Bradshaw, 1982).

The main source of acidity in mine wastes and water is iron pyrite. This may be present in three common forms: pyrite (Fe_2), marcasite (FeS_2) and pyrrhotite (Fe_nS_{n+1}). Each of these weathers at a different rate, with marcasite oxidizing nine times faster than pyrite and pyrrhotite eighteen times faster. Pyrite bearing wastes disposed of at neutral or slightly alkaline pH can weather within months or years to produce extreme acidity, assisted by the ferrous-ion oxidizing bacteria, *Thiobacillus ferrox-idans*, which thrives at pH 1.5 – 3.0 (Williamson, Johnson and Bradshaw, 1982).



Runoff and seepage from the pyritic tailings at Otjihase are causing pollution in the nearby river. Note the formation of salts. The reddish colour is from iron precipitation.

The rate of oxidation in mine wastes and in underground workings is influenced by the surface area of the material available for weathering; small particulates such as mill tailings weather faster than larger pieces of rock. Humidity, oxygen concentration, pH and the presence of sulphur oxidizing bacteria all influence the oxidation rate (Williamson, Johnson and Bradshaw, 1982).

In the case of rock fractures that contain acid-generating minerals, acid drainage occurs on their faces and other areas that are exposed to oxidation. Generally, infiltrating rainwater is the medium that carries the dissolved metals. Additionally, if the mine progressed below the level of the water table, it is normal for the water table to recover once the mine is closed and thus groundwater will come into contact with acid-generating materials. Water carrying dissolved metals can move towards the regional groundwater aquifer or daylight on surface causing contamination in groundwater or in surface water bodies respectively. The severity of the pollution will depend on a number of factors such as mean annual precipitation, dilution factors in the receiving water body and the buffering or neutralizing capacity of the host rock and/or receiving aquifers.

Considering that the sites covered in this Handbook have been abandoned or shut down and have been out of operation for several years, acid mine drainage may become a major long-term problem since there is no longer any active dewatering of the underground workings. This means that groundwater will slowly build up underground and its residence time in contact with acid-generating materials will exacerbate the problem.

The main evidence that acid drainage is occurring is the pH of the water that drains out of the mine site. Because of this, measuring this parameter is essential for assessing contamination risk.

It is important to point out that almost neutral or alkaline drainage can exist under certain conditions, with pH values more than eight. The secondary effects of alkalinity are of great significance for rehabilitation, particularly in soils and mine waste materials; deficiencies of the macro-nutrients Fe, Mn, B and Mg may occur and phosphates are removed from solution by the formation of insoluble calcium phosphates. Nitrogen, an important plant nutrient, may also be lost as ammonia by the action of strong bases on ammonium salts (Williamson *et al* 1982).

Increased solubility of the atmospheric metals aluminium and zinc causes toxicity at very high pH. Zinc begins to come into solution at pH of 9.0 and aluminium at about pH 7.8. Alkaline tailings frequently have excessive quantities of soluble salts that restrict plant growth. Therefore runoff from these types of wastes usually has a high salinity.

For these reasons, this Handbook includes assessment criteria for contamination when pH readings are Basic, i.e. when their value is greater than 8.

For more information about ARD, the following references may be useful:

The Methodological Guide to Acid Drainage in the Mining Industry, created by the National Clean Production Council - Mining Council, in November 2002.

Acid Rock drainage Technical Guide, prepared for the British Columbia Acid Mine Drainage Task Force by Steffen Robertson and Kirsten Inc. August 1989.

Williamson, NA, Johnson, MS and Bradshaw, AD (1982): *Mine Wastes Reclamation: the Establishment of Vegetation on Metal Mine Wastes.* Mining Journal Books, London, 1982.

B.2.2. Identification of Hazardous Waste inside the site

Hazardous waste found at a SD/AMS not only represents an important safety risk but could also pose a risk of contamination due to its toxicity, which could affect any sort of receptor that it comes into contact with. The Assessor must carry out a detailed inspection of the site, looking for direct and indirect evidence to determine the presence of such waste. Special care must be taken to detect the existence of buried waste that may not have proper signage.

The types of hazardous substances that an Assessor may find in a SD/AMS include the following:

- ✓ Waste with a high metal content, such as arsenic waste that comes from the roasting of concentrates, mercury waste from amalgamation processes, smelter dust and sand, waste containing copper, molybdenum, zinc, etc.
- ✓ Waste solutions that may have remained in the old plant tanks or ponds.
- ✓ Remains of consumables or reagents used in the plant processes.
- ✓ Materials with asbestos used in construction and as insulation in equipment.
- ✓ PCBs in electrical capacitors and oil in transformers.
- ✓ Oil and lubricant sediments or materials contaminated with this type of waste.
- ✓ Scrap iron and other minerals impregnated with hazardous substances.
- ✓ Waste containing explosive, corrosive or inflammable substances.
- ✓ Radioactive waste e.g. mine tailings.
- ✓ Explosives.

The type of hazardous substances that can be found in a SD/AMS is related to the type of deposit and extraction processes used and, therefore, to the substances that were used when the plant was in operation; for this reason the Assessor must compile as much information as possible regarding the minerals and processes that were used.

The Assessor must determine the existence of hazardous waste and at the same time assess the possibility that this waste could come into direct contact with receptors, either through the soil or through surface or groundwater (this last point will be dealt with in the following section).

In order to determine if mining or industrial waste present at a SD/AMS is hazardous or not, the Assessor must refer to the definitions contained in the IMDG Code for hazardous wastes. The sequential analysis described below has been based on best practice, which enables identification of the hazardous characteristics of certain types of waste (Figure 1):

- **Step 1.** When dealing with large-scale mining waste (potentially hazardous because old sites are involved) such as tailings, semi-processed material, or waste from leaching, sample taking is recommended to determine hazardousness of the material through a **Synthetic Precipitation Leaching** test for measuring toxicity.

  Such tests are required because of the potentially hazardous nature of waste that has remained at sites which were abandoned or shut down years ago. This waste probably has higher concentrations of Chemicals of Potential Concern than those found in waste generated nowadays; it is therefore useful to determine if any of the large-scale mining wastes present at the site (especially process waste such as tailings, or semi-processed ore) displays toxicity and is therefore hazardous waste.

  Where the Assessor determines that the large-scale mining waste is not potentially hazardous (possibly slag and sterile waste), it is deemed to be non hazardous waste.

- **Step 2.** If the mining waste is not large scale the Assessor should check to see if it is included in the IMDG Code. If it is not on the list, the waste is not hazardous.

- **Step 3.** The following step is to check if the waste features in the IMDG Code. If it appears on the list, the waste is hazardous.

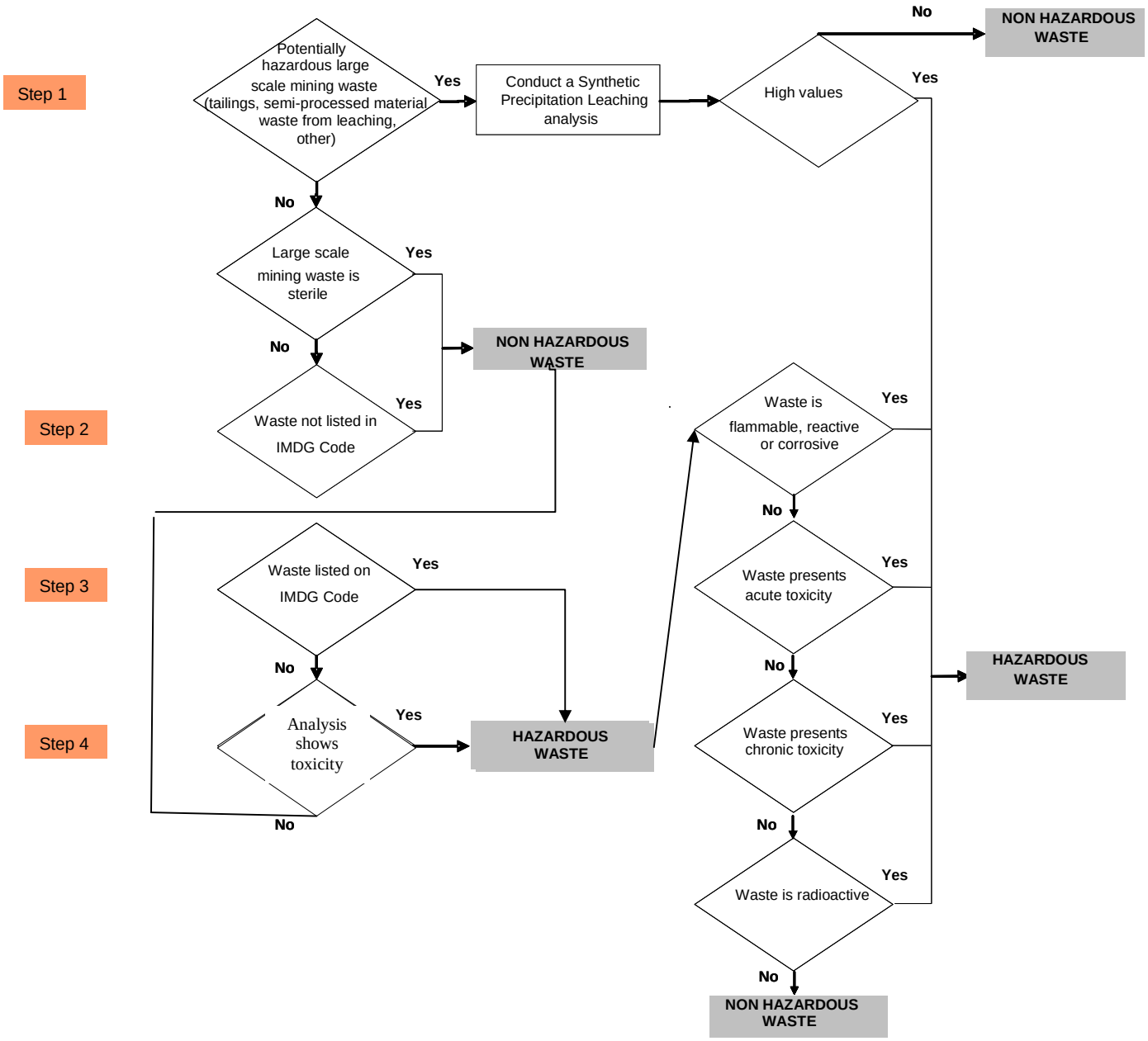
- **Step 4**. If the nature of the waste is unknown, it must be sampled to determine its chemical composition.

Finally, in order to determine if a waste is hazardous or not, it is worth bearing in mind the following:

- The toxicity of waste on the ground must be assessed. This is done using the **'Leaching Toxicity Test'.** The waste shall be considered hazardous when the test yields concentrations greater than the Maximum Permissible Concentrations, MPC.

- Alternatively, the MME can determine that waste IS NOT hazardous when, after analysis by an approved laboratory, it is found that the concentration of substances expressed in milligrams of substance per kilogram of waste, is lower than the prescribed concentrations contained in the Regulations of the Pollution and Waste Management Act.

Figure 1. Suggested flow chart for identifying Hazardous Waste



- '**Synthetic Precipitation Leaching'** is used instead of the **'Leaching Toxicity Test'** in order to determine the extrinsic toxicity of large-scale mining waste.

- The **relevant government ministries** reserve the right to sample, analyze and determine the hazardous nature of large-scale mining waste (sterile waste, low-grade ore, heap leach waste, slag and tailings), whenever they deems necessary.

B.2.3. Runoff or seepage of toxic or hazardous substances from processing plants or small-scale waste due to rainfall runoff.

Stormwater runoff from a potentially contaminated site can transport chemicals of potential concern into surface water courses and this water can also infiltrate into the groundwater. The rate of transport, degree of contamination and impact on the receptors depends on a number of factors including the following:

- ✓ The level of protection of the wastes against stormwater runoff; in other words, it is much easier for contaminants to be transported away when the wastes are uncovered, or are not enclosed, or when there is no stormwater control.

- ✓ Annual rainfall in the area, considering the possibility of unusually high rainfall in some years (the 'El Niño' phenomenon). The potential for run-off is reduced in very dry climates with annual rainfall around 200 mm, and increases progressively as annual rainfall increases.

- ✓ The slope where the abandoned site is situated, as steeper slopes provide more favourable conditions for natural runoff.

- ✓ The distance between the site and surface water sources.

- ✓ The depth of the water table. This is difficult to estimate on land but it can be obtained from wells close to the site and by interviewing local inhabitants.

In general, it is less feasible for hazardous waste to reach a receptor body when the site is located in an area with an annual rainfall of less than 200 mm. It is also less feasible in flat areas and where the nearest watercourses are more than 1 km away. On the other hand, it is more likely for hazardous waste to be transported under conditions of higher rainfall, steep slopes and where watercourses are close to the site.

The Assessor therefore must take all of these aspects into account when determining the likelihood of contaminant transport.

B.2.4 Wind drift of contaminated particulate matter

Abandoned tailings dams located in low rainfall areas usually have large expanses of dry, unconsolidated material. One of the main risks from these dams is the release of particulate matter into the atmosphere when fine particles (PM10) containing potentially harmful contaminants are transported to where they can damage the health of people and the surrounding environment.



The old tailings dam at Oamites is highly susceptible to wind erosion causing health problems at the nearby military camp. The tailings contain elevated concentrations of uranium and heavy metals (see Box 3 in Chapter 6)

Other sources that could release contaminated particulate matter into the atmosphere include small-scale accumulations of hazardous waste and, eventually, heap leach waste with fine material on the surface.

Airborne particulate matter (PM10) can be inhaled by people visiting the mine site or living in the surrounding area, putting their health at risk. This scenario is particularly relevant in cases where human receptors live less than 1 km away, or in zones 1 to 3 km away in the direction the wind usually blows. It is advisable to interview local inhabitants and authorities to determine whether particulate matter from the site's waste dumps has reached receptors located in the area of influence.

The emission of particulate matter from a tailings dam or other type of dump will depend on factors such as:

- ✓ Wind speed and direction: the force required to keep the material in suspension and the direction it is carried in.
- ✓ The moisture content of the material, as it can only be suspended from a dry surface.
- ✓ The material's grain size.

In order for particulate matter to be transported, fine material capable of being suspended by wind action must be present in the deposit. In general, the most common particulate matter in risk assessments is matter with a diameter of less than 10 microns (PM10), as this particle size can be breathed in, causing adverse health effects on different receptors.

Because special equipment is required to measure PM10, it is recommended that soils be classified using a 200 mesh (75 microns). Classification of fine material can be done on site by using the mesh to determine if most of the material in the deposit being assessed has the smaller grain size.

Where the deposits assessed, especially tailings, show cementing, agglomeration or any other feature that produces cohesion of the fine particulate matter present, the Assessor may assume that this material will not be suspended, even when a high percentage of fine material is present. The Assessor should also take into account the time of year, as more fine material may be present during dry periods than in the rainy season, when rain can favour agglomeration.

In general, the Assessor should consider the existence of fine material when it is found in dust form or could easily turn into dust.

The possibility of these substances being released and transported through the air is considerably reduced when coverings or other wind protection measures are placed over contaminated material. In general, the most efficient protection is provided by large grained materials (rocks and coarse and fine gravel) when they are at least 30 cm thick or when they are placed across the prevailing wind direction in 'windrows'. These two conditions combined should offer resistance to wind erosion and as a consequence should prevent contaminated particulate matter from entering into suspension.

Other effective coverings include dense vegetation, chemical binders and synthetic materials such as geotextiles, geomembranes and others.

The Assessor must determine whether such cover exists and how efficient it is, in order to adjust the likelihood of occurrence of a Hazard Scenario to real levels in line with the conditions found at the deposit site.

Finally, in order to determine if a waste is hazardous or not, it is worth bearing in mind the following:

- The toxicity of waste on the ground must be assessed. This is done using the **'Leaching Toxicity Test'.** The waste shall be considered hazardous when the test yields concentrations greater than the Maximum Permissible Concentrations, MPC.

- Alternatively, the MME can determine that waste IS NOT hazardous when, after analysis by an approved laboratory, it is found that the concentration of substances expressed in milligrams of substance per kilogram of waste, is lower than the prescribed concentrations contained in the Regulations of the Pollution and Waste Management Act.

ANNEX C1

GUIDELINE CONCENTRATIONS FOR ASSESSMENT OF CHEMICALS OF POTENTIAL CONCERN IN ENVIRONMEMENTAL MEDIA

ANNEX C1

GUIDELINE CONCENTRATIONS FOR ASSESSMENT OF CHEMICALS OF POTENTIAL CONCERN IN ENVIRONMENTAL MEDIA

1 Introduction

Guidelines for drinking water in Namibia under the Water Act, 1956 (Act 54 of 1956) were adopted from the South African guidelines and the guidelines took effect from 1 April 1988. The guidelines are not standards as no publication in the Government Gazette of Namibia exists to that effect.

These guidelines are outdated and it is recommended that reference concentrations for water be obtained from credible international sources that are reviewed and updated on a regular basis.

Namibia has not developed or adopted guidelines for the assessment of contamination in sediments or soils. There are also no guidelines for assessment of air quality in Namibia. It is recommended that reference concentrations for human and ecological receptors be obtained from credible international sources that are reviewed and updated on a regular basis.

This Annexure provides references to prominent international data sources that may be used to select screening guidelines from.

2 World Health Organization

The WHO drinking water guidelines are based on human health and are intended to assist countries to develop standards, without having to conduct extensive reviews of toxicology and epidemiology. The WHO guidelines are not standards. The guidelines are supported by narratives and references to source documents from which the guidelines were developed.

The WHO also published air quality guidelines for Europe, which are widely used as reference concentrations in screening assessments for exposure to air pollutants. The guidelines are supported by narratives and references to source documents from which the guidelines were developed

References:

WHO. 2008. Guidelines for Drinking-Water Quality, Third Edition, Incorporating First and Second Addenda.
http://www.who.int/water_sanitation_health/dwq/gdwq3rev/en/index.html.

WHO. 2000. Air quality guidelines for Europe, Second Edition 2000.
http://books.google.co.za/books

WHO. 2005. Air quality guidelines - global update 2005.
http://www.who.int/phe/health_topics/outdoorair_aqg/en/index.html

3 The US Environmental Protection Agency (USEPA), Mid-Atlantic Risk Assessment

This Agency has an online Risk-Based Concentration (RBC) Table with human health-risk based guideline concentrations for tap water, residential soil, industrial soil, residential air and industrial air. The table also lists soil screening levels for protection of groundwater. The RBC is updated regularly by Oak Ridge National Laboratory under an Interagency Agreement with USEPA.

The data in the RBC Table are supported by referenced toxicological information and the algorithms used for calculating guideline concentrations are available online. This is one of the most comprehensive and valuable data sources for human health risk assessment and it is recommended that the guideline concentrations be applied in the Tier-1 assessment.

A separate table is available online for screening guidelines of contaminants in fish, based on human fish consumption.

References:

US Environmental Protection Agency (USEPA), Mid-Atlantic Risk Assessment (Serving Delaware, District of Columbia, Maryland, Pennsylvania, Virginia, and West Virginia). Risk-Based Concentration (RBC) Table. Online.
http://www.epa.gov/reg3hwmd/risk/human/index.htm
http://www.epa.gov/reg3hwmd/risk/human/pdf/MAY_2010_FISH.pdf

4 The US Environmental Protection Agency National Recommended Water Quality Criteria

USEPA's compilation of national recommended water quality criteria is presented as a summary table containing recommended water quality criteria for the protection of aquatic life and human health in surface water for approximately 150 pollutants.

Reference:

United States Office of Water, Environmental Protection Agency, Office of Science and Technology. 2009. Online.
http://www.epa.gov/waterscience/criteria/wqcriteria.html

5 The Risk Assessment Information System (RAIS)

Screening ecological benchmarks are used to identify chemical concentrations in environmental media that are at or below thresholds for effects on ecological receptors. The Environmental Sciences Division of Oak Ridge National Laboratory developed and compiled a comprehensive set of ecotoxicological screening benchmarks for surface water, sediment, and surface soil applicable to a range of aquatic organisms, soil invertebrates, and terrestrial plants. These benchmarks are provided as a searchable database. Updates are performed in collaboration with The Institute for Environmental Modeling at the University of Tennessee and the Bechtel Jacobs Corporation. Links to supporting technical reports from which the benchmarks were obtained are also provided.

The RAIS maintains links to several EPA Ecological Risk Assessment Guidance documents.

The database is online and interactive. Screening Benchmarks can be obtained for various choices of biota, sediment, soil and surface water. Descriptions of the terms and literature references are available in the Spatial Analysis and Decision Assistance (SADA) Software.

References:

The Risk Assessment Information System. Online.
http://rais.ornl.gov/cgi-bin/eco/eco_search

Spatial Analysis and Decision Assistance (SADA) Software, University of Tennessee Research Corporation. Online.
http://www.tiem.utk.edu/~sada/help/TH_439.htm

6 The National Oceanic and Atmospheric Administration (NOAA), Department of Justice, Department of the Interior

Screening Quick Reference Tables (SQuiRTs) present screening concentrations for inorganic and organic contaminants in various environmental media for human and ecological receptors. The SQuiRTs also include guidelines for preserving samples and for analytical technique options.

The SQuiRTs are organized into the following sections:

- Inorganics in Freshwater and Marine Sediment;
- Inorganics in soil;
- Inorganics in Water (groundwater and surface water);
- Organics in Sediment;
- Organics in Water and Soils;
- Analytical Methods for Inorganics;
- Analytical Methods for Organics; plus,
- Guidelines for Sample Collection & Storage; *new topics include:*
    - PCB Composition;
    - Toxic Equivalency Factors; and,
    - Carbon Range of Hydrocarbon Products

Reference:

Buchman MF 2008. NOAA Screening Quick Reference Tables, NOAA OR&R Report 08-1, Seattle WA, Office of Response and Restoration Division, National Oceanic and Atmospheric Administration, 34 pages. Online: http://response.restoration.noaa.gov/.

7 The California Wildlife Biology, Exposure Factor, and Toxicity Database (Cal/Ecotox)

The California Wildlife Biology, Exposure Factor, and Toxicity Database (Cal/Ecotox) is a compilation of physiological and ecological parameters and toxicity data for a number of California fish and wildlife. It provides a compilation of ecological, physiological data, and toxicity data for a number of California mammals, birds, amphibians, reptiles and fish.

Reference:

OEHHA. Online.
http://www.oehha.org/cal_ecotox/

8 USEPA ECOTOX Database

The ECOTOX (ECOTOXicology) database provides single chemical toxicity information for aquatic and terrestrial life.

Reference:

USEPA Aquatic Toxicity Database. Online.
http://cfpub.epa.gov/ecotox/

9 USEPA Ecological Soil Screening Level Guidance

Eco-SSLs are contaminant concentration levels that are protective of ecological receptors (e.g., mammals, birds, or plants) that might have contact with the soil, directly or indirectly.

Reference:

USEPA Soil Screening Benchmarks. Online.
http://www.epa.gov/ecotox/ecossl/index.html.

10 US Department of Energy

A report presenting toxicological benchmarks for assessment of effects of 85 chemicals on 9 representative mammalian wildlife species or 11 avian wildlife species, based on no-observed-adverse-effect levels (NOAELs) and lowest observed adverse effects levels (LOAEL).

Reference:

Sample BE, Opresko DM and Suter GW, 1996. Toxicological Benchmarks for Wildlife: 1996 Revision. Prepared for US Department of Energy. Report No ES/ER/TM-86/R3.

11 South African Water Quality Guidelines

This reference is added, because the documents present useful information that assist in the interpretation of the guidelines. It must be recognized, however, that the information dates back from 1996 and it should be prudent to refer also to other, more recent data.

Reference:

The South African Water Quality Guidelines are available from the links below as individual volumes in pdf format. This is not the official source for these documents, which is now http://www.dwaf.gov.za/Dir_WQM/docsFrame.htm.

(Enter the following in the search box: “water quality guidelines”. This will return the link to South African Water Quality Guidelines, with all the guideline pdf files in a single 10Mb ZIP file.) Alternatively, start the 10 Mb download directly.

12 South African Air Quality Guidelines

South African Ambient Air Quality Standards are available in SANS 1929:2005 Edition 1.1, published by Standards South Africa, Pretoria, 2005.

South African National Standard, Ambient air quality - Limits for common Pollutants.

13 Namibian Water Quality Guidelines

The Namibian water quality guidelines are attached as Appendix 1.

APPENDIX 1

Namibian Guideline Values

	pH	EC	SO4	Mn	Al	As	Cd	Co	Cu	Pb	V	Zn
		µS/cm	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l
Namibia guideline values												
Group A: excellent quality	6-9	1500	200	0.05	0.15	0.1	0.01	0.25	0.5	0.05	0.25	1
Group B: acceptable quality	5.5-9.5	3000	600	1	0.5	0.3	0.02	0.5	1	0.1	0.5	5
Group C: low health risk	4-11	4000	1200	2	1	0.6	0.04	1	2	0.2	1	10
Group D: high health risk, or unsuitable for human consumption	4-11	4000	1200	2	1	0.6	0.04	1	2	0.2	1	10
Standard for effluent water (maximum allowable levels)						0.5			1	1		5

THE WATER ACT,1956 (ACT 54 OF 1956) AND ITS REQUIREMENTS IN TERMS OF WATER SUPPLIES FOR DRINKING WATER AND FOR WASTE WATER TREATMENT AND DISCHARGE INTO THE ENVIRONMENT

1 INTRODUCTION

The provisions of the Water Act are intended, amongst other things, to promote the maximum beneficial use of the country's water supplies and to safeguard water supplies from avoidable pollution.

The drinking water guidelines are not standards as no publication in the Government Gazette of Namibia exists to that effect. However the Cabinet of the Transitional Government for National Unity adopted the existing South African guidelines (461/85) and the guidelines took effect from 1April 1988 under the signature of the then Secretary for Water Affairs.

The sections of the Water Act that relate to the discharge of industrial effluents are:

- Section 21(1) which states that the purification of waste water shall form an integral part of water usage and that purified effluents shall comply with the General Standard Quality restrictions as laid out in Government Gazette Regulation R553 of 5 April 1962; and
- Section 21(2) which further stipulates that this purified effluent be returned as close as possible to the point of abstraction of the original water.

Where a local authority has undertaken the duty of disposing of all effluents from an industrial process the provisions of Section 21(1) and 21(2) apply to the local authority and not the producer of the effluent. If there is difficulty in complying with these provisions then the applicant may apply for an

exemption from the conditions in terms of Section 21(5) and 22(2) of the Water Act. The Permanent Secretary after consultation with the Minister may grant the issuance of a Waste Water Discharge Permit under Sections 21(5) and 22(2) subject to such conditions as he may deem fit to impose.

After independence, the Government of the Republic of Namibia, decided that for the interim the existing guidelines will continue to be valid and to remain in use until a proper study has been conducted and new guidelines / standards have been formulated (Article 140 of Act 1 of 1990).

2 GUIDELINES FOR THE EVALUATION OF DRINKING-WATER QUALITY FOR HUMAN CONSUMPTION WITH REGARD TO CHEMICAL, PHYSICAL AND BACTERIOLOGICAL QUALITY

Water supplied for human consumption must comply with the officially approved guidelines for drinking-water quality. For practical reasons the approved guidelines have been divided into three basic groups of determinants, namely:

- Determinants with aesthetic / physical implications: TABLE 1.
- Inorganic determinants: TABLE 2.
- Bacteriological determinants: TABLE 3.
- And TABLE 4 gives the frequency for bacteriological analysis.

2.1 CLASSIFICATION OF WATER QUALITY

The concentration of and limits for the aesthetic, physical and inorganic determinants define the group into which water will be classified. See TABLES 1 and 2 for these limits. A classification in groups A,B,C and D has been applied. Individually, these groups have the following meaning:

- Group A: Water with an excellent quality
- Group B: Water with acceptable quality
- Group C: Water with low health risk
- Group D: Water with a high health risk, or water unsuitable for human consumption.

Water should ideally be of excellent quality (Group A) or acceptable quality (Group B), however in practice many of the determinants may fall outside the limits for these groups.
If water is classified as having a low health risk (Group C), attention should be given to this problem, although the situation is often not critical as yet.
If water is classified as having a higher health risk (Group D), urgent and immediate attention should be given to this matter.

Since the limits are defined on the basis of average lifelong consumption, short-term exposure (e.g. visitors) to determinants exceeding their limits is not necessarily critical, but in the case of toxic substances, such as cyanide, remedial measures should immediately be taken.

The overall quality group into which a water is classified, is determined by the determinant that complies the least with the guidelines for the quality of drinking water.

TABLE 1: DETERMINANTS WITH AESTHETIC / PHYSICAL IMPLICATIONS

DETERMINANTS	UNITS	LIMITS FOR GROUPS			
		A	B	C	D*
Colour	mg/l Pt**	20			
Conductivity	mS/m @25 °C	150	300	400	400
Total hardness	mg/l $CaCO_3$	300	650	1300	1300
Turbidity	N.T.U***	1	5	10	10
Chloride	mg/l Cl	250	600	1200	1200
Chlorine (free)	mg/l Cl	0,1- 5,0	0,1 – 5,0	0,1 – 5,0	5,0
Fluoride	mg/l F	1,5	2,0	3,0	3,0
Sulphate	mg/l SO_4	200	600	1200	1200
Copper	µg/l Cu	500	1000	2000	2000
Nitrate	mg/l N	10	20	40	40
Hydrogen Sulphide	µg/l H_2S	100	300	600	600
Iron	µg/l Fe	100	1000	2000	2000
Manganese	µg/l Mn	50	1000	2000	2000
Zinc	mg/l Zn	1	5	10	10
pH****	pH-unit	6,0 – 9,0	5,5 – 9,5	4,0 – 11,0	4,0 – 11,0

* All values greater than the figure indicated.

** Pt = Platinum Units

*** Nephelometric Turbidity Units

**** The pH limits of each group exclude the limits of the previous group

TABLE 2: INORGANIC DETERMINANTS

DETERMINANTS	UNITS	LIMITS FOR GROUPS			
		A	B	C	D*
Aluminium	µg/l Al	150	500	1000	1000
Ammonia	mg/l N	1	2	4	4
Antimony	µg/l Sb	50	100	200	200
Arsenic	µg/l As	100	300	600	600
Barium	µg/l Ba	500	1000	2000	2000
Beryllium	µg/l Be	2	5	10	10
Bismuth	µg/l Bi	250	500	1000	1000
Boron	µg/l B	500	2000	4000	4000
Bromine	µg/l Br	1000	3000	6000	6000
Cadmium	µg/l Cd	10	20	40	40
Calcium	mg/l Ca	150	200	400	400

DETERMINANTS	UNITS	LIMITS FOR GROUPS			
Calcium	mg/l $CaCO_3$	375	500	1000	1000
Cerium	µg/l Ce	1000	2000	4000	4000
Chromium	µg/l Cr	100	200	400	400
Cobalt	µg/l Co	250	500	1000	1000
Cyanide (free)	µg/l CN	200	300	600	600
Gold	µg/l Au	2	5	10	10
Iodine	µg/l I	500	1000	2000	2000
Lead	µg/l Pb	50	100	200	200
Lithium	µg/l Li	2500	5000	10000	10000
Magnesium	mg/l Mg	70	100	200	200
Magnesium	mg/l $CaCO_3$	290	420	840	840
Mercury	µg/l Hg	5	10	20	20
Molybdenum	µg/l Mo	50	100	200	200
Nickel	µg/l Ni	250	500	1000	1000
Potassium	mg/l K	200	400	800	800
Selenium	µg/l Se	20	50	100	100
Silver	µg/l Ag	20	50	100	100
Sodium	mg/l Na	100	400	800	800
Tellurium	µg/l Te	2	5	10	10
Thallium	µg/l Tl	5	10	20	20
Tin	µg/l Sn	100	200	400	400
Titanium	µg/l Ti	100	500	1000	1000
Tungsten	µg/l W	100	500	1000	1000
Uranium	µg/l U	1000	4000	8000	8000
Vanadium	µg/l V	250	500	1000	1000

* All values greater than the figure indicated.

2.2 BACTERIOLOGICAL DETERMINANTS

The bacteriological quality of drinking water is also divided into four groups, namely:

- Group A: Water which is bacteriologically very safe
- Group B: Water which is bacteriologically still suitable for human consumption
- Group C: Water which is bacteriologically a risk for human consumption, which requires immediate action for rectification
- Group D: Water, which is bacteriologically unsuitable for human consumption.

TABLE 3: BACTERIOLOGICAL DETERMINANTS

DETERMINANTS	LIMITS FOR GROUPS			
	A**	B**	C	D*
Standard plate counts per 1 ml	100	1000	10000	10000
Total coliform counts per 100 ml	0	10	100	100
Faecal coliform counts per 100 ml	0	5	50	50
E. coli counts per 100 ml	0	0	10	10

* **All values greater than the figure indicated.**

** **In 95% of the samples.**

NB If the guidelines in group A are exceeded, a follow-up sample should be analysed as soon as possible.

2.3 FREQUENCY FOR BACTERIOLOGICAL ANALYSIS OF DRINKING-WATER SUPPLIES

The recommended frequency for bacteriological analysis of drinking water is given in Table 4.

TABLE 4: FREQUENCY FOR BACTERIOLOGICAL ANALYSIS

POPULATION SERVED	MINIMUM FREQUENCY OF SAMPLING
More than 100 000	Twice a week
50 000 – 100 000	Once a week
10 000 – 50 000	Once a month
Minimum analysis	Once every three months

3 GENERAL STANDARDS FOR WASTE / EFFLUENT WATER DISCHARGE INTO THE ENVIRONMENT

All applications in terms of Section 21(5) and 22(2), for compliance with the requirements of Section 21(1) and 21(2) of the Water Act (Act 54 of 1956) that purified water shall comply with the General Standard as laid out in Government Gazette Regulation R553 of
5 April 1962, are subject to these effluent quality guidelines.

TABLE 5 GENERAL STANDARDS FOR ARTICLE 21 PERMITS (EFFLUENTS)

Determinants	Maximum allowable levels
pH	5,5 – 9,5
Dissolved Oxygen (DO)	a saturation of at least 75% should be present; in Windhoek saturation is approx. 9 mg/l O_2
Typical faecal Coli.	no typical coli should be counted per 100 ml
Temperature	35°C
Chemical Oxygen Demand (COD)	75 mg / l as O
Oxygen Absorbed * (OA)	10 mg / l as O
Biological Oxygen Demand (BOD)	no value given
Total Dissolved Solids (TDS)	not more than 500 mg /l more than influent
Total Suspended Solids (TSS)	25 mg/l
Sodium	not more than 90 mg/l Na more than influent

Fats, Oil & Grease (FOG)	2,5 mg/l (!gravimetric method)
Chlorine, residual	0,1 mg/l as Cl_2
Free & Saline Ammonia	10 mg/l as N
Arsenic	0,5 mg/l as As
Boron	1,0 mg/l as B
Chromium, hexavalent	50 µg/l as Cr(VI)
Chromium, total	500 µg/l as Cr
Copper	1,0 mg/l as Cu
Lead	1,0 mg/l as Pb
Sulphide	1,0 mg/l as S
Fluoride	1,0 mg/l as F
Zinc	5,0 mg/l as Zn
Phenolic Compounds	100 µg/l as phenol
Cyanide	500 µg/l as CN
Phosphate	1,0 mg/l as **

* Also known as Permanganate Value (PV)
** This guideline was obtained from

Herewith, the Guidelines for the Evaluation of Drinking Water for Human Consumption with regard to Chemical, Physical and Bacteriological Quality, as well as the General Standards for Article 21* Permits, are confirmed and remain in force until further notice:

- For the disposal of industrial or domestic waste water and effluent, a permit application in terms of Sections 21(1) and 21(2) is required, and obtaining the advice of the Ministry of Health and Social Services is a prerequisite for the issuing of a permit.
- The Permanent Secretary in consultation with the Minister may, in writing, issue or cancel a permit, amend, delete and/or replace any clause in any permit.
- Any duly appointed official or representative of the Department of Water Affairs shall have the right of access to the premises of a permit holder for inspections and effluent sampling purposes.
- A permit does not absolve the permit holder from compliance with the provisions of the Public Health Act or any other law.
- Contravention of failure to comply with any of the permit conditions shall constitute an offence and shall render the permit holder liable to prosecution under Section 21(8) of the Water Act 56, 1956 (Act 54 of 1956).

Issued under my hand with the authority vested in my office,

Dr V Shivute
PERMANENT SECRETARY

ANNEX C2

BASIC CONSIDERATIONS FOR REVIEWING STUDIES IN THE DETAILED RISK ASSESSMENT FOR CONTAMINATION

ANNEX C2

BASIC CONSIDERATIONS FOR REVIEWING STUDIES IN THE DETAILED RISK ASSESSMENT FOR CONTAMINATION (DRAs)

	YES	NO	N/A
General			
1. Does the document properly structured?			
2. Is the information clear, concise and easy to follow?			
3. Have the objectives of the site-specific risk assessment been described?			
4. Is the assessment scope indicated (e.g., Area of Study, assessment complexity, necessary data and design)?			
5. Does the executive summary reflect the methodologies applied, the findings, conclusions and recommendations?			
Problem Formulation/ Hazard Identification – Site Description			
6. Has a general map of the site been included, including coordinates, scale, borders, topography, and features such as fences, dams and structures, and does it show the geographical relationship between the site and potential receptors?			
7. Has an adequate description of the mining site's history been included?			
8. Has the current and/or potential future use of the site been identified and described?			
9. Has a qualitative description of the nature of the contamination been included (e.g., a general indication of potential sources, types and concentrations of contaminants, exposure pathways and potential receptors)?			
10. Have the site's key features for soils and sediments been documented – e.g., particle size, carbon content, clay content, density, porosity, etc.?			
11. Have hydrogeological parameters been documented, e.g., hydraulic gradient, hydraulic conductivity, relative placement of rock layer, depth of saturation, direction of groundwater flow, etc.?			
12. Have basic water quality parameters been documented, e.g., hardness, pH, dissolved oxygen, temperature, total suspended solids, as well as basic hydrological characteristics e.g. flow and depth of rivers, and dam parameters such as area, volume and depth, etc.?			
13. Have meteorological parameters been documented, e.g., wind velocity and direction, temperature, humidity, precipitation, etc.?			

14. Has a conceptual model appropriate to the site been formulated?			
Site description – Data Collection			
15. Has an appropriate sampling plan been developed?			
16. Were the required components of the environment (surface water, groundwater, soil, sediments, air) sampled?			
17. Did sampling cover all areas of concern (as identified in the simplified risk assessment)?			
18. Did sampling include points throughout potential migration routes, e.g., between the contaminated source and potential points of exposure?			
19. Were sampling positions located consistent with the nature of the contamination e.g., at the appropriate depth?			
20. Was groundwater monitoring sufficient to identify contamination plumes?			
21. Were charts included indicating location, type and identification code for each sample?			
22. Did sampling include appropriate background samples for the components of the environment involved, e.g., areas near the site free of contamination from the site or from other anthropogenic sources, which are similar to the site in terms of topography, geology, meteorology and other physical characteristics?			
23. Did the sampling methodology include an appropriate quality control and assurance (QC/QA) program, e.g., duplicates, field blanks, trip blanks, etc.?			
Site description – Data Assessment			
24. Were appropriate analytical methods used?			
25. Were the laboratory's detection limits adequate?			
26. Were any chemicals associated with the site eliminated from the study without proper justification?			
27. Were uncertainties, limitations and gaps in quality of the sampling programme documented?			
28. Was the direction of the groundwater flow correctly identified?			
29. Does the report integrate sampling results and data interpretation in a reasonable conceptual model?			
30. Were credible guideline concentrations employed in the assessment?			
Human Health Risk Assessment – Toxicological Assessment			
31. Was any chemical eliminated from the human health risk assessment			

without justification? Should certain of the excluded contaminants be considered in the assessment?			
32. Was an analysis of potential adverse effects on human receptors provided? Was the analysis adequate?			
33. Were appropriate toxicity values used, based on credible data sources?			
34. Do toxicity values correspond to the exposure route of interest?			
35. If a toxicity value was adopted from a regulatory agency, was the basis for the toxicity value provided?			
36. Were sources of uncertainty regarding the toxicological assessment described?			
Human Health Risk Assessment – Exposure Assessment			
37. Were current and potential future land use scenarios considered?			
38. Were on-site and off-site receptors considered?			
39. Were all potential sensitive populations considered (e.g., senior citizens, infants, children, etc.)?			
40. Were all significant contamination sources considered?			
41. Were all contaminant release mechanisms considered, e.g., volatilization, short-term dust emissions, surface runoff, leaching into groundwater, etc.?			
42. Were all of the site-specific characteristics considered, including topography, hydrogeology, and hydrological and meteorological parameters?			
43. Were all direct and indirect pathways of exposure considered?			
44. Was there a justifiable reason provided for excluding any pathway or route of exposure?			
45. Were appropriate values used to calculate exposure (e.g., age, body weight, frequency and duration of exposure)?			
46. If a model was used to calculate exposure, were the main features and considerations associated with the model provided? Was the model appropriate?			
47. Were both the general equations and examples of calculations included?			
48. Were uncertainties adequately addressed?			
49. Were all the references of data sources and methodologies cited?			
Human Health Risk Assessment – Quantification of Risk			
50. Did the risk assessment take into account all the chemicals that were			

evaluated for exposure?			
51. Was the method used to quantify the risk appropriate?			
52. Were the risks appropriately added together according to the paradigm for non-carcinogens and carcinogens?			
53. Was the interpretation of risk appropriate, objective and well supported?			
54. Were the sources of uncertainty adequately described?			
55. Were all references used cited?			
56. Are human health risk conclusions justifiable considering the paradigm for human health risk assessment?			
Ecological Risk Assessment – Stressor-Response Assessment			
57. Did the study follow appropriate guidelines for stressor-response assessment?			
58. Were credible data sources consulted to obtain guideline concentrations for the assessment of stressor-response and risk?			
59. Does the selection of species adequately reflect the presence of sensitive species?			
60. Were any of the following receptors identified? • Rare, endangered or endemic species • species protected by law • species killed for human consumption • species considered health indicators for the ecological community?			
61. Was an analysis of potential adverse effects on ecological receptors provided? Was the analysis adequate?			
62. Were the sources of uncertainty adequately described?			
Ecological Risk Assessment – Exposure Assessment			
63. Were the current and potential future scenarios for land use considered?			
64. Were the receptors adequately taken into account?			
65. Were the on-site and off-site recipients (e.g., birds that may occasionally visit the site) considered?			
66. Was the home range for terrestrial animals taken into account?			
67. Were all the significant sources of contamination considered?			
68. Were all the mechanisms for contamination release considered, such			

as volatilization, short-term dust emissions, surface runoff, leaching into groundwater, etc.?			
69. Were appropriate values used in calculating exposure (e.g., food and water ingestion rates)?			
70. Were all pathways of direct and indirect exposure taken into consideration?			
71. Was there a justifiable reason to exclude any exposure pathway?			
72. Were different food types and intake rates taken into account?			
73. If models were used to calculate exposure, were the main features and considerations associated with the models described? Was the model appropriate?			
74. Were both the general equations and examples of calculations included?			
75. Were uncertainties properly addressed?			
76. Were all the references used cited?			
Ecological Risk Assessment – Quantification of Risk			
77. Did the risk quantification consider all the chemicals assessed for exposure?			
78. Were risks properly summed only through the exposure pathways and routes of exposure?			
79. Was the risk assessment appropriate, objective and well supported?			
80. Were uncertainty sources properly described?			
81. Were all the references used cited?			
82. Are ecological risk conclusions justifiable considering the paradigm for ecological risk assessment?			

ANNEX D1

BASIC CONSIDERATIONS FOR REVIEWING STUDIES IN THE DETAILED RISK ASSESSMENT FOR SAFETY

ANNEX D1

BASIC CONSIDERATIONS FOR REVIEWING STUDIES IN THE DETAILED RISK ASSESSMENT (DRAs) FOR SAFETY PARAMETERS

	Yes	No	Not applicable
Text of geotechnical report			
1. Has the location of the mining operation, or a map indicating its location, been included?			
2. Is a summary of the scope and purpose of the study provided?			
3. Is a concise description of the area's topography and geology provided?			
4. Is there a list of the laboratory tests and field studies on which the report is based?			
5. Are the general features of the subsoil, rocks and groundwater described?			
6. Is the following information (generally provided in appendices) included?			
a) Records of drilling and test drilling			
b) Soil profiles			
c) Laboratory test data			
d) Photographs			
Underground plans and profiles			
7. Does the report provide underground plans and profiles of the study area?			
8. Do the plans include the findings of the field investigation?			
9. Does the report meet the minimum criteria regarding points to be studied, as detailed in Table 5.2?			
10. Do correctly numbered drill holes and shafts appear on a plan, with indications of elevation and location?			
11. Does the underground profile contain a textual or graphic description of the types of soil and rock present?			
12. Does the underground profile show groundwater levels and date of measurement?			
Record of test drilling results, or underground profile			

13. Is there a record of the depth and type of samples taken from test drilling?			
14. Are the results of SPT testing, percentage of recovery of the sampled core material, and RQD values provided?			
15. If CPTs have been performed, are charts provided showing cone strength and angle of friction as a function of depth?			
Laboratory data			
16. Were the laboratory tests for the classification of soils (e.g., moisture content, gradation, Atterberg limits) performed with representative samples to confirm the on-site visual identification of soils?			
17. Are the results of laboratory tests (cut resistance, consolidation, etc.) included or summarized?			

A. INFORMATION REQUIRED TO PERFORM DETAILED SUBSIDENCE RISK ASSESSMENT

	Yes	No	Not applicable
Description of the operating site			
1. Is settling, subsidence or other failure associated with underground operations described?			
2. Is the type of underground operation (room and pillar, etc.) described?			
Estimation of geological parameters			
3. Have the following field tests been performed to ascertain the presence of voids, and the characteristics of the underground strata?			
a) GPR (Ground Penetrating Radar)			
b) TDR (Time Domain Reflectometry)			
c) Resistance analysis			
d) Gravity surveys			
e) RQD			
f) Shear strength parameters			
Estimation of hydraulic parameters			
4. Have studies been made to determine the depth and profile of the underground aquifer?			
5. Have studies been made to ascertain drainage patterns in the area of the mine, and have the patterns been indicated on a map?			
Assessment of stability			
6. Is the geometry of underground works and access adits to the surface available?			
7. Is there a verification of the rock mass strength and general stability, based on the dimensions of rock bridging, pillars, stopes, etc.?			
Assessment of consequences			
8. Are estimates provided of the area that could be affected by subsidence?			

B. INFORMATION REQUIRED FOR PERFORMING DETAILED STABILITY RISK ASSESSMENT

	Yes	No	Not applicable
Description of the operating site			
1. Is the existence of sliding, settling, erosion, flows of liquids, or other failures in the operating area described?			
2. Is there a description of measures that are in place at the site to protect against erosion?			
Estimation of geotechnical parameters			
3. Have the following field or laboratory tests been performed to ascertain the properties of the material of the dump and its foundation?			
a) Standard penetration tests (SPTs)			
b) Cone Penetration Tests (CPTs)			
c) Classification of the material of the deposit, founding material, moisture content, specific gravity, angle of repose			
d) Liquid limit, plastic limit, index of plasticity			
Estimation of hydraulic parameters			
4. Have studies been made to determine the phreatic surface in thedam?			
5. Have permeability tests been made in the field and in the laboratory?			
Assessment of stability			
6. Are the details of the calculations of the operation's safety factor provided?			
7. Is there mention of the design criteria for which said safety factor was calculated (seismic activity, moisture, etc.)?			
8. Are the embankments designed with a minimum pseudo-static safety factor of 1.2?			
Assessment of consequences			
9. Are estimates of the distances or areas of influence of the simulated failures provided?			

C. INFORMATION REQUIRED TO PERFORM DETAILED SLOPE FAILURE (COLLAPSE OF PIT) RISK ASSESSMENT

	Yes	No	Not applicable
Description of the operating site			
1. Is the existence of sliding, settling, erosion, or other failures in the operating area described?			
2. Is there a description of measures that are in place at the site to protect against erosion?			
Estimation of geotechnical parameters			
3. Have the following field or laboratory studies been performed to determine the properties of the in-situ rock mass conditions?			
a. RQD			
b. Confined compression tests			
c. Geological map of cracks, faults and fracture systems			
d. Orientation of faults, shears and defects			
Estimation of hydraulic parameters			
4. Have studies been performed to determine the phreatic level in the pit's slopes?			
Assessment of stability			
5. Are the details of the calculation of the safety factor in the pit's slopes provided?			
6. Is there mention of the design criteria for which said safety factor was calculated (seismic activity, moisture content, etc.)? Probability of seismic disturbance incorporated in design?			
Assessment of consequences			
7. Are estimates of the distances or areas of influence of the simulated failures provided?			

D. INFORMATION REQUIRED TO PERFORM DETAILED RISK ASSESSMENT FOR COLLAPSE OF TAILINGS STORAGE FACILITIES

	Yes	No	Not applicable
Description of the operating site			
1. Is the existence of sliding, settling, erosion, or other failures in the operating area described?			
2. Is there a description of measures that are in place at the site to protect against erosion?			
Estimation of geotechnical parameters			
3. Have the following field or laboratory studies been performed to determine the properties of the tailings deposit?			
a) Standard Penetration Tests (SPTs)			
b) Cone Penetration Tests (CPTs)			
c) Particle size analysis, moisture content, specific gravity, permeability			
d) Properties of foundation soils			
e) Liquid limit, plastic limit, index of plasticity			
Estimation of hydraulic parameters			
4. In connection with tailings, have studies been performed to determine the phreatic level in the wall and reservoir?			
5. Have studies been performed to determine the drainage pattern in the area?			
6. Has pore pressure been estimated?			
Assessment of stability			
7. Are details of the calculation of the deposit's safety factor provided?			
8. Is there mention of the design criteria for which said safety factor was calculated (seismic activity, phreatic level, etc.)? Probability of seismic disturbance incorporated in design?			
9. Is the tailings deposit designed with a minimum pseudo-static safety factor of 1.2?			
Assessment of consequences			
10. Are estimates of the distances or areas of influence of the simulated failures provided?			

ANNEX E

RISK ASSESSMENT RECORD FORM (RARF)

ANNEX E Cover page 1	RISK ASSESSMENT RECORD FORM RISK ASSESSMENT HANDBOOK FMA/P ASSESSMENT COVER PAGE	PAGE 1

A. IDENTIFICATION OF SHUT DOWN OR ABANDONED MINE SITE (SD/AMS)

				MIDS CODE:	
SITE NAME		REGION:		COMMUNITY:	
MINING COMPANY (if known)		ADDRESS (if known)			
CONTACT PERSON (if available)		ADDRESS / PHONE / MAIL			
IS MINE ABANDONED OR CLOSED?					

B. ADVISORS, REVIEWERS AND APPROVAL

	NAME POSITION	SIGNATURE	DATE	SPECIALIST ROLE IN THE ASSESSMENT
Assessor 1:				
Assessor 2:				
Assessor 3:				
Assessor 4:				
Advisor 5:				
Advisor 6:				
Advisor 7:				
Assessor 8:				
REVIEWER:				
APPROVED BY				

ANNEX E Cover page 2	RISK ASSESSMENT RECORD FORM RISK ASSESSMENT HANDBOOK SD/AMS ASSESSMENT COVER PAGE	PAGE 2

C. SHUT DOWN OR ABANDONED MINE SITE COMPONENTS (Section 4.1.2.1, a)

COMPONENT	FACILITY TYPE (STOCKPILE OR SITE)	FACILITY NAME	FACILITY CODE	GENERAL DESCRIPTION OF FACILITY, STOCKPILE OR SITE	UNIT IDENTIFICATION AND CHARACTERISATION	CO-ORD SOUTH	CO-ORD EAST	ALTITUDE

ANNEX E BASELINE SHEET 1	RISK ASSESSMENT RECORD FORM RISK ASSESSMENT HANDBOOK SD/AMS CHARACTERISATION OF THE SD/AMS ENVIRONMENT	

1. INFORMATION COLLECTION (Section 3.2.1)

1.1 Information available on Mine Inventory Data Sheet (MIDS)

	Yes/No	MIDS Code	
MIDS available			(Specify sample number)
The MIDS includes a water quality laboratory analysis			
The MIDS includes a laboratory analysis of solid residues			

(Observations)

1.2. Public Services or Third Party Interviews/Information

SOURCE TYPE	INFORMATION SOURCE (name, contact details)	DATE	INTERVIEWER	TYPE OF INFORMATION GATHERED
Ministry of Mines and Energy				
Geological Survey of Namibia				
Ministry of Environment and Tourism				
Mining Company				
Abenab villagers				

ANNEX E BASELINE SHEET 2	RISK ASSESSMENT RECORD FORM RISK ASSESSMENT HANDBOOK SD/AMS CHARACTERISATION OF THE SD/AMS ENVIRONMENT	

2. MAP PREPARATION (Section 3.2.2)		
2.1 Data Collected	**Yes/No**	(Specify what has been used to compile the Base Map)
Sheet 1:50,000 or 1:250,000		
Aerial photography (stereo pairs or 1:10,000 orthophographs)		
Satellite images		
Other cartographic sources		
2.2 Risk Assessment Base Map Preparation (RABM)	(Specify base map characteristics)	
Scale:		
Projection system (Geographic Coord. / UTM):		
Preparation process:		
Digital file names:		
Is there a copy of the map or image in the MIDS file?		

3. DEFINITION OF THE AREA OF STUDY (Section 3.2.3) (see Note below)		
3.1 Area of the mine site		
Area directly affected by the mine (ha)		
3.2 Areas that have in the past or might in future be directly or indirectly affected by contamination or catastrophic events	**Yes/No**	(Justify)
Affected or potentially affected surface water courses		
Affected or potentially affected groundwater areas		
Area affected by wind driven dust and gas dispersion (soils and air)		
Area that could be affected by a catastrophic event on site		
Families that commonly consume agricultural, game and fish products, (crops, meat and fish) produced in the Area of Study		
Applied safety zone (buffer). Required in case of uncertainty related to the study area limits.		

Note: the area to analyze must be defined ahead of time, prior to the field visit. Once the information gathered in the field is available, the size of the Area of Study may be adjusted

ANNEX E BASELINE SHEET 3	RISK ASSESSMENT RECORD FORM RISK ASSESSMENT HANDBOOK SD/AMS CHARACTERISATION OF THE SD/AMS ENVIRONMENT

4. IDENTIFICATION AND DESCRIPTION OF RECEPTORS IN THE AREA OF STUDY (Section 3.2.4)			
a. People		**Yes/No**	Spec
a.1 - Does anyone live in the Area of Study, now or in the past?			
- Settlement type			
- Is surface water being collected for human consumption?			
- Is groundwater being obtained from boreholes or wells for human consumption?			
- Are there any fountains or springs located downstream of the site?			
a.2. - Are there any site visitors?			
- Estimated number of vistors/site users per day, week, month or year			
- Motivation for entry			
- City or settlement of origin			
- Age			
- Information source			
b. Environment		**Yes/No**	SPEC
b.1. Is there any aquatic life that has been or may be affected?			
- Name of river, stream, water course or dam (if any, otherwise give it an identifying name)			
- Presence of living species of fish, invertebrates, molluscs, amphibians etc			
- Presence of protected species			
- Surface area of water body and/or length of stream/river that flows through the Area of Study			
- Information sources consulted in section b.1			
b.2. - Has the terrestrial flora been affected?			
- Ecosystem type(s)			
- Use of plant species			
- Presence of protected species of flora			
- Abundancy estimation			

ANNEX E BASELINE SHEET 3	RISK ASSESSMENT RECORD FORM RISK ASSESSMENT HANDBOOK SD/AMS CHARACTERISATION OF THE SD/AMS ENVIRONMENT

- Conservation status		
- Presence of invasive and/or alien species		
- Information sources consulted in section b.2		
b.3. - Has the terrestrial fauna been affected?		
- Typical species present		
- Are any of the species harvested for human consumption and how many people consume these products on a regular basis?		
- Presence of protected species of fauna		
- Abundancy estimation		
- Conservation status		
- Presence of invasive and/or alien species		
- Information sources consulted in section b.2		
b.4. - Is the site in or adjacent to protected or sensitive areas?		
- Presence or proximity of these areas - state name and distance to mine site		
- Protection category		
- Natural or cultural value		
- Importance of protected or sensitive area at a local, regional and national level		
- Presence of endemic or protected species		
- Component of the natural environment that might be affected by safety or contamination emitted by SD/AMS		
- Area of sensitive environment contained in the Area of Study		
- Information sources consulted in section b.3		
c. Will any economic activities be adversely affected?	Yes/No	Speci
c.1 - Agriculture -crop farming		
- Type of crop production (specify crops), now and in the past (if information is available for the latter)		
- Area and location of crop farming in relation to SD/AMS		

ANNEX E BASELINE SHEET 3	RISK ASSESSMENT RECORD FORM RISK ASSESSMENT HANDBOOK SD/AMS CHARACTERISATION OF THE SD/AMS ENVIRONMENT

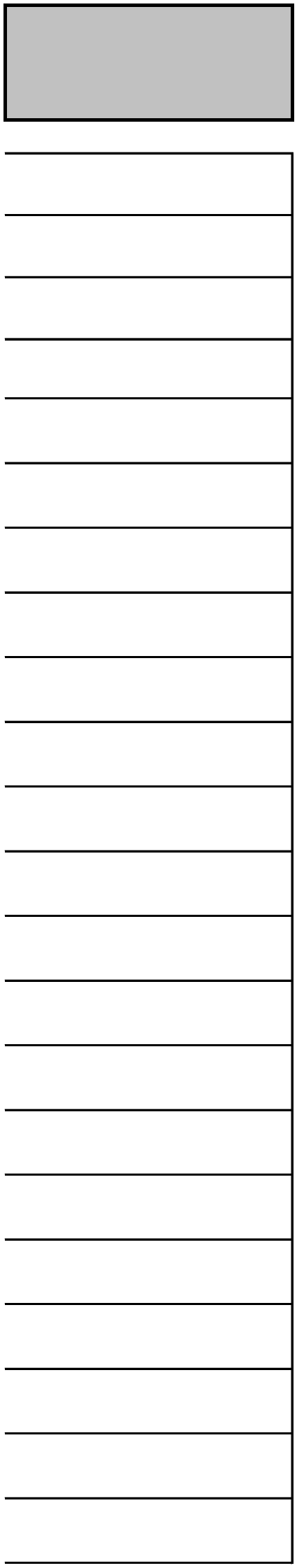
- Location of water sources used for irrigation water			
- Production level			
- Number of people who regularly eat crops produced in affected area (now and in the past)			
- Number of people working in agriculture and distribution			
c.2 - Agriculture - Livestock and game farming			
- Production type and species			
- Area and location of stock/game farming activities in relation to the SD/AMS			
- Location of boreholes used for livestock and game watering			
- Production level			
- Number of people who may consume animal products from the affected area			
- Number of people working in livestock/game rearing and distribution			
c.3 - Tourism			
- Types of tourism carried out in study area			
- Number of people employed in the affected tourism operations			
- Number of people who visit the Area of Study per year			
- Number of people employed in the tourist industry who are permanently resident in the Area of Study			
c.4 - Aquaculture and fishery			
- Species produced			
- Location of fishing/aquaculture operations in relation to the SD/AMS			
- Production level			
- Number of people who may regularly eat aquaculture or fish products			
- Information sources consulted in section c			

ANNEX E BASELINE SHEET 3	RISK ASSESSMENT RECORD FORM RISK ASSESSMENT HANDBOOK SD/AMS CHARACTERISATION OF THE SD/AMS ENVIRONMENT

6. SUMMARY OF RECEPTORS PRESENT IN SD/AMS	Summarize the
SAFETY	
CONTAMINATION	

ify details (Name/Quantity)

ify details (Name, quantity)



e identified receptors

ANNEX E: SHS STEP 1	RISK ASSESSMENT RECORD FORM RISK ASSESSMENT HANDBOOK SD/AMS SIMPLIFIED RISK ASSESSMENT - SAFETY	

STEP 1. SAFETY HAZARD SCENARIO (SHS) IDENTIFICATION (Section 4.1.2.1)

FACILITY TYPE (STOCKPILE OR SITE)	FACILITY NAME	FACILITY CODE	SHS STANDARD CODE	SHS DESCRIPTION (according to Handbook)	SHS SITE CODE	SHS DESCRIPTION
0	0	0				
0	0	0				
0	0	0				
0	0	0				
0	0	0				
0	0	0				
0	0	0				
0	0	0				
0	0	0				
0	0	0				
0	0	0				
0	0	0				

ANNEX E: SHS STEP 1	RISK ASSESSMENT RECORD FORM RISK ASSESSMENT HANDBOOK SD/AMS SIMPLIFIED RISK ASSESSMENT - SAFETY	

STEP 1. SAFETY HAZARD SCENARIO (SHS) IDENTIFICATION (Section 4.1.2.1)

FACILITY TYPE (STOCKPILE OR SITE)	FACILITY NAME	FACILITY CODE	SHS STANDARD CODE	SHS DESCRIPTION (according to Handbook)	SHS SITE CODE	SHS DESCRIPTION
0	0	0				

ANNEX E: SHS STEP 2	RISK ASSESSMENT RECORD FORM RISK ASSESSMENT HANDBOOK SD/AMS SIMPLIFIED RISK ASSESSMENT - SAFETY	

STEP 2. ASSESSMENT OF THE LIKELIHOOD OF OCURRENCE (Section 4.1.2.2.)

FACILITY NAME	SHS SITE CODE	SHS DESCRIPTION	APPLIED GUIDE	PROBABILITY INDEX	JUSTIFICATION
0	0	0			
0	0	0			
0	0	0			
0	0	0			
0	0	0			
0	0	0			
0	0	0			
0	0	0			
0	0	0			

0	0	0			

ANNEX E: SHS STEP 3.1	RISK ASSESSMENT RECORD FORM RISK ASSESSMENT HANDBOOK SD/AMS SIMPLIFIED RISK ASSESSMENT - SAFETY

STEP 3. ASSESSMENT OF THE SEVERITY OF CONSEQUENCES (Section 4.1.2.3)

3.1. HUMAN CONSEQUENCES

FACILITY NAME	SHS SITE CODE	SHS DESCRIPTION	SEVERITY OF CONSEQUENCES FOR PEOPLE	JUSTIFICATION
0	0	0		
0	0	0		
0	0	0		
0	0	0		
0	0	0		
0	0	0		
0	0	0		
0	0	0		
0	0	0		
0	0	0		

ANNEX E: SHS STEP 3.2	RISK ASSESSMENT RECORD FORM RISK ASSESSMENT HANDBOOK SD/AMS SIMPLIFIED RISK ASSESSMENT - SAFETY

STEP 3. ASSESSMENT OF THE SEVERITY OF CONSEQUENCES (Section 4.1.2.3)

3.2. ENVIRONMENTAL CONSEQUENCES

			TERRESTRIAL FAUNA & FLORA	
FACILITY NAME	SHS SITE CODE	SHS DESCRIPTION	SEVERITY	JUSTIFICATION
0	0	0		
0	0	0		
0	0	0		
0	0	0		
0	0	0		
0	0	0		
0	0	0		
0	0	0		
0	0	0		
0	0	0		

ANNEX E: SHS STEP 3.3	RISK ASSESSMENT RECORD FORM RISK ASSESSMENT HANDBOOK SD/AMS SIMPLIFIED RISK ASSESSMENT - SAFETY

STEP 3. ASSESSMENT OF THE SEVERITY OF THE CONSEQUENCES (Section 4.1.2.3)

3.3. CONSEQUENCES ON ECONOMIC ACTIVITIES

			AGRICULTURE (crops)		LIVESTOCK AND GAME FARMING		TOURISM	
FACILITY NAME	SHS SITE CODE	SHS DESCRIPTION	SEVERITY	JUSTIFICATION	SEVERITY	JUSTIFICATION	SEVERITY	JUSTIFICATION
0	0	0						
0	0	0						
0	0	0						
0	0	0						
0	0	0						
0	0	0						
0	0	0						
0	0	0						

ANNEX E: STEP 4	RISK ASSESSMENT RECORD FORM RISK ASSESSMENT HANDBOOK SD/AMS SIMPLIFIED RISK ASSESSMENT - SAFETY	

STEP 4. ASSESSING THE MAGNITUDE OF THE RISK (Section 4.1.2.4)

(cells will fill automatically)

4.1. SUMMARY TABLE

				SEVERITY OF CONSEQUENCES				
				PEOPLE	ENVIRONMENT	ECONOMIC ACTIVITIES		
FACILITY NAME	SHS SITE CODE	SHS DESCRIPTION	PROBABILITY	SAFETY	TERRESTRIAL FAUNA AND FLORA	AGRICUL-TURE (crops)	LIVESTOCK & GAME	TOURISM
				pe	tf	ag	ga	to
0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0
0	0	0	0	0				
			Negligible		0	0	0	0
0	0	0	0	0				

	0	0	Negligible		0	0	0	0

ANNEX E: CHS STEP 1	RISK ASSESSMENT RECORD FORM RISK ASSESSMENT HANDBOOK SD/AMS SIMPLIFIED RISK ASSESSMENT - CONTAMINATION

STEP 1. FORMULATION OF THE PROBLEM (Section 4.2.2.2)

1.1. CONTAMINATION MODEL DESCRIPTION FOR FACILITIES, STOCKPILES OR SITES.

Source of contamination	Mechanisms for release	Transport or residence medium	Exposure pathways	Potential direct receptors	Indirect receptors
Minerals (underground / surface mines)	**Wind action**	**Air**	**Inhalation**	**People**	**People**
Tailings	**Water action**	**Surface water** (including irrigation)	**Ingestion of food**	**Terrestrial fauna**	**Terrestrial fauna** (higher in foodchain)
Leaching waste	**Leaching** (incl acid drainage)	**Groundwater** (including irrigation)	**Skin contact**	**Aquatic life** (natural ecosystem)	**Game and Livestock**
Waste rock, low grade ore	**Evaporation or gaseous release**	**Soil**	**Direct ingestion**	**Plants and fodder crops**	
Small scale industrial and mining waste	**Physical removal**	**Man-made transport**	**Uptake by plants**	**Crops**	
				Game and Livestock	
				Aquaculture and fish species	

(Link with lines the blocks that correspond to each column)

Contamination model description

Tailings material can be blown through wind action resulting in direct inhalation, ingestion of wind blown dust by animals on forage plants and soil, which could in turn be transferred to humans through consumption of animal products.
Water is being used by people for drinking, bathing and washing and also by animals.
Some of the toxic concentrate material is being physically removed by people without dust masks or other PPE. This dust can be inhaled and will come into contact with skin.

ANNEX E: CHS STEP 2	RISK ASSESSMENT RECORD FORM RISK ASSESSMENT HANDBOOK SD/AMS SIMPLIFIED RISK ASSESSMENT - CONTAMINATION	

STEP 2. IDENTIFICATION OF CONTAMINATION HAZARD SCENARIOS (CHS) (Section 4.2.2.2)

FACILITY TYPE (STOCKPILE OR SITE)	FACILITY NAME	FACILITY CODE	STANDARD CHS CODE	CHS DESCRIPTION (according to the Handbook)	CHS SITE CODE	CHS DESCRIPTION
0	0	0				
0	0	0				
0	0	0				
0	0	0				
0	0	0				
0	0	0				
0	0	0				
0	0	0				
0	0	0				
0	0	0				

0	0	0				

ANNEX E: CHS STEP 3	RISK ASSESSMENT RECORD FORM RISK ASSESSMENT HANDBOOK SD/AMS SIMPLIFIED RISK ASSESSMENT - CONTAMINATION	

STEP 3. ESTIMATION OF THE PROBABILITY INDEX (Section 4.2.2.3)

FACILITY NAME	CHS SITE CODE	CHS DESCRIPTION	APPLIED GUIDE	PROBABILITY INDEX	JUSTIFICATION
0	0	0			
0	0	0			
0	0	0			
0	0	0			
0	0	0			
0	0	0			
0	0	0			
0	0	0			
0	0	0			

0	0	0			
0	0	0			

ANNEX E: CHS STEP 4.1	RISK ASSESSMENT RECORD FORM RISK ASSESSMENT HANDBOOK SD/AMS SIMPLIFIED RISK ASSESSMENT - CONTAMINATION	

STEP 4. ESTIMATION OF THE SEVERITY OF CONSEQUENCES (Section 4.2.2.5)

4.1. CONSEQUENCES FOR PEOPLE

FACILITY NAME	CHS SITE CODE	CHS DESCRIPTION	SEVERITY OF CONSEQUENCES FOR PEOPLE	JUSTIFICATION
0	0	0		
0	0	0		
0	0	0		
0	0	0		
0	0	0		
0	0	0		
0	0	0		
0	0	0		
0	0	0		
0	0	0		
0	0	0		

ANNEX E: CHS STEP 4.2	RISK ASSESSMENT RECORD FORM RISK ASSESSMENT HANDBOOK SD/AMS SIMPLIFIED RISK ASSESSMENT - CONTAMINATION	

STEP 4. ESTIMATION OF THE SEVERITY OF CONSEQUENCES contd. (Section 4.2.2.5)

4.2. ENVIRONMENTAL CONSEQUENCES

			AQUATIC LIFE		TERRESTRIAL FAUNA & FLORA		PROTECTED OR SENSITIVE AREAS	
FACILITY NAME	CHS SITE CODE	CHS DESCRIPTION	SEVERITY	JUSTIFICATION	SEVERITY	JUSTIFICATION	SEVERITY	JUSTIFICATION
0	0	0						
0	0	0						
0	0	0						
0	0	0						
0	0	0						
0	0	0						
0	0	0						
0	0	0						
0	0	0						
0	0	0						

0	0	0						
0	0	0						

ANNEX E: CHS STEP 4.3	RISK ASSESSMENT RECORD FORM RISK ASSESSMENT HANDBOOK SD/AMS SIMPLIFIED RISK ASSESSMENT - CONTAMINATION	

STEP 4. ESTIMATION OF THE SEVERITY OF CONSEQUENCES contd. (Section 4.2.2.5)

4.3. CONSEQUENCES FOR ECONOMIC ACTIVITIES

			AGRICULTURE (crops)		LIVESTOCK & GAME		FISHERIES AND AQUACULTURE		TOURISM	
FACILITY NAME	CHS SITE CODE	CHS DESCRIPTION	SEVERITY	JUSTIFICATION	SEVERITY	JUSTIFICATION	SEVERITY	JUSTIFICATION	SEVERITY	JUSTIFICATION
0	0	0								
0	0	0								
0	0	0								
0	0	0								
0	0	0								
0	0	0								
0	0	0								
0	0	0								
0	0	0								
0	0	0								
0	0	0								
0	0	0								

ANNEX E: CHS STEP 5	RISK ASSESSMENT RECORD FORM RISK ASSESSMENT HANDBOOK SD/AMS SIMPLIFIED RISK ASSESSMENT - CONTAMINATION	

STEP 5. ASSESSING THE MAGNITUDE OF THE RISK (Section 4.2.2.5)

(cells will fill automatically)

5.1. SUMMARY TABLE

				SEVERITY OF CONSEQUENCES							
				PEOPLE	ENVIRONMENT			ECONOMIC ACTIVITIES			
FACILITY NAME	CHS SITE CODE	CHS DESCRIPTION	PROBABILITY	PUBLIC HEALTH	AQUATIC LIFE	TERRESTRIAL FAUNA & FLORA	PROTECTED AND SENSITIVE AREAS	AGRICUL-TURE	LIVESTOCK & GAME	FISHERIES AND AQUACULT-URE	TOURISM
				pe	aq	tf	pa	ag	ga	ac	to
0	0	0	0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0	0	0	0

ANNEX E: MATRIX	RISK ASSESSMENT RECORD FORM RISK ASSESSMENT HANDBOOK SD/AMS RISK ASSESSMENT MATRIX	

RISK REGISTRATION FOR SAFETY AND CONTAMINATION (Section 4.3)

	SEVERITY OF CONSEQUENCES				
PROBABILITY INDEX	NEGLIGIBLE (A)	LOW (B)	MODERATE (C)	HIGH (D)	CATASTROPHIC (E)
HIGH (4)					
MEDIUM (3)					
LOW (2)					
NEGLIGIBLE (1)					

ANNEX E: CRA-1	RISK ASSESSMENT RECORD FORM RISK ASSESSMENT HANDBOOK SD/AMS CUMULATIVE RISK ASSESSMENT	

CUMULATIVE RISK ASSESSMENT (CRA) (Section 4.4 and Figure 2-2)

CRA-1. WHEN TO CARRY OUT A CRA.

	Yes / No	(Justify)
1.1. Does the Area of Study overlap with that of another SD/AMS?		

If the answer (1.1) is positive, proceed with questions (1.2 … 1.5).
If the answer is negative, please go to the next page.

	(Revised findings
1.2. Check if the site's Hazard Scenarios might be affected by Hazard Scenarios belonging to the other site(s).	
1.3. Check if the study area should be corrected to accommodate the combined Hazard Scenarios.	
1.4. Check the site's Ocurrence of Probability values for consequences taking into account the cumulative effects.	
1.5. Check risk magnitudes registered for SD/AMS.	

ANNEX E: CRA-2	RISK ASSESSMENT RECORD FORM RISK ASSESSMENT HANDBOOK SD/AMS CUMULATIVE RISK ASSESSMENT - SAFETY	

CUMULATIVE RISK ASSESSMENT - SAFETY

CRA-2. REVIEW OF THE PROBABILITY OF OCCURRENCE AND SEVERITY OF CONSEQUENCES FOR SAFETY HAZARD SCENARIOS.

				SEVERITY OF CONSEQUENCES							
				PEOPLE	ENVIRONMENT			ECONOMIC ACTIVITIES			
FACILITY NAME	SHS SITE CODE	SHS DESCRIPTION	PROBABILITY	SAFETY	AQUATIC LIFE	TERRESTRIAL FAUNA & FLORA	PROTECTED & SENSITIVE AREAS	AGRICUL-TURE	LIVESTOCK & GAME	FISHERIES AND AQUACUL-TURE	TOURISM
				pe	aq	tf	pa	ag	ga	ac	to
0	0	0									
0	0	0									
0	0	0									
0	0	0									
0	0	0									
0	0	0									
0	0	0									
0	0	0									
0	0	0									

ANNEX E: CRA-3	RISK ASSESSMENT RECORD FORM RISK ASSESSMENT HANDBOOK SD/AMS CUMULATIVE RISK ASSESSMENT - CONTAMINATION	

CUMULATIVE RISK ASSESSMENT - CONTAMINATION

CRA-3. REVIEW OF THE PROBABILITY OF OCCURRENCE AND SEVERITY OF CONSEQUENCES FOR CONTAMINATION HAZARD SCENARIOS.

				SEVERITY OF CONSEQUENCES							
				PEOPLE	ENVIRONMENT			ECONOMIC ACTIVITIES			
FACILITY NAME	SHS SITE CODE	SHS DESCRIPTION	PROBABILITY	SAFETY	AQUATIC LIFE	TERRESTRIAL FAUNA & FLORA	PROTECTED & SENSITIVE AREAS	AGRICUL-TURE	LIVESTOCK & GAME	FISHERIES AND AQUACUL-TURE	TOURISM
				pe	aq	tf	pa	ag	ga	ac	to
0	0	0									
0	0	0									
0	0	0									
0	0	0									
0	0	0									
0	0	0									
0	0	0									
0	0	0									
0	0	0									

ANNEX E: CRA MATRIX	RISK ASSESSMENT RECORD FORM RISK ASSESSMENT HANDBOOK SD/AMS CUMULATIVE RISK ASSESSMENT MATRIX	

CUMULATIVE RISK ASSESSMENT

CRA-4. RISK RECORD FOR SAFETY AND CONTAMINATION

	SEVERITY OF CONSEQUENCES				
PROBABILITY INDEX	**NEGLIGIBLE (A)**	**LOW (B)**	**MODERATE (C)**	**HIGH (D)**	**CATASTROPHIC (E)**
HIGH (4)					
MEDIUM (3)					
LOW (2)					
NEGLIGIBLE (1)					

ANNEX E: CLASSIFI-CATION	RISK ASSESSMENT RECORD FORM RISK ASSESSMENT HANDBOOK SD/AMS	

SITE CLASSIFICATION

	Yes/No	(Mark corresponding issues)	
The highest risks are located in cells			
a4, a5, a7, a8, a9		THE SITE IS CLASSIFIED AS "MINING LIABILITY"	END OF PROCESS
b1, b2, b3, b4, b5, b6		THE SITE IS CLASSIFIED AS "NON-MINING LIABILITY"	END OF PROCESS
a1 a2, a3, a6		Go to question 2.2	
b7, b8, b9, b10, b11		Go to question 2.3	

Assessor enters comments on the final site classification

NEED TO PERFORM A DETAILED RISK ASSESSMENT (DRA) (Section 4.5)

	Yes / No	(Justify)
2.2. Is there certainty on assessing AT LEAST ONE of the risks located in the cells a1, a2, a3, a6?		

If the anwer is YES… The SITE IS A MINING LIABILITY — END OF PROCESS

	Yes / No	(Justify)
2.3. Is there certainty on assessing ALL the risks located in b7… b11 ?		

If the answer is YES… The SITE IS NOT A MINING LIABILITY — END OF PROCESS

If the answer in 2.2. / 2.3 is NO A Detailed Risk Assessment is required for uncertain hazard scenarios. (see Chapters 5 and 6)

ANNEX E: APP 1 DRA	RISK ASSESSMENT RECORD FORM RISK ASSESSMENT HANDBOOK SD/AMS	

APPENDIX 1. DETAILED RISK ASSESSMENT

Hazard scenario identification requiring a DRA

SHS CODE or SHS	HAZARD SCENARIO	DESCRIPTION	UNCERTAINTY REASON

DRA Technical specifications

SHS CODE or SHS	DRA OBJECTIVES	SCOPE	TYPE OF SPECIALIST REQUIRED	ESTIMATED COSTS

DRA documentation

MME/GSN Responsible party	
Record date	
Entered by	
Reviewed by	
Approved by	

Once you´re done with the DRAs, RETURN TO CLASSIFICATION

APPENDIX 2 : NOTES

A. Add comments on site access and safety conditions (for the Assessor).

B. Add comments on measurements and estimates obtained during the assessment.

ANNEX E: PHOTO LOG	RISK ASSESSMENT RECORD FORM RISK ASSESSMENT HANDBOOK SD/AMS	

APPENDIX 3. PHOTOS

PHOTOS	INSTALLATION / SITE	DESCRIPTION (photo)	DATE	HAZARD SCENARIO	CO-ORD. SOUTH	CO-ORD. EAST

ANNEX E Cover page 1	RISK ASSESSMENT RECORD FORM RISK ASSESSMENT HANDBOOK FMA/P ASSESSMENT COVER PAGE	PAGE 1

A. IDENTIFICATION OF SHUT DOWN OR ABANDONED MINE SITE (SD/AMS)

				MIDS CODE:	2
SITE NAME	Abenab Mine	REGION:	Otjozondjupa	COMMUNITY:	Abenab village
MINING COMPANY (if known)	Tsumeb Corporation Limited	ADDRESS (if known)	n/a		
CONTACT PERSON (if available)	Jerry Mbwale	ADDRESS / PHONE / MAIL	n/a		
IS MINE ABANDONED OR CLOSED?	Abandoned				

B. ADVISORS, REVIEWERS AND APPROVAL

	NAME POSITION	SIGNATURE	DATE	SPECIALIST ROLE IN THE ASSESSMENT
Assessor 1:	Moses		03 August 2011	Contamination team
Assessor 2:	Alina		03 August 2011	Contamination team
Assessor 3:	Rudolf		03 August 2011	Contamination team
Assessor 4:	Rosina		03 August 2011	Contamination team
Advisor 5:	Godfrey		03 August 2011	Safety team
Advisor 6:	Kaarina		03 August 2011	Safety team
Advisor 7:	Ewaldine		03 August 2011	Safety team
Assessor 8:	Nekwaya		03 August 2011	Safety team
REVIEWER:	Bryony Walmsley		03 August 2011	Trainer
APPROVED BY				

C. SHUT DOWN OR ABANDONED MINE SITE COMPONENTS (Section 4.1.2.1, a)

COMPONENT	FACILITY TYPE (STOCKPILE OR SITE)	FACILITY NAME	FACILITY CODE	GENERAL DESCRIPTION OF FACILITY, STOCKPILE OR SITE	UNIT IDENTIFICATION AND CHARACTERISATION	CO-ORD SOUTH	CO-ORD EAST	ALTITUDE
Mine	Open pit mine	Breccia pipe	OP1	Roughly circular pit approx 120m in diameter. Almost vertical walls covered in vegetation; some benches still apparent. Filled with water at a depth of 80-100m	Fenced off, but still several access points and steps leading down to last bench above water	-19,283	18,083	
Plant	Process plant	Concentrator plant	P1	Large number of dilapidated buildings from top of slope to foot of hill. Unsafe structures, high walls, open tanks, pits and sumps	Open access to all areas. Plant area includes: concentrator area, analytical lab, workshops, storage areas etc			
Large-scale mine wastes	Waste rock, low grade ore	Waste rock dumps	LW1	Several waste rock dumps with material of various sizes lying at natural angle of repose and mostly overgrown	Open access to top and bottom of dumps			
Large-scale mine wastes	Tailings dumps (dry)	Tailings dump	LW2	Two main areas of tailings disposal: approx 500m to NW; and slurried out from the plant on top of waste rock, covering an area of about 18ha	Highly eroded and widely dispersed. Good growth of vegetation over parts, especially on NW dump			
Small-scale mining and industrial wastes	Concentrate waste	White concentrate wastes	SW1	Concentrate wastes containing 3.5% Pb, 1% As, 40% Zn, and strong smell of sulphur found on top of and adjacent to tailings/waste rock dump	Light grey to white, fine powder and consolidated sediment layer			
Small-scale mining and industrial wastes	Concentrate waste	Light grey concentrate wastes	SW2	Wastes containing Pb (410ppm), As (26ppm), V (219ppm), Cu (145ppm) found in approx 20 marked, rusty small drums	Light grey material			
Small-scale mining and industrial wastes	Concentrate waste	Dark grey concentrate wastes	SW3	Wastes containing 0.2% Pb, 347ppm As, 0.7% Zn, 0.2% Cu, 81ppm Hg, 0.3% Ni found in unmarked, rusty drums	Dark grey fine grained material. Considerable plant growth in this material			
Small-scale mining and industrial wastes	Scrap metal	Plant area	SW4	Scrap metal lying everywhere with sharp and serrated edges	Open access to plant; signs of scrap metal collection			
Infrastructure	Water reservoirs and pipelines	Plant area	I1	Concrete water tank 20mx6mx4m deep divided into two. Vertical sides; no escape route; contains water of 1-2m depth	Dead bird and fish visible. Many small live fish visible. Water green in colour with abundant algae; no apparent use			
Infrastructure	Water reservoirs and pipelines	Plant area	I2	Round water tank of approx 30m diameter and 2-3m high; contains water 1-2m in depth. Drum has been placed to provide access out	Water green in colour; no odour; signs of fishing. Used for stock watering			
Small-scale mining and industrial wastes	Resin and/or hydrocarbons	Veld	SW5	Highly toxic resin from burning of invader bush (including Tamboti wood) in kiln was slurried onto bare soil	Strong odour; no plant growth; resin crust 10-15cm thick has been broken up by animals			

ANNEX E BASELINE SHEET 1	RISK ASSESSMENT RECORD FORM RISK ASSESSMENT HANDBOOK SD/AMS CHARACTERISATION OF THE SD/AMS ENVIRONMENT	

1. INFORMATION COLLECTION (Section 3.2.1)

1.1 Information available on Mine Inventory Data Sheet (MIDS)

	Yes/No	MIDS Code	
MIDS available	Yes	2	(Specify sample number)
The MIDS includes a water quality laboratory analysis	No		
The MIDS includes a laboratory analysis of solid residues	No		

(Observations)

1.2. Public Services or Third Party Interviews/Information

SOURCE TYPE	INFORMATION SOURCE (name, contact details)	DATE	INTERVIEWER	TYPE OF INFORMATION GATHERED
Ministry of Mines and Energy				
Geological Survey of Namibia	**Library**			**Vol 2 of inventory of abandoned mines (date unknown but post-1997)**
Ministry of Environment and Tourism				
Mining Company				
Abenab villagers	??	03. Aug	Team	**Number of residents; economic activity, safety issues**

ANNEX E BASELINE SHEET 2	RISK ASSESSMENT RECORD FORM RISK ASSESSMENT HANDBOOK SD/AMS CHARACTERISATION OF THE SD/AMS ENVIRONMENT	

2. MAP PREPARATION (Section 3.2.2)		
2.1 Data Collected	**Yes/No**	(Specify what has been used to compile the Base Map)
Sheet 1:50,000 or 1:250,000	No	
Aerial photography (stereo pairs or 1:10,000 orthophographs)	No	
Satellite images	Yes	**Google image 2010**
Other cartographic sources		
2.2 Risk Assessment Base Map Preparation (RABM)	(Specify base map characteristics)	
Scale:		
Projection system (Geographic Coord. / UTM):		
Preparation process:		
Digital file names:		
Is there a copy of the map or image in the MIDS file?		

3. DEFINITION OF THE AREA OF STUDY (Section 3.2.3) (see Note below)		
3.1 Area of the mine site	Mine site abandoned in 1947 following 25 years of mining. Produced 56,000 t vanadium cincentrate at a grade of 18.5% V2O5	
Area directly affected by the mine (ha)	**130 ha**	
3.2 Areas that might be directly or indirectly affected by contamination or catastrophic events	**Yes/No**	(Justify)
Potentially affected surface water courses	No	**Karst landscape; surface runoff ephemeral after storm events; only surface water at base of pit (groundwater)**
Potentially affected groundwater areas	No	**Quality unknown but used for drinking purposes by residents of village. High buffering capacity limits potential for metals to go into solution.**
Area affected by wind driven dust and gas dispersion (soils and air)	Yes	**Tailings have been dispersed widely in landscape; heaps of ash-like material; very toxic resin; pollution potential unknown**
Area that could be affected by a catastrophic event on site	No	**Dumps are relatively stable**
Families that commonly consume agricultural, game and fish products, (crops, meat and fish) produced in the Area of Study	Yes	**About 20 people live in the old mine village. They graze cattle and goats on the AMS. Evidence of fishing in the water tanks (nets). Probably hunt game as well**
Applied safety zone (buffer). Required in case of uncertainty related to the study area limits.	?	**Not measured or surveyed fully on site. Need data on grass uptake of metals**

Note: the area to analyze must be defined ahead of time, prior to the field visit. Once the information gathered in the field is available, the size of the Area of Study may be adjusted

ANNEX E BASELINE SHEET 3	RISK ASSESSMENT RECORD FORM RISK ASSESSMENT HANDBOOK SD/AMS CHARACTERISATION OF THE SD/AMS ENVIRONMENT

4. IDENTIFICATION AND DESCRIPTION OF RECEPTORS IN THE AREA OF STUDY (Section 3.2.4)			
a. People		**Yes/No**	Spec
a.1 - Does anyone live in the Area of Study?		Yes	
- Settlement type		**Informal settlement in aban**	
- Is surface water being collected for human consumption?		**No**	
- Is groundwater being obtained from boreholes or wells for human consumption?		**Yes. Water is being pumpe**	
- Are there any fountains or springs located downstream of the site?		**Do not know**	
a.2. - Are there any site visitors?		Yes	
- Estimated number of vistors/site users per day, week, month or year		**About 20 people visit daily. once per day**	
- Motivation for entry		**There are 6 families reside the site on a daily basis to make charcoal, collect woo**	
- City or settlement of origin		**Abenab informal settlemen**	
- Age		**Young and old (6 families)**	
- Information source		**Visual observations. Interv**	
b. Environment		**Yes/No**	SPEC
b.1. Is there any aquatic life that has been or may be affected?		**Yes**	
- Name of river, stream, water course or dam (if any, otherwise give it an identifying name)		**Pool at base of pit; water ta**	
- Presence of protected species		**unknown**	
- Surface area of water body and/or length of stream/river that flows through the Area of Study		**Approx 1.2 ha**	
- Information sources consulted in section b.1		**Visual observations.**	
b.2. - Has the terrestrial flora been affected?		?	**Don't know if toxic substan**
- Ecosystem type(s)		**Karstveld. Mixed woodland**	
- Use of plant species		**Fodder for cattle and goats**	
- Presence of protected species of flora		**Unlikely**	
- Abundancy estimation		**n/a**	
- Conservation status		**n/a**	

ANNEX E BASELINE SHEET 3	RISK ASSESSMENT RECORD FORM RISK ASSESSMENT HANDBOOK SD/AMS CHARACTERISATION OF THE SD/AMS ENVIRONMENT		
- Presence of invasive and/or alien species			Yes - lantana and much bu (Dichrostachys cinerea)
- Information sources consulted in section b.2			Atlas of Namibia; visual ob
b.3. - Has the terrestrial fauna been affected?		?	Don't know if toxic substan uptake by wild
- Typical species present			In an area of high biodivers Most likely species are spri gemsbok, leopard, but few
- Are any of the species harvested for human consumption and how many people consume these products on a regular basis?			Yes. It is likely that small a hunted and eaten by the ap
- Presence of protected species of fauna			Unlikely
- Abundancy estimation			n/a
- Conservation status			n/a
- Presence of invasive and/or alien species			?
- Information sources consulted in section b.2			Atlas of Namibia; visual ob
b.4. - Is the site in or adjacent to protected or sensitive areas?		No	
- Presence or proximity of these areas - state name and distance to mine site			
- Protection category			
- Natural or cultural value			
- Importance of protected or sensitive area at a local, regional and national level			
- Presence of endemic or protected species			
- Component of the natural environment that might be affected by safety or contamination emitted by SD/AMS			
- Area of sensitive environment contained in the Area of Study			
- Information sources consulted in section b.3			
c. Will any economic activities be adversely affected?		Yes/No	Speci
c.1 - Agriculture -crop farming		No	
- Type of crop production (specify crops)			
- Area and location of crop farming in relation to SD/AMS			
- Location of water sources used for irrigation water			

ANNEX E BASELINE SHEET 3	RISK ASSESSMENT RECORD FORM RISK ASSESSMENT HANDBOOK SD/AMS CHARACTERISATION OF THE SD/AMS ENVIRONMENT

- Production level		
- Number of people who regularly eat crops produced in affected area		
- Number of people working in agriculture and distribution		
c.2 - Agriculture - Livestock and game farming	Yes	
- Production type and species	Cattle, goats, donkeys	
- Area and location of stock/game farming activities in relation to the SD/AMS	Evidence of cattle, goats ar	
- Location of boreholes used for livestock and game watering	Water pumped from undeg	
- Production level	Cattle are sold commercial	
- Number of people who may consume animal products from the affected area	Cattle products - number u	
- Number of people working in livestock/game rearing and distribution	About 10	
c.3 - Tourism	No	
- Types of tourism carried out in study area		
- Number of people employed in the affected tourism operations		
- Number of people who visit the Area of Study per year		
- Number of people employed in the tourist industry who are permanently resident in the Area of Study		
c.4 - Aquaculture and fishery	Yes	
- Species produced	Unknown - probably barbel	
- Location of fishing/aquaculture operations in relation to the SD/AMS	Evidence of fishing nets ar	
- Production level	Subsistence	
- Number of people who may regularly eat aquaculture or fish products	Approx 20 people	
- Information sources consulted in section c	Visual observations; discu residents	

ANNEX E BASELINE SHEET 3	RISK ASSESSMENT RECORD FORM RISK ASSESSMENT HANDBOOK SD/AMS CHARACTERISATION OF THE SD/AMS ENVIRONMENT

6. SUMMARY OF RECEPTORS PRESENT IN SD/AMS

Summarize the

SAFETY

Safety hazards present all over site, particularly the open pit which is inadequately fenced, the old plant area where t
and high walls, tanks etc and unstable waste rock dumps

CONTAMINATION

The contamination risks are unknown because there are no data on water quality, which is being used for drinking a
community, nor on 'soil' (tailings) chemistry and whether plant species used for forage by livestock and wildlife are b

ify details (Name/Quantity)
ıdoned mine village
d from underground for potable
Some may visit more than
ıt and it seems that they visit wash, collect water, herd cattle, ıd
t
iews with visitors
IFY DETAILS (Name, quantity)
ınks on top of hill
there has been any uptake of ces by plants
:; browse for wildlife

sh encroachment
servations
there has been any uptake of ces by plants, with subsequent l animals
sity, but with low endemism. ingbok, kudu, hartebeest, signs of wild animals seen
nd medium size mammals are pprox 20 residents
servations
ify details (Name, quantity)

ıda donkeys all over the site
round to circular tank at top of h
ly; goats are probably for subsis
nknown; Goats - probably all the
(catfish)
ound tanks at top of hill.
ssions with Abenab village

e identified receptors

there are many unsafe structures

nd washing by the local
ioaccumulating heavy metals

ANNEX E: SHS STEP 1	RISK ASSESSMENT RECORD FORM RISK ASSESSMENT HANDBOOK SD/AMS SIMPLIFIED RISK ASSESSMENT - SAFETY	

STEP 1. SAFETY HAZARD SCENARIO (SHS) IDENTIFICATION (Section 4.1.2.1)

FACILITY TYPE (STOCKPILE OR SITE)	FACILITY NAME	FACILITY CODE	SHS STANDARD CODE	SHS DESCRIPTION (according to Handbook)	SHS SITE CODE	SHS DESCRIPTION
Open pit mine	Breccia pipe	OP1	SHS 12	Risk of falling from elevated unsafe structures or heights.	OP1-SHS12	Although the open pit is fenced, there are gaps in the fence and access is unrestricted. Very high vertical pit walls
Process plant	Concentrator plant	P1	SHS 12	Risk of falling from elevated unsafe structures or heights.	P1-SHS12	High walls over 10m high; unrestricted access
Process plant	Concentrator plant	P1	SHS 13	Falling of unsafe remnant structures and other elements onto people.	P1-SHS13	Dilapidated buildings with loose bricks, unsafe roof trusses
Waste rock, low grade ore	Waste rock dumps	LW1	SHS 12	Risk of falling from elevated unsafe structures or heights.	LW1-SHS12	Undercut edge of waste rock dump
Tailings dumps (dry)	Tailings dump	LW2	SHS 12	Risk of falling from elevated unsafe structures or heights.	LW2-SHS12	Deep gullies in eroded tailings which were slurried onto waste rock dumps; evidence of frequent access
Concentrate waste	White concentrate wastes	SW1				
Concentrate waste	Light grey concentrate wastes	SW2				
Concentrate waste	Dark grey concentrate wastes	SW3				
Scrap metal	Plant area	SW4	SHS 14	Physical contact with unsafe remnant structures or other elements that may cause injury or damage.	SW4-SHS14	Glass shards and sharp pieces of scrap metal lying everywhere; unprotected sumps
Water reservoirs and pipelines	Plant area	I1	SHS 4	Drowning in pools, ponds, tanks.	I1-SHS4	Concrete water tank 20mx6mx4m deep divided into two. Vertical sides; no escape route; contains water of 1-2m depth
Water reservoirs and pipelines	Plant area	I2	SHS 4	Drowning in pools, ponds, tanks.	I2-SHS4	Round water tank of approx 30m diameter and 2-3m high; contains water 1-2m in depth. Drum has been placed to provide access out

ANNEX E: SHS STEP 1	RISK ASSESSMENT RECORD FORM RISK ASSESSMENT HANDBOOK SD/AMS SIMPLIFIED RISK ASSESSMENT - SAFETY	

STEP 1. SAFETY HAZARD SCENARIO (SHS) IDENTIFICATION (Section 4.1.2.1)

FACILITY TYPE (STOCKPILE OR SITE)	FACILITY NAME	FACILITY CODE	SHS STANDARD CODE	SHS DESCRIPTION (according to Handbook)	SHS SITE CODE	SHS DESCRIPTION
Resin and/or hydrocarbons	Veld	SW5				

ANNEX E: SHS STEP 2	RISK ASSESSMENT RECORD FORM RISK ASSESSMENT HANDBOOK SD/AMS SIMPLIFIED RISK ASSESSMENT - SAFETY	

STEP 2. ASSESSMENT OF THE LIKELIHOOD OF OCURRENCE (Section 4.1.2.2.)

FACILITY NAME	SHS SITE CODE	SHS DESCRIPTION	APPLIED GUIDE	PROBABILITY INDEX	JUSTIFICATION
Breccia pipe	OP1-SHS12	Although the open pit is fenced, there are gaps in the fence and access is unrestricted. Very high vertical pit walls	**Guideline 7**	**Medium**	**Although steep, walls appear quite stable around edges; access not on a daily basis**
Concentrator plant	P1-SHS13	Dilapidated buildings with loose bricks, unsafe roof trusses	**Guideline 7**	**High**	**Many dangerous structures; unrestricted access; appears to be daily access by adults and children**
Tailings dump	LW2-SHS12	Deep gullies in eroded tailings which were slurried onto waste rock dumps; evidence of frequent access	**Guideline 7**	**High**	**Steep gullies and slopes more than 1.5m high; daily access**
White concentrate wastes	0	0			
Light grey concentrate wastes	0	0			
Dark grey concentrate wastes	0	0			
Plant area	SW4-SHS14	Glass shards and sharp pieces of scrap metal lying everywhere; unprotected sumps	**Guideline 7**	**High**	**Broken glass and scrap metal lying all over site; unrestricted and frequent access by all, including children**
Plant area	I1-SHS4	Concrete water tank 20mx6mx4m deep divided into two. Vertical sides; no escape route; contains water of 1-2m depth	**Guideline 7**	**High**	**Unrestricted access to tank for people (low wall)**
				Negligible	**Stock/game cannot access tank due to wall**

Plant area	I2-SHS4	Round water tank of approx 30m diameter and 2-3m high; contains water 1-2m in depth. Drum has been placed to provide access out	**Guideline 7**	**High**	**Makeshift ladder used to access tank**
				Negligible	**Stock/game cannot access tank due to high walls**

ANNEX E: SHS STEP 3.1	RISK ASSESSMENT RECORD FORM RISK ASSESSMENT HANDBOOK SD/AMS SIMPLIFIED RISK ASSESSMENT - SAFETY

STEP 3. ASSESSMENT OF THE SEVERITY OF CONSEQUENCES (Section 4.1.2.3)

3.1. HUMAN CONSEQUENCES

FACILITY NAME	SHS SITE CODE	SHS DESCRIPTION	SEVERITY OF CONSEQUENCES FOR PEOPLE	JUSTIFICATION
Breccia pipe	OP1-SHS12	Although the open pit is fenced, there are gaps in the fence and access is unrestricted. Very high vertical pit walls	**High**	**A fall from the edge of the pit will likely be fatal**
Concentrator plant	P1-SHS13	Dilapidated buildings with loose bricks, unsafe roof trusses	**Low**	**Falls of loose building material unlikely to cause permanent disability**
Tailings dump	LW2-SHS12	Deep gullies in eroded tailings which were slurried onto waste rock dumps; evidence of frequent access	**Negligible**	**Slopes are not that high or steep to cause major injury**
White concentrate wastes	0	0		
Light grey concentrate wastes	0	0		
Dark grey concentrate wastes	0	0		
Plant area	SW4-SHS14	Glass shards and sharp pieces of scrap metal lying everywhere; unprotected sumps	**Low**	**An injury from broken glass or rusty metal may need some medical attention**
Plant area	I1-SHS4	Concrete water tank 20mx6mx4m deep divided into two. Vertical sides; no escape route; contains water of 1-2m depth	**High**	**If someone were to fall into this tank, there is no way out. If the depth of water is greater than the person who has fallen in (e.g. a child), they will drown.**
Plant area	I2-SHS4	Round water tank of approx 30m diameter and 2-3m high; contains water 1-2m in depth. Drum has been placed to provide access out	**High**	**Although a drum has been placed in this tank a small child would not be able to climb out. If the water depth is too deep a child might drown.**

ANNEX E: SHS STEP 3.2	RISK ASSESSMENT RECORD FORM RISK ASSESSMENT HANDBOOK SD/AMS SIMPLIFIED RISK ASSESSMENT - SAFETY

STEP 3. ASSESSMENT OF THE SEVERITY OF CONSEQUENCES (Section 4.1.2.3)

3.2. ENVIRONMENTAL CONSEQUENCES

			TERRESTRIAL FAUNA & FLORA	
FACILITY NAME	**SHS SITE CODE**	**SHS DESCRIPTION**	**SEVERITY**	**JUSTIFICATION**
Breccia pipe	OP1-SHS12	Although the open pit is fenced, there are gaps in the fence and access is unrestricted. Very high vertical pit walls	**Low**	**A kudu was reported to have fallen and drowned in the pool (due to hunting?)**
Concentrator plant	P1-SHS13	Dilapidated buildings with loose bricks, unsafe roof trusses	**Negligible**	**Unlikely for animals to be injured or killed**
Tailings dump	LW2-SHS12	Deep gullies in eroded tailings which were slurried onto waste rock dumps; evidence of frequent access	**Negligible**	**Unlikely for animals to be injured or killed**
White concentrate wastes	0	0		
Light grey concentrate wastes	0	0		
Dark grey concentrate wastes	0	0		
Plant area	SW4-SHS14	Glass shards and sharp pieces of scrap metal lying everywhere; unprotected sumps	**Negligible**	**Unlikely for animals to be injured or killed**
Plant area	I1-SHS4	Concrete water tank 20mx6mx4m deep divided into two. Vertical sides; no escape route; contains water of 1-2m depth	**Low**	**Evidence of a dead bird in pool of water. Any animal falling into this tank will drown**
Plant area	I2-SHS4	Round water tank of approx 30m diameter and 2-3m high; contains water 1-2m in depth. Drum has been placed to provide access out	**Low**	**Any animal falling into this tank will drown**
Veld	0	0		

ANNEX E: SHS STEP 3.3	RISK ASSESSMENT RECORD FORM RISK ASSESSMENT HANDBOOK SD/AMS SIMPLIFIED RISK ASSESSMENT - SAFETY

STEP 3. ASSESSMENT OF THE SEVERITY OF THE CONSEQUENCES (Section 4.1.2.3)

3.3. CONSEQUENCES ON ECONOMIC ACTIVITIES

			AGRICULTURE (crops)		LIVESTOCK AND GAME FARMING		TOURISM	
FACILITY NAME	SHS SITE CODE	SHS DESCRIPTION	SEVERITY	JUSTIFICATION	SEVERITY	JUSTIFICATION	SEVERITY	JUSTIFICATION
Breccia pipe	OP1-SHS12	Although the open pit is fenced, there are gaps in the fence and access is unrestricted. Very high vertical pit walls	None	No crop farming	Low	No reports of cattle falling into pit, but possibility exists	None	No tourists visit this site
Concentrator plant	P1-SHS13	Dilapidated buildings with loose bricks, unsafe roof trusses	None	No crop farming	Negligible	Unlikely to cause injuries to stock	None	No tourists visit this site
Tailings dump	LW2-SHS12	Deep gullies in eroded tailings which were slurried onto waste rock dumps;	None	No crop farming	Negligible	Unlikely to cause injuries to stock	None	No tourists visit this site
White concentrate wastes	0	0						
Light grey concentrate wastes	0	0						
Dark grey concentrate wastes	0	0						
Plant area	SW4-SHS14	Glass shards and sharp pieces of scrap metal lying everywhere; unprotected	None	No crop farming	Negligible	Unlikely to cause injuries to stock	None	No tourists visit this site
Plant area	I1-SHS4	Concrete water tank 20mx6mx4m deep divided into two. Vertical sides; no	None	No crop farming	Low	If stock were to fall in, they would drown	None	No tourists visit this site
Plant area	I2-SHS4	Round water tank of approx 30m diameter and 2-3m high; contains water 1-2m in depth.	None	No crop farming	Low	If stock were to fall in, they would drown	None	No tourists visit this site

ANNEX E: STEP 4	RISK ASSESSMENT RECORD FORM RISK ASSESSMENT HANDBOOK SD/AMS SIMPLIFIED RISK ASSESSMENT - SAFETY	

STEP 4. ASSESSING THE MAGNITUDE OF THE RISK (Section 4.1.2.4)

(cells will fill automatically)

4.1. SUMMARY TABLE

				SEVERITY OF CONSEQUENCES				
				PEOPLE	ENVIRONMENT	ECONOMIC ACTIVITIES		
FACILITY NAME	SHS SITE CODE	SHS DESCRIPTION	PROBABILITY	SAFETY	TERRESTRIAL FAUNA AND FLORA	AGRICUL-TURE (crops)	LIVESTOCK & GAME	TOURISM
				pe	tf	ag	ga	to
Breccia pipe	OP1-SHS12	Although the open pit is fenced, there are gaps in the fence and access is unrestricted. Very high vertical pit walls	Medium	High	Low	None	Low	None
Concentrator plant	P1-SHS13	Dilapidated buildings with loose bricks, unsafe roof trusses	High	Low	Negligible	None	Negligible	None
Tailings dump	LW2-SHS12	Deep gullies in eroded tailings which were slurried onto waste rock dumps; evidence of frequent access	High	Negligible	Negligible	None	Negligible	None
White concentrate wastes	0	0	0	0	0	0	0	0
Light grey concentrate wastes	0	0	0	0	0	0	0	0
Dark grey concentrate wastes	0	0	0	0	0	0	0	0
Plant area	SW4-SHS14	Glass shards and sharp pieces of scrap metal lying everywhere; unprotected sumps	High	Low	Negligible	None	Negligible	None
Plant area	I1-SHS4	Concrete water tank 20mx6mx4m deep divided into two. Vertical sides; no escape route; contains water of 1-2m depth	High	High				
			Negligible		Low	None	Low	None
Plant area	I2-SHS4	Round water tank of approx 30m diameter and 2-3m high; contains water 1-2m in	High	High				

	[illegible]	contains water 1-2m in depth. Drum has been placed to provide access out	**Negligible**		**Low**	**None**	**Low**	**None**

ANNEX E: CHS STEP 1	RISK ASSESSMENT RECORD FORM RISK ASSESSMENT HANDBOOK SD/AMS SIMPLIFIED RISK ASSESSMENT - CONTAMINATION

STEP 1. FORMULATION OF THE PROBLEM (Section 4.2.2.2)

1.1. CONTAMINATION MODEL DESCRIPTION FOR FACILITIES, STOCKPILES OR SITES.

Source of contamination	Mechanisms for release	Transport or residence medium	Exposure pathways	Potential direct receptors	Indirect receptors
Minerals (underground / surface mines)	**Wind action**	**Air**	**Inhalation**	**People**	**People**
Tailings	**Water action**	**Surface water** (including irrigation)	**Ingestion of food**	**Terrestrial fauna**	**Terrestrial fauna** (higher in foodchain)
Leaching waste	**Leaching** (incl acid drainage)	**Groundwater** (including irrigation)	**Skin contact**	**Aquatic life** (natural ecosystem)	**Game and Livestock**
Waste rock, low grade ore	**Evaporation or gaseous release**	**Soil**	**Direct ingestion**	**Plants and fodder crops**	
Small scale industrial and mining waste	**Physical removal**	**Man-made transport**	**Uptake by plants**	**Crops**	
				Game and Livestock	
				Aquaculture and fish species	

(Link with lines the blocks that correspond to each column)

Contamination model description

Tailings material can be blown through wind action resulting in direct inhalation, ingestion of wind blown dust by animals on forage plants and soil, which could in turn be transferred to humans through consumption of animal products.
Water is being used by people for drinking, bathing and washing and also by animals.
Some of the toxic concentrate material is being physically removed by people without dust masks or other PPE. This dust can be inhaled and will come into contact with skin.

ANNEX E: CHS STEP 2	RISK ASSESSMENT RECORD FORM RISK ASSESSMENT HANDBOOK SD/AMS SIMPLIFIED RISK ASSESSMENT - CONTAMINATION	

STEP 2. IDENTIFICATION OF CONTAMINATION HAZARD SCENARIOS (CHS) (Section 4.2.2.2)

FACILITY TYPE (STOCKPILE OR SITE)	FACILITY NAME	FACILITY CODE	STANDARD CHS CODE	CHS DESCRIPTION (according to the Handbook)	CHS SITE CODE	CHS DESCRIPTION
Open pit mine	Breccia pipe	OP1	CHS 2	Presence of drainage that could percolate and contaminate groundwater, affecting persons, environment or economic activity.	OP1-CHS2	Open pit pool is in direct contact with groundwater. Groundwater is being pumped for human and animal consumption
Process plant	Concentrator plant	P1				
Waste rock, low grade ore	Waste rock dumps	LW1				
Tailings dumps (dry)	Tailings dump	LW2	CHS 7	Surface activity involving tailings, stockpiles or contaminated soils, which could affect persons, environment or economy activity through inhalation, accidental ingestion or skin contact.	LW2-CHS7	Livestock and game are eating the vegetation growing in tailings, which have a high metal content. The vegetation could be bioaccumulating some of these metals
Concentrate waste	White concentrate wastes	SW1	CHS 8	Movement of particulate material due to wind, which could affect persons (inhalation), environment or economic activity.	SW1-CHS8	People were seen removing white powdery concentrate using shovels and a wheelbarrow without any PPE
Concentrate waste	Light grey concentrate wastes	SW2	CHS 6	Movement of hazardous wastes remaining in structures, equipment or contaminated soil, which could contaminate the soil, affecting persons (via ingestion or skin contact), environment or economic activity.	SW2-CHS6	Toxic material in rusty drums is polluting the soil
Concentrate waste	Dark grey concentrate wastes	SW3	CHS 6	Movement of hazardous wastes remaining in structures, equipment or contaminated soil, which could contaminate the soil, affecting persons (via ingestion or skin contact), environment or economic activity.	SW3-CHS6	Toxic material in rusty drums is polluting the soil
Scrap metal	Plant area	SW4				
Water reservoirs and pipelines	Plant area	I1	CHS 3	Presence, in operational areas, of contaminated water that could be used for drinking or other purposes (irrigation, bathing, drinking water for animals).	I1-CHS3	Evidence of fishing in tanks
Water reservoirs and pipelines	Plant area	I2	CHS 3	Presence, in operational areas, of contaminated water that could be used for drinking or other purposes (irrigation, bathing, drinking water for animals).	I2-CHS3	Water used for drinking, washing, bathing by community and by livestock. Evidence of fishing in tanks

Resin and/or hydrocarbons	**Veld**	**SW5**	**CHS 6**	**Movement of hazardous wastes remaining in structures, equipment or contaminated soil, which could contaminate the soil, affecting persons (via ingestion or skin contact), environment or economic activity.**	**SW5-CHS6**	**Toxic resin deposited on the soil surface has prevented vegetation growth. Inhalation of fumes could be dangerous to people and livestock**

ANNEX E: CHS STEP 3	RISK ASSESSMENT RECORD FORM RISK ASSESSMENT HANDBOOK SD/AMS SIMPLIFIED RISK ASSESSMENT - CONTAMINATION	

STEP 3. ESTIMATION OF THE PROBABILITY INDEX (Section 4.2.2.3)

FACILITY NAME	CHS SITE CODE	CHS DESCRIPTION	APPLIED GUIDE	PROBABILITY INDEX	JUSTIFICATION
Breccia pipe	OP1-CHS2	Open pit pool is in direct contact with groundwater. Groundwater is being pumped for human and animal consumption	**GUIDE 2**	**Low**	**No water quality data available. High buffering capacity (pH probably >7.5) and so solution of heavy metals unlikely. People drinking water without any apparent ill effects. NEEDS VALIDATING**
Concentrator plant	0	0			
Waste rock dumps	0	0			
Tailings dump	LW2-CHS7	Livestock and game are eating the vegetation growing in tailings, which have a high metal content. The vegetation could be bioaccumulating some of these metals	**GUIDE 7**	**High**	**No data on soils or vegetation are available. Much evidence of livestock present on areas covered with windblown and eroded tailings. NEEDS VALIDATION**
White concentrate wastes	SW1-CHS8	People were seen removing white powdery concentrate using shovels and a wheelbarrow without any PPE	**GUIDE 8**	**Medium**	**The amount of concentrate is quite small and so although contact may be daily for a short period of time, this will average out to a medium frequency over a year**
Light grey concentrate wastes	SW2-CHS6	Toxic material in rusty drums is polluting the soil	**GUIDE 6**	**Low**	**Number of drums and area of contamination is small, well concealed and overgrown with vegetation**
Dark grey concentrate wastes	SW3-CHS6	Toxic material in rusty drums is polluting the soil	**GUIDE 6**	**Low**	**Number of drums and area of contamination is small, well concealed and overgrown with vegetation**
Plant area	0	0			
Plant area	I1-CHS3	Evidence of fishing in tanks	**GUIDE 3**	**Low**	**Water quality unknown, Frequency of fishing unknown. NEEDS VALIDATION**

Plant area	I2-CHS3	Water used for drinking, washing, bathing by community and by livestock. Evidence of fishing in tanks	**GUIDE 3**	**Medium**	**Water used every day by villagers, but water quality unknown. No complaints by villagers, but sample had a bad odour. NEEDS VALIDATION**
Veld	SW5-CHS6	Toxic resin deposited on the soil surface has prevented vegetation growth. Inhalation of fumes could be dangerous to people and livestock	**GUIDE 6**	**High**	**Frequent access by livestock to the resin area. Resin crust being broken up by hoof action. Effects on soil, livestock, groundwater and humans unknown. NEEDS VALIDATION**

ANNEX E: CHS STEP 4.1	RISK ASSESSMENT RECORD FORM RISK ASSESSMENT HANDBOOK SD/AMS SIMPLIFIED RISK ASSESSMENT - CONTAMINATION	

STEP 4. ESTIMATION OF THE SEVERITY OF CONSEQUENCES (Section 4.2.2.5)

4.1. CONSEQUENCES FOR PEOPLE

FACILITY NAME	CHS SITE CODE	CHS DESCRIPTION	SEVERITY OF CONSEQUENCES FOR PEOPLE	JUSTIFICATION
Breccia pipe	OP1-CHS2	Open pit pool is in direct contact with groundwater. Groundwater is being pumped for human and animal consumption	**Negligible**	**No contact with pool in open pit**
Concentrator plant	0	0		
Waste rock dumps	0	0		
Tailings dump	LW2-CHS7	Livestock and game are eating the vegetation growing in tailings, which have a high metal content. The vegetation could be bioaccumulating some of these metals	**Moderate**	**All the villagers (including children) consume livestock products**
White concentrate wastes	SW1-CHS8	People were seen removing white powdery concentrate using shovels and a wheelbarrow without any PPE	**Low**	**Only about 2-5 people will excavate this material**
Light grey concentrate wastes	SW2-CHS6	Toxic material in rusty drums is polluting the soil	**Negligible**	**Limited quantity and no signs of access by people or wildlife**
Dark grey concentrate wastes	SW3-CHS6	Toxic material in rusty drums is polluting the soil	**Negligible**	**Limited quantity and no signs of access by people or wildlife**
Plant area	0	0		
Plant area	I1-CHS3	Evidence of fishing in tanks	**Low**	**Small fish. If an fish is contaminated it will only affect a few people**
Plant area	I2-CHS3	Water used for drinking, washing, bathing by community and by livestock. Evidence of fishing in tanks	**Moderate**	**If water is contaminated, entire community will be affected**
Veld	SW5-CHS6	Toxic resin deposited on the soil surface has prevented vegetation growth. Inhalation of fumes could be dangerous to people and livestock	**Negligible**	**Area is far from residential area**

ANNEX E: CHS STEP 4.2	RISK ASSESSMENT RECORD FORM RISK ASSESSMENT HANDBOOK SD/AMS SIMPLIFIED RISK ASSESSMENT - CONTAMINATION	

STEP 4. ESTIMATION OF THE SEVERITY OF CONSEQUENCES contd. (Section 4.2.2.5)

4.2. ENVIRONMENTAL CONSEQUENCES

			AQUATIC LIFE		TERRESTRIAL FAUNA & FLORA		PROTECTED OR SENSITIVE AREAS	
FACILITY NAME	CHS SITE CODE	CHS DESCRIPTION	SEVERITY	JUSTIFICATION	SEVERITY	JUSTIFICATION	SEVERITY	JUSTIFICATION
Breccia pipe	OP1-CHS2	Open pit pool is in direct contact with groundwater. Groundwater is being pumped for human and animal consumption	**Moderate**	**Impacts unknown, but colour of water indicates algal growth resulting from eutrophication and low oxygen**				
Concentrator plant	0	0						
Waste rock dumps	0	0						
Tailings dump	LW2-CHS7	Livestock and game are eating the vegetation growing in tailings, which have a high metal content. The vegetation could be bioaccumulating some of these metals			**Moderate**	**Some bird life, but few signs of wildlife**		
White concentrate wastes	SW1-CHS8	People were seen removing white powdery concentrate using shovels and a wheelbarrow without any PPE						
Light grey concentrate wastes	SW2-CHS6	Toxic material in rusty drums is polluting the soil						
Dark grey concentrate wastes	SW3-CHS6	Toxic material in rusty drums is polluting the soil						
Plant area	0	0						
Plant area	I1-CHS3	Evidence of fishing in tanks	**Moderate**	**Very limited biodiversity. Dead fish and birds evident**				

Plant area	I2-CHS3	Water used for drinking, washing, bathing by community and by livestock. Evidence of fishing in tanks						
Veld	SW5-CHS6	Toxic resin deposited on the soil surface has prevented vegetation growth. Inhalation of fumes could be dangerous to people and livestock			**High**	**Almost no vegetation growing in this area, even after more than60 years**		

ANNEX E: CHS STEP 4.3	RISK ASSESSMENT RECORD FORM RISK ASSESSMENT HANDBOOK SD/AMS SIMPLIFIED RISK ASSESSMENT - CONTAMINATION	

STEP 4. ESTIMATION OF THE SEVERITY OF CONSEQUENCES contd. (Section 4.2.2.5)

4.3. CONSEQUENCES FOR ECONOMIC ACTIVITIES

			AGRICULTURE (crops)		LIVESTOCK & GAME		FISHERIES AND AQUACULTURE		TOURISM	
FACILITY NAME	CHS SITE CODE	CHS DESCRIPTION	SEVERITY	JUSTIFICATION	SEVERITY	JUSTIFICATION	SEVERITY	JUSTIFICATION	SEVERITY	JUSTIFICATION
Breccia pipe	OP1-CHS2	Open pit pool is in direct contact with groundwater. Groundwater is being pumped for human and animal consumption								
Concentrator plant	0	0								
Waste rock dumps	0	0								
Tailings dump	LW2-CHS7	Livestock and game are eating the vegetation growing in tailings, which have a high metal content. The vegetation could be bioaccumulating some of these metals			**Low**	**Less than 20% of total area covered in tailings**				
White concentrate wastes	SW1-CHS8	People were seen removing white powdery concentrate using shovels and a wheelbarrow without any PPE								
Light grey concentrate wastes	SW2-CHS6	Toxic material in rusty drums is polluting the soil								
Dark grey concentrate wastes	SW3-CHS6	Toxic material in rusty drums is polluting the soil								
Plant area	0	0								
Plant area	I1-CHS3	Evidence of fishing in tanks					**Negligible**	**Fish probably not sold**		
Plant area	I2-CHS3	Water used for drinking, washing, bathing by community and by livestock. Evidence of fishing in tanks			**Negligible**		**Negligible**	**Fish probably not sold**		
Veld	SW5-CHS6	Toxic resin deposited on the soil surface has prevented vegetation growth. Inhalation of fumes could be dangerous to people and livestock			**Low**	**<20% of grazing area lost due to contaminatio n**				

ANNEX E: CHS STEP 5	RISK ASSESSMENT RECORD FORM RISK ASSESSMENT HANDBOOK SD/AMS SIMPLIFIED RISK ASSESSMENT - CONTAMINATION	

STEP 5. ASSESSING THE MAGNITUDE OF THE RISK (Section 4.2.2.5)

(cells will fill automatically)

5.1. SUMMARY TABLE

				SEVERITY OF CONSEQUENCES							
				PEOPLE	ENVIRONMENT			ECONOMIC ACTIVITIES			
FACILITY NAME	CHS SITE CODE	CHS DESCRIPTION	PROBABILITY	PUBLIC HEALTH	AQUATIC LIFE	TERRESTRIAL FAUNA & FLORA	PROTECTED AND SENSITIVE AREAS	AGRICUL-TURE	LIVESTOCK & GAME	FISHERIES AND AQUACULT-URE	TOURISM
				pe	aq	tf	pa	ag	ga	ac	to
Breccia pipe	OP1-CHS2	Open pit pool is in direct contact with groundwater. Groundwater is being pumped for human and animal	Low	Negligible	Moderate	0	0	0	0	0	0
Concentrator plant	0	0	0	0	0	0	0	0	0	0	0
Waste rock dumps	0	0	0	0	0	0	0	0	0	0	0
Tailings dump	LW2-CHS7	Livestock and game are eating the vegetation growing in tailings, which have a high metal content. The vegetation could	High	Moderate	0	Moderate	0	0	Low	0	0
White concentrate wastes	SW1-CHS8	People were seen removing white powdery concentrate using shovels and a wheelbarrow without any PPE	Medium	Low	0	0	0	0	0	0	0
Light grey concentrate wastes	SW2-CHS6	Toxic material in rusty drums is polluting the soil	Low	Negligible	0	0	0	0	0	0	0
Dark grey concentrate wastes	SW3-CHS6	Toxic material in rusty drums is polluting the soil	Low	Negligible	0	0	0	0	0	0	0
Plant area	0	0	0	0	0	0	0	0	0	0	0
Plant area	I1-CHS3	Evidence of fishing in tanks	Low	Low	Moderate	0	0	0	0	Negligible	0
Plant area	I2-CHS3	Water used for drinking, washing, bathing by community and by livestock. Evidence of fishing in tanks	Medium	Moderate	0	0	0	0	Negligible	Negligible	0
Veld	SW5-CHS6	Toxic resin deposited on the soil surface has prevented vegetation growth. Inhalation of fumes could be dangerous to people and livestock	High	Negligible	0	High	0	0	Low	0	0

ANNEX E: MATRIX	RISK ASSESSMENT RECORD FORM RISK ASSESSMENT HANDBOOK SD/AMS RISK ASSESSMENT MATRIX	

RISK REGISTRATION FOR SAFETY AND CONTAMINATION (Section 4.3)

	SEVERITY OF CONSEQUENCES				
PROBABILITY INDEX	**NEGLIGIBLE (A)**	**LOW (B)**	**MODERATE (C)**	**HIGH (D)**	**CATASTROPHIC (E)**
HIGH (4)	P1-SHS13tf, ga; LW2-SHS12pe,tf,ga; SW4-SHS14tf,ga; SW5-CHS6pe	P1-SHS13pe; SW4-SHS12pe; LW2-CHS7ga; SW5-CHS6-ga	LW2-CHS7pe,tf	I1-SHS4pe; I2-SHS4pe; SW5-CHS6tf	
MEDIUM (3)	I2-CHS3ga,ac	OP1-SHS12tf,ga; SW1-CHS8pe		OP1-SHS12pe	
LOW (2)	OP1-CHS2pe; SW2-CHS6pe; SW3-CHS6pe; I1-CHS3ac	I1-CHS3pe	OP1-CHSaq; I1-CHS3aq		
NEGLIGIBLE (1)		I1-SHS4tf,ga; I2-SHS4tf,ga			

ANNEX E: CRA-1	RISK ASSESSMENT RECORD FORM RISK ASSESSMENT HANDBOOK SD/AMS CUMULATIVE RISK ASSESSMENT	

CUMULATIVE RISK ASSESSMENT (CRA) (Section 4.4 and Figure 2-2)

CRA-1. WHEN TO CARRY OUT A CRA.

	Yes / No	(Justify)
1.1. Does the Area of Study overlap with that of another SD/AMS?	**No**	

If the answer (1.1) is positive, proceed with questions (1.2 … 1.5).
If the answer is negative, please go to the next page.

	(Revised findings
1.2. Check if the site's Hazard Scenarios might be affected by Hazard Scenarios belonging to the other site(s).	
1.3. Check if the study area should be corrected to accommodate the combined Hazard Scenarios.	
1.4. Check the site's Ocurrence of Probability values for consequences taking into account the cumulative effects.	
1.5. Check risk magnitudes registered for SD/AMS.	

ANNEX E: CRA-2	RISK ASSESSMENT RECORD FORM RISK ASSESSMENT HANDBOOK SD/AMS CUMULATIVE RISK ASSESSMENT - SAFETY	

CUMULATIVE RISK ASSESSMENT - SAFETY

CRA-2. REVIEW OF THE PROBABILITY OF OCCURRENCE AND SEVERITY OF CONSEQUENCES FOR SAFETY HAZARD SCENARIOS.

				SEVERITY OF CONSEQUENCES							
				PEOPLE	ENVIRONMENT			ECONOMIC ACTIVITIES			
FACILITY NAME	SHS SITE CODE	SHS DESCRIPTION	PROBABILITY	SAFETY	AQUATIC LIFE	TERRESTRIAL FAUNA & FLORA	PROTECTED & SENSITIVE AREAS	AGRICUL-TURE	LIVESTOCK & GAME	FISHERIES AND AQUACUL-TURE	TOURISM
				pe	aq	tf	pa	ag	ga	ac	to
Breccia pipe	OP1-SHS12	Although the open pit is fenced, there are gaps in the fence and access is unrestricted. Very high vertical pit walls									
Concentrator plant	P1-SHS13	Dilapidated buildings with loose bricks, unsafe roof trusses									
Tailings dump	LW2-SHS12	Undercut edge of waste rock dump									
White concentrate wastes	0	Deep gullies in eroded tailings which were slurried onto waste rock dumps; evidence of frequent access									
Light grey concentrate wastes	0	0									
Dark grey concentrate wastes	0	0									
Plant area	I1-SHS4	0									
Plant area	I2-SHS4	Glass shards and sharp pieces of scrap metal lying everywhere; unprotected sumps									

ANNEX E: CRA-3	RISK ASSESSMENT RECORD FORM RISK ASSESSMENT HANDBOOK SD/AMS CUMULATIVE RISK ASSESSMENT - CONTAMINATION	

CUMULATIVE RISK ASSESSMENT - CONTAMINATION

CRA-3. REVIEW OF THE PROBABILITY OF OCCURRENCE AND SEVERITY OF CONSEQUENCES FOR CONTAMINATION HAZARD SCENARIOS.

				SEVERITY OF CONSEQUENCES							
				PEOPLE	ENVIRONMENT			ECONOMIC ACTIVITIES			
FACILITY NAME	SHS SITE CODE	SHS DESCRIPTION	PROBABILITY	SAFETY	AQUATIC LIFE	TERRESTRIAL FAUNA & FLORA	PROTECTED & SENSITIVE AREAS	AGRICUL-TURE	LIVESTOCK & GAME	FISHERIES AND AQUACUL-TURE	TOURISM
				pe	aq	tf	pa	ag	ga	ac	to
Breccia pipe	OP1-CHS2	Open pit pool is in direct contact with groundwater. Groundwater is being pumped for human and animal									
Concentrator plant	0	0									
Waste rock dumps	0	0									
Tailings dump	LW2-CHS7	Livestock and game are eating the vegetation growing in tailings, which have a high metal content. The vegetation could									
White concentrate wastes	SW1-CHS8	People were seen removing white powdery concentrate using shovels and a wheelbarrow without any PPE									
Light grey concentrate wastes	SW2-CHS6	Toxic material in rusty drums is polluting the soil									
Dark grey concentrate wastes	SW3-CHS6	Toxic material in rusty drums is polluting the soil									
Plant area	0	0									

ANNEX E: CRA MATRIX	RISK ASSESSMENT RECORD FORM RISK ASSESSMENT HANDBOOK SD/AMS CUMULATIVE RISK ASSESSMENT MATRIX	

CUMULATIVE RISK ASSESSMENT

CRA-4. RISK RECORD FOR SAFETY AND CONTAMINATION

	SEVERITY OF CONSEQUENCES				
PROBABILITY INDEX	**NEGLIGIBLE (A)**	**LOW (B)**	**MODERATE (C)**	**HIGH (D)**	**CATASTROPHIC (E)**
HIGH (4)					
MEDIUM (3)					
LOW (2)					
NEGLIGIBLE (1)					

ANNEX E: CLASSIFI-CATION	RISK ASSESSMENT RECORD FORM RISK ASSESSMENT HANDBOOK SD/AMS	

SITE CLASSIFICATION

	Yes/No	(Mark corresponding issues)	
The highest risks are located in cells			
a4, a5, a7, a8, a9	Yes	THE SITE IS CLASSIFIED AS "MINING LIABILITY"	END OF PROCESS
b1, b2, b3, b4, b5, b6		THE SITE IS CLASSIFIED AS "NON-MINING LIABILITY"	END OF PROCESS
a1 a2, a3, a6		Go to question 2.2	
b7, b8, b9, b10, b11		Go to question 2.3	

Assessor enters comments on the final site classification

The main risks relate to the dangers of the open pit, which is inadequately fenced off to prevent access to people and the water tanks at the top of the hill which hold a high risk for drowning. There is insuffient information to assess with certainty whether the tailings material poses a risk to livestock and game through uptake by plants - THIS NEEDS TO BE VALIDATED by first taking grass and leaf samples for analysis. The workers removing the concentrate and/or tailings from the top of the waste rock must be eqipped with Personal Protective Equipment (masks and gloves and overalls) immediately. There is also uncertainty regarding the risk posed by the resin to soil, groundwater, people and the environment. THIS NEEDS TO BE VALIDATED. A sample must be analysed. There is also uncertainty regarding the quality of the water being used by the local residents and stock. THIS NEEDS TO BE VALIDATED by taking water samples for analysis.

NEED TO PERFORM A DETAILED RISK ASSESSMENT (DRA) (Section 4.5)

	Yes / No	(Justify)
2.2. Is there certainty on assessing AT LEAST ONE of the risks located in the cells a1, a2, a3, a6?		

If the anwer is YES…	The SITE IS A MINING LIABILITY	END OF PROCESS

	Yes / No	(Justify)
2.3. Is there certainty on assessing ALL the risks located in b7… b11 ?		

If the answer is YES…	The SITE IS NOT A MINING LIABILITY	END OF PROCESS

If the answer in 2.2. / 2.3 is NO	A Detailed Risk Assessment is required for uncertain hazard scenarios. (see Chapters 5 and 6)

ANNEX E: APP 1 DRA	RISK ASSESSMENT RECORD FORM RISK ASSESSMENT HANDBOOK SD/AMS	

APPENDIX 1. DETAILED RISK ASSESSMENT

Hazard scenario identification requiring a DRA

SHS CODE or SHS	HAZARD SCENARIO	DESCRIPTION	UNCERTAINTY REASON

DRA Technical specifications

SHS CODE or SHS	DRA OBJECTIVES	SCOPE	TYPE OF SPECIALIST REQUIRED	ESTIMATED COSTS

DRA documentation

MME/GSN Responsible party	
Record date	
Entered by	
Reviewed by	
Approved by	

Once you´re done with the DRAs, RETURN TO CLASSIFICATION

APPENDIX 2 : NOTES

A. Add comments on site access and safety conditions (for the Assessor).

B. Add comments on measurements and estimates obtained during the assessment.

ANNEX E: PHOTO LOG	RISK ASSESSMENT RECORD FORM RISK ASSESSMENT HANDBOOK SD/AMS	

APPENDIX 3. PHOTOS

PHOTOS	INSTALLATION / SITE	DESCRIPTION (photo)	DATE	HAZARD SCENARIO	CO-ORD. SOUTH	CO-ORD. EAST

ANNEX F

FIELD GUIDE

ANNEX F: GUIDE FOR PREPARING AND IMPLEMENTING THE FIELD VISIT

A. Activities to be undertaken prior to site visit

	Yes
1. Have you gathered the pertinent information (MIDS, Safety folder, etc.) ?	
2. Have you prepared the Risk Assessment Base Map (RABM)?	
3. Have you identified the receptors prior to the visit?	
4. Have you established communication with the owner of the farm or the person in charge of coordinating the site visit?	
5. Are there aspects of the assessment that require interviews? If so, have you prepared them, that is, have you defined the objectives, expected results, information sources and the way to contact people?	

B. Equipment to be taken on site

Safety equipment

Sun glasses and sun blocker	
Safety boots / shoes	
Helmet	
Plastic gloves	
Water	
Cellphone	
Lantern or torch	
Institutional jacket or ID	
Cap	

Measurement equipment

Inclinometer	
GPS	
Geologist´s hammer and small shovel	
50 m measuring tape.	
Plastic bags (20 x letter size) and ties	
pH meter	
Conductivity meter	
Bottles for water samples	
Bailer	
String	

Other

Light rucksack	
Maps & Google images	
RA Record Forms	
Safety haz. scenario list	
Manual Guides	
Clip board	
Camera, binoculars	
Permanent marker	
Notebook and pen	
Field guides/books	

C. Field work protocol

	Done	Observations
1. Check you have adequate **transportation** and equipment (pick-up 4x2 or 4x4, spare tyre, etc.). Consult locals in case of doubt.		
2. Report to your office on location of your visit, transportation used, participants and estimated time of return.		
3. Check you have appropriate equipment.		
4. When you arrive at the site check the location's personal safety conditions.		
5. Hold a meeting with **local persons** accompanying you (person in charge).		
6. At the site hold a preliminary **general inspection** (brief walk over)		
7. Identify site **components**, assigning a name to each of them (Cover **Page 2 of Annex E**).		
8. Identify facilities, stockpiles and works on the site, assign a code to each. Carry out measurements that allow you to understand dimensions. Record GPS points defining location for each facility (Complete Cover page 2 in Annex E). Take photos that illustrate the state of each facility, stockpile and work.		
9. Identify and characterize **receptors** (**Complete Baseline Sheet 3**).		

ANNEX F: GUIDE FOR PREPARING AND IMPLEMENTING THE FIELD VISIT

C. Field work protocol

	Done	Observations
10. Check which Safety Hazard Scenarios are found at each facility, stockpile or work area. Record each hazard by taking photos (Complete SHS Step 1).		
11. Identify on the guide (Probability Index) each Safety Hazard Scenario (SHS Step 2).		
12. Carry out specific measurements required by each guide applicable to this site. Record measurements on the appropriate guide.		
13. Check Contamination Hazard Scenarios at each facility, stockpile and work area. Record each with photos (Complete CHS Step 2).		
14. Identify the Probability Index Guide related to each Contamination Hazard Scenario (CHS Step 3).		
15. Carry out specific measurements for each site, record measurements on each form.		
16. Take samples in the bags prepared for **solid materials,** if the material could constitute a Hazardous Residue and if it might be needed for the DRA for contamination. Write down the location where the sample was taken (GPS coordinates), the date, an ID number and the environmental characteristics. Mark the bag with the sample number, using a permanent marker.		
17. Take samples of liquids in the bottles**,** if some might constitute a Hazardous Liquid Residue or contaminated water, and it could be required for the DRA of contamination. Write down the location where the sample was taken (GPS coordinates), the date, an ID number and the environmental characteristics. Mark the bottle with the sample number, using a permanent marker.		
18. At the end of the visit, check your notes before you leave the location. Write down doubtful aspects, indicate reasons for uncertainty and why you think a DRA may be necessary		
18. If there is a site person in charge and you have identified a risk of accidents, please inform him/her.		
19. Take notes on the RARF (**Appendix 2 - Site Notes**) on aspects related to the Assessor's personal safety or site access, and whether a new visit must take place.		
20. Check whether you have all the equipment and materials you brought with you.		

ANNEX G

SHUT DOWN AND ABANDONED MINE SITE INVENTORY DATA SHEET (MIDS)

ANNEX G: SHUT DOWN AND ABANDONED MINE SITE INVENTORY DATA SHEET

Map ID	Name	Operator (s)	Location	Lat	Long	Primary mineral (s) /commodity(s)	Group	Secondary mineral(s) / commodity(s)	Regional Geology	Site Geology	Mining method	Ore processing	Ore Quantity / Production statistics	Mining remnants	Closure date	Environmental hazards
1	(Carnicho mining) Sonnberg Diamondmante		Orange river	-28,00000	17,00000	Diamond	Alluvial diamonds	Unknown							Unknown	
2	Abenab	Tsumeb Corporation limited (TCL)	20km E of Tsumeb on Grootfontein road	-19,28300	18,10000	Vanadium (V)	Fe, Mn, V, Ti	Descloizite, Calcite	Located in Otavi Group, Damara sequence, Maiberg Formation	Faulted contact between laminated grey limestone and grey dolomite. Cylindrical orebody ± 425 m	Open pit, cylindrical pipe mined to depth of 215m	Production of vanadium concentrate	56 600 t of concentrate with a grade of 18.5% Vanadium Oxide, from 1922-1948, 1360 000 t was mined from a breccia pipe	Excess of 1.0m tons in various dumps. Waste dumps mainly large solid rock	30. Apr 05	Aesthetic pollution caused by delapidated buildings, old machinery, rust sheet iron etc. possibly wind blown pollution.
3	Abenab West Mine	Tsumeb Corporation limited (TCL)	35km N of Grootfontein, 300m SW of Abenab breccia pipe	-19,28300	18,08300	Vanadium (Descloizite, Sphalerite, Galena, Pyrite, Tennantite, Enargite, Jordanite, Covellite)	Fe, Mn, V, Ti	Galena, Willemite, Cerussite, Limonite, Chalcocite, Chalcopyrite	Damara sequence-Auros formation on steeply dipping (45 - 70°) southern limb of the ENE striking Tsumeb syncline	Mined along strike of 730 m x 6 m wide on the southern limb of Tsumeb syncline.	Open pit	Crushing, Milling, Flotation-concentrate.	66 890 t of concentrate containing 13% Vanadium Oxide and 72% lead. 13100 t of concentrate: 55-72% lead	± 300 000 t	1958	Aesthetic pollution caused by dumps/waste material
4	Ai-Ais Mine		Farm Kanabean 331 Karas district	-28,11700	17,53300	Pb Zn Ag	Pb, Zn		The pipes which intrude Nama age sediments and appear to underlie Karoo age rocks, have brecciation age of ± 550.	Comprises a number of mineralised quartz and calcite veins which appear to be related to the syenite and granite of the Bremen Complex.					Unknown	
5	Ameib Mine	Falls within Reefton (pty) Ltd EPL	Farm Ameib 60, 30km N of Usakos	-21,78300	15,60000	Cassiterite (Sn)	Sn, Li, Be, W, Nb, Ta, REE	Unknown	Biotite schists of Kuiseb formation, intruded by quartz/feldspar pegmatites. Damara sequence	Numerous NE - SW striking pegmatite. Main orebody 100 m long x 5.5 m wide. Dips 30° N. Mined to 30 m	Open pit	Blasting and Crushing	Not known	Tailings dumped in the adjacent stream	Unknown	Tailings dumped in the river.
6	Anderson Henderson Mine	Last owner TCL	Farm Naob 69 13km SSW Usakos	-22,10000	15,55000	Malachite, Bornite, Chalcopyrite, Chalcocite (Cu)	Cu	Cobaltite, Gold (Au)	Mineralisation along a contact zone between granitic gneiss and mafic schist	Mineralisation strikes EW for ± 350 m and dips southwards	Underground	Blasting, Crushing and hand sorting	Reserves estimated at 150 000 t @ 2.0% copper	Rock dumps, open excavations, and remnants of waste rocks and taillings.	1968	Open workings are dangerous
7	Arandis Tin Mine(Annaberg)	Unknown	36km N Arandis, through Trekkopje Farmyard	-22,13300	15,00000	Cassiterite, Arsenopyrite, Pyrrhotite, Bornite, Pyrite (Sn)	Sn, Li, Be, W, Nb, Ta, REE	60 different minerals recorded in hydrothermal veins within Karibib marbles	Karoo dolorites common. Karibib Marbles-nearby granite forming contact-pneumatolytic ore. Intrusive pegmatites into quartz-feldspathic schists	Karibib Marbles cut by hydrothermal quartz vein-also as fillings and cavities in the limestone up to 2 m wide	Limited underground operations	Crushing	14 t Cassiterite concentrate	Tailings, waste material flows to desert	Unknown	Pollution of desert below old plant
8	Aranos Basin			-24,25000	19,16700	Coal	Fossil fuel									
9	Arriesdrif			-28,50000	16,71700	Diamond	Alluvial diamonds									
10	Asis Ost Mine	Omeg (1910-15), TCL (1974-76), Ongopolo (current)	2 km E of Kombat, 39 km E of Otavi, north of road to Grootfontein	-19,71700	17,68300	Chalcopyrite, Galena (Cu, Pb)	Pb, Zn	Malachite, Bornite, Vanadate, chalcocite	Kombat formation slates overlying dolomites of the Otavi group	Calcitisation and brecciaation extend in a 300 m zone north of slate/dolomite contact. (orebody lies within this zone). Mineralisation in steeply dipping calcitised shear zones trenching east-west	Underground	Unknown	34 913 t of Cu/Pb ore grading 1.26 % Cu and 0.25 % Pb	Waste rock dump	Unknown	No long-term danger due to the calcareous nature of the bedrock; sinkholes
11	Auchas Mine		Farm Auchas 347 Luderitz	-28,25000	16,75000	Diamond	Alluvial diamonds								Unknown	
12	Aukam Graphite Mine	Unknown	Aukam farm 112 Bethanie district Karas	-22,56700	17,65000	Amorphous Graphite	Industrial minerals	Alachite, Sulphur	Altered shear zone in coarse granites and gneisses of Namaqualand metamorphic complex	Kaolinized shear zone with veins and lenses of graphite. Three main bodies mined	Open cast pit and underground workings	Blasting, Crushing and hand sorting	25 000 t of graphite ore	Oil drums, scrap metal and cables	04. Okt 74	No potential for ground water or surface water pollution
13	Aukam Tin Mine	Unknown	Aukam farm 112 Bethanie district Karas	-26,96700	16,81700	Cassiterite (Sn)	Sn, Li, Be, W, Nb, Ta, REE	Muscovite, Quartz, Albite		Cassiterite associated with mica rich zones in pegmatites. Colluvial cassiterite also present	Underground	Blasting, Crushing and gravity separation	± 5 000 t at 2.2 %. Total of 123 t at 55 %, 12- 14 000 t of rock and ore removed	8 000 t of waste rock and 1 000 t of tailings	1986	Mine waste and tailings are inert and can only be a dust pollutant
14	Baltika Mine			-19,63300	17,53300	V	Fe, Mn, V, Ti									
15	Berg Aukas Mine	rights held by Ongopolo & Processing Limited, (previously TCL)	17km ENE Grootfontein	-19,51700	18,20000	Sphalerite, Galena, Pyrite (Pb, Zn, V)	Pb, Zn	Descloizite, Willemite, Cerussite, Smithsonite, Goethite	Berg Aukas syncline consists of dolomites of Berg Aukas and Gauss Formation underlain by Nosib Group and Grootfontein Metamorphic Complex	Berg Aukas Syncline plunges westwards. North Ore Horizon-largely oxidised replacement lenses. Central Ore-body-located in solution cavities controlled by steeply dipping north-south fractures	Underground	Gravity concentrations , Flotation and Milling	1.6 Mt of ore produced. ± 1.6 Mt of ore reserves still remain @ 0.6 Vanadium Oxide, 5.0% of Pb and 17% of Zn, tonnes hoisted 1599 525 t	437 655 t of mining waste, waste dumps and some scrap metal on dumps	Unknown	Concrete pads polluted, waste dumps cause air pollution and pollution of the groundwater.
16	Black Range Deposit	Previously Rossing Uranium Ltd	38 km west of Usakos, Farm Black Range 72	-21,91700	15,16700	Graphite	Industrial minerals		The graphite member is located in the core zone of a broad overturned antiform.	Large disseminated flake graphite deposit is hosted by strongly weathered Silimanite-Muscovite-cordierite and quartz-feldspar-graphite gneisses of the sukses Formation.						
17	Blydskap Deposit			-19,88300	14,83300	fluorite,Ba	Industrial minerals									

Map ID	Name	Operator (s)	Location	Lat	Long	Primary mineral (s) /commodity(s)	Group	Secondary mineral(s) / commodity(s)	Regional Geology	Site Geology	Mining method	Ore processing	Ore Quantity / Production statistics	Mining remnants	Closure date	Environmental hazards
18	Bobos Mining Area (Alt Bobs Mine)	Last owner TCL	24km Tsumeb, farm Uris 481	-19,33300	17,50000	Cupreferrous descloizite (Cu)	Pb, Zn	Vanadium, Manganese, Calcite (V, Mn)	Elandshock and Hüttenberg Formations. Dolomites of the Damara Sequence	"Sand sack" type deposits-cavities and depressions up to 25 m deep filled with aeolian sand, vanadium bearing clay, wall rock fragments and iron and copper concretions	Open pit	No processing on site, transported to Uris Mine	±50 000t / ± 40 000 t	Small dumps	Unknown	Visual pollution by old dumps
19	Bogenfels			-27,43330	15,40000	Diamond	Alluvial diamonds									
20	Border Prospect			-19,48300	17,95000	Zn Pb	Pb, Zn									
21	Brandberg West Mine	Tsumeb Corporation limited (TCL) 1945 - 80	Lower Ugab River, Erongo Region	-21,00000	14,15000	Tin and Tungsten (Sn, W)	Sn, Li, Be, W, Nb, Ta, REE	Unknown	Turolites and metasediments of lower Ugab Group. Damara Sequence	Hydrothermal quartz vein deposits intruded into quartz-biotite schists	Open cast pit with smaller excavations	Blasting, Crushing and mechanical separation	14 000 t of concentrate, grading 32 - 56 % Tin oxide and 14,5 - 19 % tungsten oxide,	Solid waste and scrap metal, delapidated structures, 4.5 million bench cubic meters	1980	Water in pit is polluted; high visual pollution next to tourist road; open workings are dangerous
22	Charlottenfelder			-24,22600	14,62500	Diamond	Alluvial diamonds							Scrap metal and delapidated buildings		
23	Conception Bay			-24,00000	14,44000	Diamond	Alluvial diamonds							Scrap metal, waste, old boats and buildings		
24	Copper Valley Mine		65 NW Khorixas	-20,21700	14,41700	Cu Pb Au	Cu									
25	Crystal Tin Mine		Farm Kompaneno 104	-21,21700	15,81700	Cu Zn	Cu			consists of quartzo-feldspathic rock which occasionally carries cassiterite.			9 to 10 t of metallic tin has extracted.		Unknown	
26	Dan Mines Amethyst	Dan mines	E Platveld Otjiwarongo District, Farm Okaruhuipta 336	-20,09333	17,16777	Amethyst quartz	Industrial minerals	Calcite, Quartz	Swakop Group limestones and marbles-gently folded	North-south striking quartz zones. Thin veinlets form an anastomering network in the marbles. Dark violet,transluscent amethyst	Hand sorting and excavation	Hand sorted and stockpiled	Uknown	90% of material mined is waste rock	Unknown	Dumps cause minor visual pollution
27	Doppelgipfel Quarry			-22,41700	15,08300	Wollastonite	Industrial minerals									
28	Elbe Copper Prospect	Previously Falconbridge of Africa	40km W Okahandja, on farm Elbe 10 and Ombojongupa 9	-22,01700	16,60000	Chalcopyrite, Pyrrrhotite, Sphalerite (Cu, Zn)	Cu	Malachite, limonite, Barite, Magnetite, Chalcocite	Damara sequence-Kusib formation marbles, quartzite, quartz-biotite schist and calc-silicates. Intruded by granites	1 500 m long gossan. Complex folds plunging 45° to south-west. Orebody located in pyroclastic or sedimentary "breccia". Altered granite lenses both concordant and cross-cutting have been observed. Four gossan located to date	Open pit	Not worked	3 291 776 t @ 1.57% Cu , 1.48% Zn, 10.06 g/t Ag , 0.55% Av (Cut-off 1% Cu)	Unknown	Unknown	Old trenches/pits
29	Engo Valley Deposit			-18,10000	12,01700	U	U									
30	Etemba Mine			-21,45000	15,05000	Sn	Sn, Li, Be, W, Nb, Ta, REE									
31	Etiro Pegmatite Mine		20km N Karibib	-21,76700	15,95000	Be Nb Ta	Sn, Li, Be, W, Nb, Ta, REE									
32	Eureka Deposit			-22,03300	15,25000	REE	Sn, Li, Be, W, Nb, Ta, REE									
33	Gamikaubmund Mine			-22,36700	15,73300	Au, Cu,Mo	Au									
34	Ganschow Pegmatite			-21,33300	15,20000	Sn	Sn, Li, Be, W, Nb, Ta, REE									
35	Garob Mine		100km N Karasburg	-27,46700	19,00000	F Pb	Industrial minerals									
36	Gelbingen			-19,41700	14,75000	Cu Pb Zn	Cu									
37	Giftkuppe Deposit			-21,68300	15,95000	Ti	Fe, Mn, V, Ti									
38	Goabeb Quarry			-21,86700	15,51700	Wollastonite	Industrial minerals									
39	Goanikontes Deposit			-22,68400	14,83300	U	U									
40	Golden Valley	Unknown	SW Rehoboth	-23,38300	17,05000	Gold hosted in hematite, limonite, Pyrite, Malachite (Au)	Au	Unknown	Host rocks are metapelite/psammitic units with intercalated metavolcanics. Marienhof Formation	Gold mineralisation associated with quartz veins on granite/metasediment contacts. Typically hydrothermal. Very erratic	Underground	Crushing and milling	Produced 29.6 kg of gold, excavation volume is not known	Old tanks and scrap	Unknown	Taillings being washed down by the river. Minor negative impact on the environment.

41	Gorob Mine	Unknown	~120km E Walvisbay, close to Kuiseb River	-23,55000	15,40900	Pyrite, Chalcopyrite, Pyrrhotite, Sphalerite, Galena (Cu, Pb)	Cu	Unknown		Mineralisation is typical proximal volcanogenic sulphides. These now associated with magnetite quartz schists. 8 major ore bodies have been located and drilled	Extensive surface exploration -trenching and drilling	Unknown	Reserves 3.3 m tonnes @ 1,93% Cu, Reserves estimate at 4.7 m tonnes @ 2% Cu	waste dump	28/02/1982	Located in the Namib Naukluft Park
42	Gross Otavi Mine	Previuosly TCL, (Omeg). Now a privately owned game farm	Farm Antvoro 518, 21km E of otavi on Grootfontein road	-19,66700	17,61700	Vanadium (V)	Fe, Mn, V, Ti	Unknown								
43	Haib Deposit			-28,70000	17,91700	Cu Mo Au	Cu									
44	Harasib			-19,48300	17,83300	Pb Zn V	Pb, Zn									
45	Helikon I Mine	S.W.A Lithium (Pty) Ltd.	Farm Okongava 72, SE of Karibib	-22,05000	16,01700	Lepidolite, Petalite, Amblygonite (Li)	Sn, Li, Be, W, Nb, Ta, REE	Tantalite, Beryl, Topaz (Nb,Li, Be)			Hand cobbing	Excavated and hand sorted	Estimated 900 000 cubic metres of ore mined	Rock dumps and remains of buildings	06. Jun 82	Impact on grazing
46	Henderson Mine		Farm Naob 69 Usakos	-22,10000	15,55000	Cu Au	Cu		Mineralisation along a contact zone between granitic gneiss and mafic schist	Mineralisation strikes EW for ± 350 m and dips southwards	Underground	Blasting, Crushing and hand sorting	Reserves estimated at 150 000 t @ 2.0% copper	Rock dumps, open excavations,and remnants of waste rocks and taillings.	1968	Open workings are dangerous
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47	Hohewarte Deposit			-22,65000	17,40000	Cu Pb Zn	Cu									
48	Homidigams mine			-21,35000	15,18300	Sn	Sn, Li, Be, W, Nb, Ta, REE									
49	Hope Mine	Unknown	100km E Walvis Bay	-23,57000	15,26400	Chalcopyrite, Pyrite, Cornite, Chalcocite (Cu)	Cu	Molybdenite, Silver (Mo, Ag)	Matchless Amphibolite Belt-basic rocks and schists of Karibib Formation. Damara sequence.	Mineralisation as stringers and lenses in magnetite quartzite sequence over a strike of 420 m. Depth is over 1 000 m. Folded into a nose of a regional syncline. Intense folding and shearing	Extensive surface and underground exploration carried out	Unknown	Estimates of over 1.2 m tonne @ ± 3 % Cu + 13.5 g/t Ag	Extensive tips of rock from underground development	04. Feb 82	No significant negative environmental impact
50	Husab Mine	Unknown	20km S Rossing Mine, close to road D1903	-22,66700	15,08300	Flourite (F)	Industrial minerals	Unknown	Abbabos Metamorphic Complex lower Proterozoic (2500 - 2900 Ma)	Fluorite occurs in NW-SW striking quartz veins. Dips steeply to the NW.	Underground	Unknown	11 000 t of concentrate exported, 60-70 000 t mined and hand sorted, average grade 40% Fluorite	Waste dumps flattened, no scrap or waste materials are seen.	28. Nov 73	Located in the Namib Naukluft Park
51	Ida Mine		55km E Swakopmund	-22,71700	15,03300	Cu U	Cu									
52	Jan Jonker Mine		farm Kos 28	-23,13500	16,20100	Cu W Au	Cu									
53	Jerusalem fluorite Mine		farm Jerusalem 73	-28,36700	19,56700	F	Industrial minerals									
54	Joumbira			-20,80000	16,71700	Cu Pb Zn	Pb, Zn									
55	Kainkagchas Mine		farm Valencia 122	-22,31700	15,25000	Cu	Cu									
56	Kalkfeld Complex			-20,81700	16,13300	REE,Fe	Sn, Li, Be, W, Nb, Ta, REE									
57	Karavatu Mine/Uris Mine on Strike	Omeg-now Ongopolo Mining & Processing	24 km Tsumeb, Farm Bobos 544	-20,34333	17,50750	Cupriferous descloizite (Cu)	Cu	Vanadium, Manganese, Calcite (V, Mn)	Elandshock and Hüttenberg Formations. Dolomites of the Damara Sequence	"Sand sack" type deposits-cavities and depressions up to 25 m deep filled with aeolian sand, vanadium bearing clay, wall rock fragments and iron and copper concretions	Open pit	5234 t of concentrate averaging 11.87 % vanadium oxide	Uknown	Old machinery and remains of processing plant	1943	Not much evidence of tailings, visual degradation
58	Karlowa Pegmatites	Hoffmann (et.al)	30 km South of Brandberg Mountain, Namib Desert	-21,46666	14,51722	Cassiterite, Tantalum (Sn,Ta)	Sn, Li, Be, W, Nb, Ta, REE	Spodumene, Quatrz, Felsdpar, Mica (Li)	Central portion of the Cape-Cross to Uis pegmatite field is underlain by foliated metasedimentary rocks of the Amis River Formation. Striking NE-SW.	The pegmatites are controlled by intrusion into pre-existing zones of weakness resulting from shearing and block faulting in a structural half-graben	Open pit	Hand cobbing	Unknown	Low dumps adjacent to old pegmatite surface workings, rusted petrol drums	Unknown	Scattered trenching and pitting
59	Khan Mine	Ohlthaver and List	60km NE of Swakopmund	-22,50000	15,00000	Sphalerite, Bornite, Chacopyrite, Chalcocite (Cu)	Cu	Malachite, Azurite	Khan Formation. Damara sequence. Upper proterozoic	Mineralisation in pegmatite. Cutting calc-silicate granulites.	Underground	Crushing, milling and flotation	40 - 50 + concentrate per day. 45 - 55 % Cu, 160 g/t Ag and 1.0 g/t, Tailings estimated @ 8 400 cubic metres, rock dumps ± 700 cubic metres	Tailings and Rock dumps	28. Feb 75	Open workings are a hazard
60	Klein Aub Mine	Last owner Metorex (Pty) Ltd.	farm Klein Aub 350, 85km SW of Rehoboth	-23,80000	16,63300	Chalcocite (Cu)	Cu	Bornite, Chalcopyrite, Djurleite, silver (Ag)	Klein Aub Formation. Sinclair Sequence. Midole proterozoic	Stratiform copper mineralisation in calcareous argillites. Associated with concordant shear zones. Resulting in a series of ore horizons.	Underground	Crushing, milling and flotation	Estimated 220 000 t of concentrate produced 45 - 56 % Cu and 70 g/t Ag, Tailings and rock waste- 2.0 Mt ± 50 % used underground	Concrete structures and foundations remain, volumes of scrap metal and tailings	31. Mrz 87	Contamination via wind blown dust from the tailings. Open workings are dangerous

61	Klein Aukas Mine		farm Klein Aukas 66	-22,01700	15,61700	Pb Zn Ag	Pb, Zn		The marble hosting the deposit overlie quartzite and schist of the Nosib Group, and these were intrudee by small masses of Salem granite.	weak lead-zinc mineralisation is confined to unit 6, 40 m thick which consists of dolomite marble with abundant tremolite and wollastonite. The ore deposit developed in the 3 to 10 m thick central portion of the unit.	Opencast working				Unknown	
62	Klein Spitzkoppe Granite Quarry	Unknown	S of Klein Spitzkoppe	-22,01700	15,61700	Granite (Dimension stone)	Industrial minerals	Unknown	Intrusive granites		Quarrying	Drilling then splitting into blocks	Unknown	Large open cast quarry	Unknown	Waste blocks of granite pose visual pollution
63	Kobos Copper Mine		farm Kobos 321 Rehoboth	-23,53300	16,65000	Cu Zn	Cu								Unknown	
64	Kolmanskop			-26,70000	15,23300	Diamond	Alluvial diamonds									
65	Kombat mine (T.C.L)	Formerly Ongopolo Mining and Processing	Kombat	-19,71101	17,71032	Cu Pb	Cu			The ore bodies are located on the northern miogeosynclinal shelf of the Damara Orogen in relatively unmetamorphosed dolostone of the upper Otavi Group of Damara Sequence. The orebodies are situated on the northern limb of the canoe-shape, doubly plunging Otavi Valley synclinorium in dolostones of Hüttenberg Formation,	Underground				Unknown	
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66	Kompaneno mine			-21,26700	15,76700	Sn W	Sn, Li, Be, W, Nb, Ta, REE									
67	Kopermyn	Unknown	20km NE Kamanjab	-19,41700	15,16700	Chalcopyrite, Pyrite (Cu, Ag)	Cu	Malachite, Chalcocite, Covellite	Khabendos Group - Otjovazandu Formation. On northern limb of a dome shape inliers of Volcano - Sedimentary rocks.	Upper rhyolitic Volcanic breccia (hosting Cu mineralisation) . Lower quartz feldspar porphyry, considered to be a felsic Volcanic centre with a mafic Volcanic pile-similar to CanaDiamondn VMS deposit	Underground	On site production of concentrates	1969 - 75 100 000 t 2 % Cu, 10 g/t Ag. 1940 - 1961, 3 000 t Cu averaging 7 % Cu. Dumping material may contain over 4 000 t @ 6.3 % Cu	Large waste rock dumps and extensive tailings area	30. Nov 75	Contamination via wind blown dust from the tailings. Visual pollution from old waste dumps
68	Krantzberg Mine	Nord Mining and Exploration, Canada.	15km WSW Omaruru on farm Pristelwitz	-21,48200	15,78400	Woframite (Sn, W)	Sn, Li, Be, W, Nb, Ta, REE	Cassiterite (Sn)	Kuiseb Formation biotite schists intruded by Pan African granites. Overlain by lavas of Erongo Complex.	The tin-tungsten mineralisation is developed along the contact zone between the schists and the granites.	Underground	Not known. Appears to have being crushing, grinding and flotation	Most of the 1 Mt was ore. Average 0.4 - 0.5 % WO+B529. Reserves 130 000 t remain, ~ 1 Mt of ore was removed	Two tailings dams, Rock dumps of limited extent	02. Jul 80	Aesthetically the surface area of the mine is a mess and constrains revegetation
69	Kuiseb Deposit			-23,20000	14,68300	Gypsum	Industrial minerals									
70	Kunene Complex			-17,13400	13,18700	Ti ,Fe	Fe, Mn, V, Ti									
71	Lofdal Tantalite	P.de Villet (Uis)-(EPL)	farm Lofdal 491 Khorixas	-20,29166	14,63055	Tantalite (Nb)	Sn, Li, Be, W, Nb, Ta, REE	Malachite (Cu)	Huab Metamorphic Complex-metasedimentary and metavolcanic rocks with quartz veining.	Ferruginous chlorite carbonate schists with quartz veining. Pegmatites with tantalite. Also in area rare-earth pegmatites.	Open pit	Hand sorting	Uknown	None	Unknown	Blasting and dump spoils create visual environmental pollution
72	Lorelei	Unknown	20km NE Sendelings Drift, on the D212 road.	-28,08300	16,95000	Porph- copper-Molydenite (Cu, Mo)	Cu	Bornite, Pyrite	Orange River volcanics intruded by granite-aplites of Vioolsdrift suite.	Chalcopyrite and molybdenite as disseminated mineralisation in the granite contact rocks. Outcrop area 60 × 30 m.	Open pit	Blasting, Crushing, milling and flotation and smelting	0.3 - 0.4 % Cu. MO 30 - 40 ppm. Volume not known, Several hundred tonnes only	Foundations remain, tailings/sludge	Unknown	Tailing/sludge causing pollution or water contamination, pit and shaft require filling.
73	Marinkas Quelle Deposit			-28,15000	17,43300	REE	Sn, Li, Be, W, Nb, Ta, REE									
74	Matchless Mine	Last owners TCL	45km W Windhoek, Farm Friedenau16	-22,68300	16,85000	Pyrite, Chalcopyrite, Sphalerite (Cu, Zn)	Cu	Marcosite, Bornite, Galena (Pb, Ag, Au)	Late proterozoic (900 - 450 Ma). Matchless Amphibolite Belt. Damara sequence.	Besshi type ore bodies within an amphibolite/basic schist sequence . Ore is structurally controlled and occurs in 3 to 4 shoots. 800 m of surface Gossan.	Underground	Crushing, milling and flotation	1.35 Mt of ore produced @ 2.3 % Cu; 6 9 g/t Ag; 0.5 - 1 g/t Au and 14 % S. 20 Mt remain underground, 1.35 Mt of ore; 1.65 Mt of waste; 121 000 t of concentrate	Concrete structures remain, tailings dam and waste rock	30. Nov 83	Serious surface water pollution is present from run-off from the mine's tailings dam and the reworked rock dumps

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75	Meob Bay			-24,50000	14,61700	Diamond	Alluvial diamonds							Old buildings.		
76	Mile 72 Deposit			-21,85000	14,10000	U	U									
77	Moewe Bay			-19,36700	12,71700	Diamond	Alluvial diamonds									
78	Mon Repos Quarry			-22,10000	15,66700	Wollastonite	Industrial minerals									
79	Nainais (Tin-Tan) Mine	Last owner Imcor	Usakos area, road D1930	-21,45000	15,06700	Cassiterite (Sn)	Sn, Li, Be, W, Nb, Ta, REE	Columbite, Petalite, Spodumene, Beryl. Tantalite, Tourmaline (Nb, Li, Be)	Quartz-feldspar pegmatites into metasediments of Swakop Group. Damara sequence.	Mineralisation in a series of albite-muscovite dykes cross cutting NE-SW. Striking biotite schists and quartzofeldspathic pegmatites.	Open pit	Crushing and milling with gravity separation of tin	± 615 t of tin concentrate was produced between 1936 - 86. Columbite - Ta 5.7 t 1983 - 86, Av. Grade of 0.9 % indicates that over 60 000 t of ore was removed, absence of waste rock	Old mine buildings, several steep sided cuts are present. Inert tailings	1986	Most significant negative impacts are the deep, steep sided cuttings
80	Namib Lead	Namib Lead Mines (Pty) Ltd	7.5km NE Namib Siding	-22,52700	14,75400	Sphalerite, Galena, Pyrrhotite, Pyrite (Pb, Zn)	Pb, Zn	Ag	Highly folded calcareous rocks of Damara age adjacent to Kuiseb schists. High grade greenschist facies.	"Sedex" type mineralisation in marbles and calc-silicate metasediments. Four main ore bodies present of which two have been extensively mined.	Underground	Crushing, milling and flotations. Reworking by crushing, magnetic separation and cyclones	100 000 t of Pb/Zn produced before 1992. Ore reserves of 300 000 t @ 5.5 % Zn and 1.5 % Pb, Estimated 1.8 Mt mined. Tailings volume 4.0 cubic metres of which 1.25 cuic metres has been reworked	Ventilation shafts present, tailings and process plant and buildings	Unknown	Dangerous chemicals remain on site, reworked tailings liable to collapse. Significant dust pollution.
81	Natas Mine	Unknown	150km SW Windhoek, on the Farm Natas 20	-23,16700	16,26700	Scheelite (W)	Sn, Li, Be, W, Nb, Ta, REE	Au with Ag	Intrusive pegmatites into late Pan African granites.	Mineralisation associated with quartzo-feldspathic pegmatites cutting boitite schists. Main body is 80 m × 1.0 m and dips 40 - 50° N. Mineralisation erratic	Surface workings of subsiDiamondry pegmatites and underground workings of the main pegmatite	Crushing, Milling and gravity separation	Estimates of yield are 2 - 3 % scheelite + 0.2 to 4.8 g/t Au. Gold contains ± 18 % Ag	Processing plant still on site, tailings and scrap metal	31. Mai 79	Presence of open workings and mine adits
82	Neuras Gold Working			-23,45000	17,03300	Au	Au									
83	Neuwerke-Askevold South Area			-19,75000	17,58300	Cu	Cu									
84	Neuwerke-Askevold South Area			-19,75200	17,46600	Cu	Cu									
85	Nomgams Mine			-21,36700	15,16700	Sn Li	Sn, Li, Be, W, Nb, Ta, REE									
86	Nonidas Quarry	Marmorwerke, Karibib	15 km E Swakopmund	-22,61666	14,66666	Marble (MBL)	Industrial minerals		Marble horizon within calcsillicate rocks of Damara sequence	Epidote marble	Excavation	Cut into slabs or tiles	World class material	Scrap metal, cables, discarded blocks on site, Wastage ranges from 30 to 70 %	Unknown	Only negative impacts are visual
87	Nosib Block			-19,58300	17,83300	Zn Pb V	Pb, Zn									
88	Nosib Mine		farm no. 655 Tsumeb	-19,43300	17,78300	Zn Pb U	Pb, Zn		The Nosib Valley is an eroded anticline, the core of which consists of granite and gneiss of the Grootfontein Metamorphic Complex. .	Vanadium -bearing "mud ore" was mined along the contact between the Nosib and Otavi Group, stratigraphically below this a highly sheared breccia (possibly tillite) in which scattered chalcocite, sphalerite , galena , decloizite and gangue minerals are present in a sericitised matrix					Unknown	
89	Nui-Sie Pan			-22,90000	19,78300	Sepiolite	Industrial minerals									
90	Oamites Mine	Unknown	50km S of Windhoek	-22,95000	17,08300	Bornite, Chalcopyrite (Cu)	Cu	Chalcocite, Digenite, Covellite, Galena (Pb, Ag)	Oamites Formation , Nossib Group, Damara sequence.	Strata bound mineralisation in conglomerates and quartzites along fault zone Mine on the middle of 3 orebodies along 2.5 km of strike. Subvertical.	Underground	Crushing, milling and flotation	6.6 Mt ore produced 36 % Cu concentrate with 15 g/t Ag	Concrete foundations and structures, tailings dumps and rock waste, Estimated 5.5 Mt of tailings in two dumps. Rockwaste ± 450 000 t	31. Dez 84	Wind erosion of the two tailings dams is a major pollution problem
91	Olifantasfontain Deposit			-19,41000	18,07800	Pb,Zn	Pb, Zn									
92	Omburu Fluorite	Unknown	35km NE of Omaruru, Farm Omburo West 1143	-21,25000	16,15000	Flourite, Quartz (F)	Industrial minerals	Unknown	Marbles and calc silicate rocks of Swakop Group. Intruded by Salem Granites. Damara sequence.	Post Karoo veins into marbles and granites. Associated with older north-south faulting	Open workings	Blasting, Crushing, milling and flotation	32 000 t acid grade concentrate, 100 000 cubic metres. Reserves 600 000 t @ 35.40 % calcium fluorite	Foundations, tanks and buildings remain	1975	Side walls of the old excavations are weak and subject to erosion
93	Ondumakorume Complex			-20,76700	16,25000	REE	Sn, Li, Be, W, Nb, Ta, REE									

Map ID	Name	Operator (s)	Location	Lat	Long	Primary mineral (s) /commodity(s)	Group	Secondary mineral(s) / commodity(s)	Regional Geology	Site Geology	Mining method	Ore processing	Ore Quantity / Production statistics	Mining remnants	Closure date	Environmental hazards
94	Ondundu Gold Mine	Gold Fields Namibia (Pty) Ltd	90km NW of Omaruru,	-20,75000	15,48300	Gold (Au)	Au	Pyrite, Arsenopyrite, Chalcopyrite, Siderite, Marcasite, Argentifferous galena, Metallic copper and Manganese (Cu)	Swakop Group , Kuiseb Formation phyllites quartzites, amphibole schists, meta-gabbros-graphite schists; tourmalinites.	Anticlinal-synclinal structure (N-S). Gold bearing quartz veins over area of 10 square kilometre. Veins parallel to bedding planes in metasediments average 2 to 60 cm in width. 2 generations of quartz veining - only older system carries gold. Free gold in some areas.	Underground	Free milling oxidised ore at shallow depth. Unrefined gold produced 1924 - 45 then refined gold thereafter	± 32 000 t. Total production 448.15 kg Au. 14 g/t Av., Est. ± 480 000 t (waste to ore ratio, 15:1)	Concrete platform of treatment plant and old buildings, old machinery and tailings dump	Unknown	Contamination of stream/watertable from the tailings dam, air pollution during high winds
95	Ongaba Deposit			-18,40100	13,48200	Fe,Mn	Fe, Mn, V, Ti									
96	Onganja Mine		65km NE Windhoek	-22,10000	17,45000	Cu	Cu								Unknown	
97	Ongeama Deposit			-22,38300	17,30000	Cu, Zn	Cu									
98	Onguati Mine	Unknown	15km NNW of Karibib, Farm Onguati 52	-21,80000	15,80000	Malachite, Azurite Chrysocolla, Chalcopyrite, pyrite (Cu)	Cu	Arsenopyrite (Ag, Au)	Karibib Formation. Swakop Group. Damara sequence	Brecciated quartz-veins in folded marbles and silicates. Lodes vary in length from 6 -60 cm long and 20 to 600 mm wide. Very erratic.	Underground	Crushing, milling and flotation	In the main mining period 1972 - 1977, 3 404 t of concentrate, 19-20% Cu was produced	Rock waste is scattered around the site, the vicinity of the ore lodes is like a rabbit warren with many open workings and rock dumps.Taillings subject to erosion, Taillings 17 500 cubic metres	1971	Visual pollutant and dangerous to animals and unaware people moving around the area,waste passed to taillings dump in adjecent valley.
99	Orange River	Previuosly De Beers, now Russians	Between Senderingsdrif and Noordoewer, along N bank	-28,61349	16,45825	Diamondmonds	Alluvial diamonds	Unknown	Miocene to recent river gravels in palaeo - terraces	Remnant terraces above present river levels (40 m at lorelei) and in bedrock traps.	Excavation	Excavetate,screening and hand sorting	Not known	10 m deep trenches	Unknown	Excavations and prospecting activities on the Orange river terraces cause visual pollution
100	Oranjemund Mining Area No.1			-28,09300	15,88500	Diamond	Alluvial diamonds									
101	Osongombo Complex			-20,88300	16,00000	REE	Sn, Li, Be, W, Nb, Ta, REE									
102	Otjihase mine	Weatherly Mining	18 km NE Windhoek	-22,38333	17,23333	Cu	Cu			Stratabound, Cuprous masive pyrite deposit, located in the middle to upper part of the metasediments of the Kuiseb Formation/Damara Sequence, closely associated with the Matchless Amphibolite Belt.	Underground				Unknown	Significant water pollution in river and dust pollution from the tailings dam affects nearby village
103	Otjimbojo Deposit			-21,70000	16,13300	Au	Au									
104	Otjimbojo Tin Mine		Farms Otjimbojo east 48, 38 km northwest of Wilhelmastal	-21,71700	16,15000	Sn	Sn, Li, Be, W, Nb, Ta, REE			4 m wide and are discordantly emplaced into biotite schist, dipping 85° southeast. The pegmatite consists of coarse grained, quartzo-feldspathic, muscovite bearing rock with numerous closely spaced bands of muscovite and quartz which occur parallel to the walls of the dyke.						
105	Otjisazu Complex			-21,91700	17,08300	Phosphate	Industrial minerals									
106	Otjonamewa Mine		4 locations around Otjonamewa/ Ais, S of the Ais dome.	-21,06700	15,01700	Fluorite	Industrial minerals		Occurs with in the Intracontinental arm of the Damara Orogen, underlain mainly by metasedimentary rocks of the Swakop Group, Salem and other granites and pegmatites of varying ages intruding the Damara lithologies.							

107	Otjozonjati Mine	Robert Carr	70km NE Windhoek, on farm Okatjemisse 144	-22,11700	17,38300	Chalcopyrite, Bornite, Pyrite (Cu)	Cu	Malachite, Chrysocolla	Quartz-biotite schists of the Khomas Group,Damara Sequence .Area is a trough striking north-east-south - west with subsequent north-south faulting.	Brecciated quartz-veins striking north-south and dipping 45° east.	Underground	Crushing, milling and flotation	Production varied between 50 and 100 t of concentrate per month, 55-65% Cu. 800 t copper have been produced	A tailings dam is present on the site which is eroding into the river.	05. Jun 88	Tailings have been eroded into the adjacent river.
108	Otjua Deposit			-21,18300	16,00000	W	Sn, Li, Be, W, Nb, Ta, REE									
109	Ovihende Deposit		10km SE of Ovihende and about 18km SW of Kaoko, Otavi	-18,41800	13,53200	Fe,Mn	Fe, Mn, V, Ti		underlain by Damara Sequence metasediments comprising of dolomite, limestone, shells, chert and quartzites of the Tsumeb and Abenab Subgroup, as well as Quartzites, conglomerates schists and dolomites of the Nossib Group.							
110	Palisandro Marble	Palisandro Marble (Pty) Ltd	40 km SE of Karibib, on farm Gamikaub	-22,23333	15,63333	Marble (MBL)	Industrial minerals		The area is underlaid by a sequence of marbles (ridges) interbedded with biotite schists and calcsillicates gneisses, intruded by granites. Damara Sequence, Swakop Group	The quarry is confined to mining white marble as a prominent ridge	Excavation	Unknown	World class material of unlimited quantity	Large quantities of broken and rejected marble	Unknown	Waste stone is stockpiled on site, creating possible visual pollution
111	Panther Beacon Salt Pan			-22,58300	14,51700	halite	Industrial minerals									
112	Paukuab/ Baukwab	Unknown	51km E of Uis, Omaruru road C36	-21,26700	15,31700	Cassiterite (Sn)	Sn, Li, Be, W, Nb, Ta, REE	Tantalite, Tourmaline, Topaz, Garnet (Nb, Be)	Pegmatites into syntolate tectonic Pan African granites and Kuiseb Formation schists	Mineralisation in zoned quartzo-feldspathic pegmatites, very erratic distribution	Open pit	Unknown	1930's production not known. 1986- 8 830 t of 70% concentrate produced.	Quantities of quartzo-feldsparthic pegmatite dumped on site, tonnage not known.	1990	Dangerous trenches and pits
113	Petalite/Molopo Mine			-21,70000	14,20000	Sn,Li,Be	Sn, Li, Be, W, Nb, Ta, REE		the country rock consists of biotite schist with minor quartzite layers of the Amis River Formation, Swakop Group.	about 120 m long and 40 m wide with 20° north-northeasterly strike. The pegmatite is steeply dipping and has a discordant contact with the metasedimentary fabric.						
114	Platveld Amethyst	Unknown	Mine is 5 km north of farmhouse, Otjiwarongo district	-19,99722	17,20805	Amethyst quartz	Semi-precious stones	Calcite	Gently folded Swakop Group limestones and marble	Amethyst in banded zones, irregular lenses and patches in drusy cavities within vein quarts. Mineralised zones 0.3 - 0.5 m drusy cavities with large crystals	Open pit	Blocks and slabs exported	Unknown	Line of dumps up to 15 m high, waste from approx. 95% of production	Unknown	Dumps create visual pollution, operation limits use of land for livestock farming
115	Pomona			-27,20000	15,33300	Diamond	Alluvial diamonds									
116	Pot Mine		50km Karibib-Otjimbingwe	-22,40000	15,83300	Cu Au	Cu								Unknown	
117	Regenstein Deposit			-22,70000	17,01700	Pb,Zn,Ag	Pb, Zn									
118	Rhineland Deposit			-19,95100	15,06800	fluorite, Ba	Industrial minerals									
119	Rubicon Mine	S.W.A Lithium (Pty) Ltd, African Eploration (Pty)Limited	30km SE Karibib, on famr Okangava 22	-22,10000	16,00000	Petalite, Lepidolite, Amblygonite (Li)	Sn, Li, Be, W, Nb, Ta, REE	Beryl, Bismuth, Nb-Tantalite, Mica, Pollucite (Be	Quartz-feldspar pegmatites into monzo-diorite and Pan African granites	Two elipsoid pegmatite bodies. 20 - 35 m wide and 200 - 300 m long strike E-W and dip 40° northward flattening with depth	Underground	Blasting, hand cobbing and sorting	An estimated 300 000 cubic metres of ore has been produced.	Several abandoned buildings, works (with oil spillage) and rock dumps exist on site.	1999	Severe visual pollution is caused by the abandoned building and dumps
120	Saddle Hill			25,95000	14,93300	Diamonds	Marine diamonds									
Map ID	**Name**	**Operator (s)**	**Location**	**Lat**	**Long**	**Primary mineral (s) /commodity(s)**	**Group**	**Secondary mineral(s) / commodity(s)**	**Regional Geology**	**Site Geology**	**Mining method**	**Ore processing**	**Ore Quantity / Production statistics**	**Mining remnants**	**Closure date**	**Environmental hazards**
121	Sandamap Deposit		Farm Sandamap 115 Brandberg District	-21,83300	15,33300	Au Ag Pb	Au								Unknown	
122	Sandamap Mine	Reefton EPL.	Farm Sandamap 115	-21,96700	15,30000	Lithium minerals, Cassiterite, Tourmaline (Li, Sn, Be)	Sn, Li, Be, W, Nb, Ta, REE	Columbite, Tantalite (Nb)	Biotite schists of Karibib formation, intruded by pegmatites. Damara sequence	Mineralisation along zones in the pegmatites. Most important- Lithium-Muscovite + Cassiterite Greissen	Open pit	Excavate ,crush and separate	0.1% tin was recorded, ± 2 500 cubic metres	Waste rock	Unknown	Negative visual pollution is present
123	Sandamap Tin Mine		Farm Sandamap 115 Brandberg District	-21,90000	15,35000	Sn	Sn, Li, Be, W, Nb, Ta, REE								Unknown	
124	Sendelingsdrif		Orange river	-28,16700	16,88300	Diamond	Alluvial diamonds									

125	Sinclair Mine	South West Copper Company (1927-32)	110km N of Aus, on farm Sinclair	-25,70000	16,35000	Bornite, Chalcopyrite (Cu)	Cu	Malachite, Azurite, Atacamite, Cuprite, Tenorite	Metamorphosed basic to andesitic lavas. Barby Formation	Mineralisation in quartz filled fractures cross cutting lavas. These veins pinch and swell giving erratic grades. 4 - 5 major fracture systems recorded	Underground	Crushing and flotation	Several hundred tonnes of concentrate, the quantity is not recorded, reserves estimated at 16 000 t @ 3% Cu. Grade very erratic	Waste dumps, offices, houses and process plant foundations remain	19. Apr 86	Building foundations are a visual pollutant.
126	SP 14 Pegmatite Mine		8.2 km east-northeast of Pentalite/Molopo Mine	-21,66700	14,25000	Li,Sn,Nb	Sn, Li, Be, W, Nb, Ta, REE			20° north-northeasterly strike, the pegmatite is steeply dipping and locally up to 8 m wide and 40 m long.The core zone is surrouded by a discontinous shell of quartz , rare metal mineralisation, mostly of columbite-tantalite and tapiolite, is limited to a coarse grained zone.					Nov 62	
127	Spencer Bay		140 km North of Luderitz	-25,83300	14,91700	Diamond	Alluvial diamonds									
128	Sphinx Mine		Karibib district	-22,33300	15,45000	Au Cu	Au								Unknown	
129	Strathmore Tin Mine	Previously Bateman Mining (Pty) Ltd	40 km NW Hentiesbay, track to Ne from Mile 72	-21,66666	14,26666	Cassiterite (Sn)	Sn, Li, Be, W, Nb, Ta, REE	spodumene, Lepidolihe, Petalite, Eucryptite, Amplygonite, (REE) (Li)	Damara Sequence. Swakop Group- metasedimentary rocks of Amis Formation	Some 180 pegmatites of various sizes intruded into pre-existing zones of weakness. Both zoned and unzoned types are present. Bedrock schists. Sn-Nb-Ta in solid solution in cassiterite	Open pit	Large processing facility dismantled and removed on closure	Uknown	Old buildings, low dumps in existence	30. Apr 82	Visual pollution
130	Swartbooisdrift Mine		approx. 40 km NE of Epembe in NE Kaokoland	-17,35000	13,80000	Sodalite	Industrial minerals		the carbonate dykes are associated with syenitic and gabbroic dykes hosted by anorthositic rocks of the Kunene complex	deep blue sodalite occurs in Carbornet dykes, the sodalite-bearing dykes are irregular in shape and vary considerably in width.						
131	Swartmodder Mine		6km S Rehoboth	-23,38300	17,08300	Cu Au	Cu								30. Apr 82	
132	Tantalite Valley(Southern Sphere)		Warmbad	-28,71666	18,80000	Ta, Scheelite	Sn, Li, Be, W, Nb, Ta, REE								30/06/1981	
133	Terrace Bay			-19,98300	13,03300	Diamond	Alluvial diamonds									
134	Thorntree		6km W Onganja	-22,11700	17,40000	Cu	Cu								10. Mai 87	
135	Toscanini Coal Deposit		Skeleton Coast N Swakopmund	-20,90000	13,50000	Coal	Fossil fuel								Unknown	
136	Tschudi Deposit	Formerly Ongopolo Mining and Processing		-20,90000	13,50000	Cu,Ag	Cu									
137	Tsomtsaub Mine		3km NE of Granschow pegmatite S of Uis-Omaruru road	-21,31700	15,23300	Sn	Sn, Li, Be, W, Nb, Ta, REE		Underlain by metasedimentary rocks of the swakop Group, Granites and pegmatites of varying ages intruding the Damara lithology, forming a prominent NE-SW strip on the Nainais-kolero pegmatite belt							
138	Tsongoari		2.5km SW of Otjiorongwari	-18,84900	13,42100	Zn,Cu,Pb	Pb, Zn		Metasediments of the Ugab Subgroup, but mainly covered by rocks of the Damara Sequence							
139	Tsumeb Mine		N Otavi Mountainland	-19,23300	17,71700	Cu Pb Zn	Cu				Underground				Unknown	
Map ID	**Name**	**Operator (s)**	**Location**	**Lat**	**Long**	**Primary mineral (s) /commodity(s)**	**Group**	**Secondary mineral(s) / commodity(s)**	**Regional Geology**	**Site Geology**	**Mining method**	**Ore processing**	**Ore Quantity / Production statistics**	**Mining remnants**	**Closure date**	**Environmental hazards**
140	Tsumeb West		2.5km SW Tsumeb	-19,25000	17,70000	Cu	Cu			Vanadium ore found as nodules in the sand filling of surface karst cavities or as coatings on dolomite boulders within the sand is a typical example of the common " sand sack" type of deposit.	Underground and opencast				Unknown	

141	Tubas Deposit			-22,88300	14,80000	U	U									
142	Tumas Deposit			-22,91700	15,11700	Gypsum	Industrial minerals									
143	Tumas Deposit		Tumas drainage basin E of walvisbay on eastern Tumas dome	-23,06900	15,20000	U	U									
144	Tzamin Copper Prospect		30km N Outjo	-19,83300	16,11700	Cu Ag	Cu								Unknown	
145	Ubib (Mine) Prospect	Unknown	on farm Ubib 76, Karibib district	-22,15000	15,58300	Copper (Cu)	Cu	Unknown			Open pit	No indications of processing	Grade 2.5 % Cu. Reserves of 100 000 t @ 1.5 % Cu, No indication of mining	No indications of mining	Unknown	Unknown
146	Ugab Salt Pans 1-4	Unknown	10 - 35 km S Ugab. Erongo region	-21,36666	13,80000	Halite	Industrial minerals		Karoo group basalts and sediments	Derived from the differential weathering of rocks in a desert/marine environment	Excavation	Cut into blocks	Lower quality than distillation/evaporation salt. Used for cattle licks, 12 -15 Mt	Domestic waste and scrap metal on site	1958	No serious pollution
147	Uis Mine	Iscor limited South Africa, now partially operated by small scale miners	Uis	-21,23300	14,88300	Cassiterite, Tantalite (Sn, Nb, Ta)	Sn, Li, Be, W, Nb, Ta, REE	Unknown	Mineralisation associated with graben feature down-throwing Swakop group metasediments between Nossob rocks to the south and younger granitic rocks to the north. Strike north-east-south-west	A whole suite of cassiterite bearing pegmatites have intruded the downthrown rocks in a series of en echelon shear zones. These range from 0.5 to 40 m wide and from 10 m to 1 000 m long and strike sub-north-south	Open pit	Crushing and screening	Av. 200 - 1600 ppm tin, 80 - 440 ppm Ta. The large remaining ore reserves indicate a potential of job creation	Domestic waste dumped on tailings dam	04. Dez 90	Stability of parts of the pit excavations is poor
148	Uis Tantalite	Previously explored by Falconbridge	14 km W of Uis	-21,30833	14,79000	Tantalite (Ta)	Sn, Li, Be, W, Nb, Ta, REE	Columbite (Nb)	Amis River Formation-knotted schists and biotite schists	Pegmatite dipping north at shallow angle (35°) 2 - 3 m wide structurally controlled- "tension gashes".	Excavations	Hand cobbing	Few kilograms of Tantalite	Waste rock left in small dumps on side of trenches	Unknown	Operation carried on without any claim or mining licence as a result it causes visual pollution
149	Usakos Tourmalines mines		S of Usakos, o nthe famr Klein Aukas 66	-22,00000	15,61700	Tourmaline	Semi-precious stones		Occurs with in the Intracontinental arm of the Damara Orogen, underlain mainly by metasedimentary rocks of the Swakop Group, extensively intruded by post Karoo Erongo granites.						Unknown	
150	Vertwall Salt Pan			-25,93300	18,98300	halite	Industrial minerals									
151	Walvis Bay Salt Works			-22,98300	14,25000	halite	Industrial minerals									
152	Waterberg Basin			-20,68400	17,37800	Coal	Fossil fuel									
153	White Rhino Quarry	Marmorwerke, Karibib	20 km S of Karibib	-22,13333	15,75000	Marble (dimension stone)	Semi-precious stones		The area is underlaid by a sequence of marbles (ridges) interbedded with biotite schists and calcsillicates gneisses, intruded by granites. Damara Sequence	The quarry is confined to mining white marble as a prominent ridge	Excavation	Required blocks are transported for cutting	Almost inexhaustible reserves, World class material	Scrap metal, old equipment, unsuitable blocks/waste remain on site, Wastage ranges from 30 to 70 %	Unknown	Minor oil spills present on site
154	White Ridge Quartz Mine		80km E Windhoek	-22,57500	17,64500	Qtz	Industrial minerals								Unknown	
155	Witkrans Gold Workings			-23,71700	16,43300	Au	Au									
156	Witvlei Pos			-22,34900	18,46900	Cu	Cu									
157	Ysterputs		Noordoewer	-28,25000	18,08330	Blue Agate	Semi-precious stones								Unknown	

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INTRODUCTION TO ENVIRONMENTAL HYDROGEOCHEMISTRY

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Chapter 1: Introduction

There is an increasing interest in environmental issues. Hydrogeochemistry is very important from viewpoint of environmental impact assessment. Both surface water and ground water are used as sources of water for many purposes. Water also is transfer medium for many inorganic and organic contaminants and for pathogenic organisms. The purpose of our text is to present a basic information necessary for treatment and interpretation of environmental hydrogeochemical data. The level of text roughly corresponds to introductory master's level and basic knowledge of chemistry, mathematics and intrudoctury hydrogeochemistry is expected.

The structure of our text is as follows: Principal ground water pollutants are briefly indicated and then basic hydrogeochemical principals are discussed. More profound treatment of introductory hydrogeochemistry can be found in books such as Drever (1997) and Langmuir (1997). Then carbonate system is discussed in more detail because buffering in contaminated water and, thus, behavior of pH-sensitive contaminants is closely linked to the behavior of carbonates. Sampling of water and solids are an important part of contaminant studies and basic principals are introduced. Especially collection of solid phase samples is often neglected, but solid phase composition can be as important as water chemistry at many contaminated sites. More quantitative interpretation of collected data is discussed in chapters about geochemical modeling and transport. Then several types of contamination are discussed, including metals, acid mine drainage, radionuclides, and organics. Geochemical problems of remediation and principal remediation methods are also introduced. More detailed treatment of the topic is covered, for example, by Appelo and Postma (1999) and by Suthersan (1996). Finally, principals of risk analysis are discussed because calculation of risk became an important part of contamination studies. We will welcome comments from readers, which could help us to improve a potential re-edition of the text.

Chapter 2: Water Pollutants

2.1 Introduction

There are many types of water pollutants. Water which is withdrawn, used for some purposes and returned, is generally polluted. For example, water contaminated by agriculture activities contains nitrates, pesticides, and pathogens; mining activities produce water with low pH, elevated concentrations of sulfate, iron and other metals; thermal plants produce water that is elevated in temperature, with low dissolved oxygen concentration and so on. Chemical industry is very important source of water pollution because produces thousands of toxic compounds. In this chapter we focus on principal water pollutants, but this review is by no means complete and more detailed information can be found at U.S. EPA Home Page and in specialized books such as Masters (1998) and Fetter (1999).

2.2 Heavy Metals

Definition of metals is based on their physical properties like high thermal and electrical conductivity, high reflectivity, ductility, and strength. From chemical viewpoint, metals are elements which can give up one or more electrons and, thus, form cations in aqueous solution. The term heavy metals generally refers to metal with specific weight greater than about 4.0 g/cm^3. Principal metals from environmental viewpoint are *mercury, lead, cadmium,* and *arsenic* (arsenic is considered as semi-metal because has both metalic and non-metalic properties). Other toxic metals are beryllium, aluminum, chromium, bismuth, cobalt, nickel, strontium, thallium, zinc, tin, selenium, and titanium. Some of them like chromium are essential nutrients at low doses, but they become toxic at high concentrations.

Metals differ from organic pollutants because they are persistent in environment. For example, benzene can be degraded by bacteria, but lead can be only transferred from water to solid phase by precipitation of minerals like cerussite, $PbCO_3$, or galenite, PbS. It can be also adsorbed on ferric oxide and hydroxides, but always stays in environment and may be later remobilized during changes of pH and Eh conditions.

Metals may be inhaled or ingested with consumed water. Their toxicity depends on *exposition pathway* (see Chapter 13). For example, mercury in liquid form is not very toxic and most of ingested mercury is excreted from human body. In contrast, mercury vapor is very toxic because enters blood stream and after passing to brain can damage central nervous system. In the case of lead the situation is inverse, e.g., the most toxic is dissolved lead present as free ion Pb^{2+} and lead vapor is not very dangerous. Typical target organ damaged by metals are kidneys because most metals are excreted via kidneys. Typical metals toxic to kidneys and called nephrotoxins are cadmium, lead, and mercury.

There are several sources of metals in environment. Principal source of metals is mining industry, where concentrations of dissolved metals like iron, zinc, arsenic, lead etc., may reach extreme values (Chapter 9). Other sources are landfills, application of fertilizers (they frequently contain metals like cadmium, electroplating (chromium), and so on. High concentrations of dissolved metals are also typical for organic contamination plumes because initially adsorbed metals are released from Fe(III) oxide and hydroxides, which are unstable in very reducing environment.

2.3 Organic Compounds

There are thousands organic compounds produced in chemical industry. However, only some of them are important from environmental viewpoint. There is a group of toxic compounds related to dissolution of commercial gas. The group is called *BTEX* on the basis of names of compounds: *B*enzene, *T*oluene, *E*thylbenzene, and *X*ylene. They have a lower specific weight than that of water and, thus, they float on water table. The BTEX comprise only a small fraction of commercial gas (less than 10 %), but they are relatively more soluble than compounds with higher molecular weight (> C7, e.g., with more than 7 atoms of carbon), and they are very carcinogenic (more in Chapter 11 and Chapter 13).

Important group of contaminants also are *chlorinated solvents* like tetrachloroethylene (PCE), trichloroethylene (TCE), 1,2-dichloroethylene (DCE), 1,2-dichloroethane (DCA), vinylchloride (VC), and carbon tetrachloride (CTC). These compounds have higher specific weight than that of water and, consequently, they sink towards the base of an aquifer. They are carcinogenic, with vinylchloride as the most toxic compound. In many cases, there is formation of TCE, 1,2-DCE, and VC from PCE as parent compound (more in Chapter 11). Some organic compounds like trichloromethane (TCM) may form as a consequence of artificial chlorination of water containing natural dissolved organic carbon compounds.

Finally, there is contamination by *polyaromatic hydrocarbons* (PAH) like naphtalene, anthracene, and benzopyrene at some sites. These compounds comprise several benzene nuclei and they are relatively insoluble, with tendency to partition into soil organic matter. Thus, their occurrence is generally limited to the proximity of contaminant sources. They are very persistent in environment and some of them like benzopyrene are strong carcinogens. More in-depth reviews of organic contaminants are in Domenico and Schwartz (1998) and Fetter (1999).

2.4 Pesticides

Pesticides are chemicals used to kill undesirables organisms. Based on their use, they can be divided into *insecticides, fungicides, herbicides,* and *rodenticides.*

There are 3 principal groups of organic pesticides: *organochlorines, organophosphates, and carbamates.* The typical organochlorine is DDT (dichlorodiphenyltrichlorethane) which was frequently used to control mosquitoes carrying malaria and yellow fever. Toxicity of DDT to humans is relatively low, but the most serious problem related to this compound was its accumulation in food chain. DDT and its metabolite dichlorodiphenyldichloroethene (DDE) interferes with the enzyme that regulates distribution of calcium in birds, with resulting very thin shells of eggs. Other common organochlorines are aldrine, dildrin, endrin, endosulfan, and heptachlor.

Organophosphates such as parathion, malathion, and diazinon, are not very persistent, but they are more toxic than organochlorines. Exposure results in a wide range of symptoms like tremor, convulsions etc.

Carbamates are derived from carbamic acid, H_2NCOOH. Common carbamates are aldicarb, carbaryl, and propoxur. Acute human exposure may cause vomiting, blurred vision, and in some cases also death.

Most of compounds indicated above are insecticides. Chlorinated hydrocarbons are also used as pesticides. Clorophenoxy compounds like 2,4,5-T, and 2,4-D are known because they were used in mixture called Agent Orange as defoliants in the Vietnam War.

2.5 Acid Deposition

Rain water is naturally slightly acidic, with pH about 5.7 (Chapter 4). This is result of presence of carbonic acid, H_2CO_3, in the air at equilibrium with p_{CO2} equal to $10^{-3.5}$ atm. However, typical pH values of precipitation in industrial zones of Europe and North America are as low as 4.0. This is referred as acid rain caused by *anthropogenic emissions* of sulfur and nitrogen oxides. Sources of emissions can be *stationary* (thermal plants burning coal with high sulfur content) or *mobile* (cars releasing emissions from combustion of fuel).

Principal input from emissions are ions H^+, NO_3^-, and SO_4^{2-}. Sulfate ions are not very detrimental, but they may contribute to high salinity of water. Nitrate ions may contribute to eutrophication of surface water bodies, and, first of all, they can cause *methemoglobinemia* in little kids as a consequence of oral consumption (see section about nutrients). Thus, their concentration in consumed water is closely controlled. Nitrogen oxides in the air also contributes to formation of *ground level ozone* (GLO), harmful for both human health and plants.

Important impact of acidification is also dissolution of aluminosilicate and aluminum hydroxide minerals. In that case, toxic aluminum is released. Concentration of aluminum is generally controlled by precipitation of amorphous aluminum hydroxide, $Al(OH)_3$. This mineral phase becomes soluble at pH about 4.2 and water

with lower pH often has high aluminum concentration. Aluminum is very detrimental for aquatic life because precipitates as $Al(OH)_3$ in more basic environment of the gills of fish and may cause their clogging.

2.6 Nutrients

Nutrients are chemicals necessary for growth of living organisms. Typical examples are carbon, nitrogen, iron, sulfur, and phosphorus. In excessive concentrations, they can be considered as pollutants because they stimulate growth of aquatic plants such as algae. Presence of algae in surface water bodies is detrimental for their use as drinking water and for recreational purposes.

Excessive growth of algae leads to *algae blooms* and to *eutrophication* of water. When algae die and decompose, they remove dissolved oxygen (DO) from water. The nutrient, which is the least available for algae growth is called a *limiting nutrient.* Carbon is generally available and either nitrogen or phosphorus are limiting nutrients for algae growth. Principal sources of nitrogen are chemical fertilizers, runoff from animal feedlots, septic systems, waste water discharge, and nitrogen deposition from atmosphere. Thus, nitrogen is rarely limiting nutrient for algae growth. In contrast, phosphorus is generally less abundant. However, concentration of phosphorus in the form of phosphate, PO_4^{3-}, may be high in agriculture runoff from heavily fertilized areas, in sewage water, and in outflow from septic systems.

Detergents produced after World War II also contained large amount of phosphate and were not biodegradable. Recent detergents are already biodegradable and phosphate present as sodium tripolyphosphate (STP) was often replaced by sodium nitrilotriacetate (NTA).

2.7 Thermal Pollution

Thermal pollution is generally related to waste waters from power plants. Water is not generally contaminated, but has higher temperature than ambient water. Thus, concentration of dissolved oxygen (DO) is lower. Also, metabolic rates of aquatic organisms double for each 10°C of increasing temperature. Increased metabolic rates also result in higher consumption of oxygen. Thus, consequences of thermal pollution are similar to the input of nutrients, e.g., water with low DO concentration with limited aquatic life. Furthermore, toxic impact of some contaminants like aluminum increases in low DO water because their input by gills increases as a consequence of higher rate of water exchange.

2.8 Pathogens

Pathogens are disease-causing organisms that can multiply and grow within bodies of humans and animals. Our text is focused on hydrogeochemistry of contamination and only brief outline of pathogens is presented here.

Growth of pathogens in body of a host is called infection. Pathogens can be broadly divided into *bacteria,* responsible for diseases like cholera, bacillary dysentery, and typhoid; *viruses,* responsible, for example, for hepatitis and poliomyelitis; *protozoa,* causing amebic dysentery and giardiasis, and *helminths* (parasitic worms), which cause diseases like schistosomiasis and dracunculiasis. Epidemics may be caused by penetration of intestinal discharges of an infected individual called carrier. Carriers themselves may not even exhibit symptoms of disease. This means that it is necessary to protect water supplies from any human and animal waste contamination. A common classification distinguishes between waterborne diseases like cholera and typhoid, which are spread by ingestion of contaminated water, water-washed diseases like scabia and trachoma, associated with lack of water to maintain cleanliness, water-based diseases, such as schistosomiasis and dracunculiasis, transmitted by contact with water without ingestion, and water-related diseases, such as dengue fever and malaria, transmitted by hosts (like mosquitoes) which depend on water, but without direct human contact with water.

Initially, coliform bacteria were considered as indicators of contamination of water by pathogens from human waste. However, it was found that presence *enteroviruses* is a better criterion for evaluation of contamination by human waste. Suggested indicators are presence of *polioviruses* and *hepatitis A* (HAV) viruses. Transport of viruses can be modeled just like transport of inorganic and organic contaminants and probably the most important modeling parameter is *inactivation rate* (e.g., removal of viruses by processes like their die-off) of viruses (Azadpour-Keeley et al., 2003).

2.9 Oxygen-demanding Wastes

Besides of nutrients and thermal pollution the DO concentration may be reduced by decomposition of *oxygen-demanding wastes.* The saturated oxygen concentration

in water is relatively low, from 8 to 15 mg/L, depending on temperature. The minimum recommended DO concentration for fish population is 5 mg/L, but cold water species require even higher concentrations of oxygen.

Oxygen-demanding wastes are generally biodegradable organic compounds which consume oxygen during their biodegradation. Biodegradable organic compounds are contained, for example, in municipal waste waters and in effluents from industries like food processing and paper production.

The most common measures of oxygen demand are *chemical oxygen demand* (COD) and *biochemical oxygen demand* (BOD). The BOD is generally measured for 5 days period and is indicated as BOD_5. The COD refers to the amount of oxygen necessary to oxidize the waste chemically and BOD refers to amount of oxygen necessary to degrade waste biologically. Because not all organic compounds can be degraded biologically, then it holds that COD > BOD.

2.10 Salts

Water accumulates a variety of dissolved solids. A commonly used measure of salinity the concentration of *total dissolved solids* (TDS). Recommended TDS for drinking water is about 500 mg/L. Limits for livestock are higher, for example beef cattle can tolerate concentration up to 10,000 mg/L. In temperate and cold climate, one of sources of salinity can be related to the *application of road salts* in winter. Concentrations of cations like Na is generally lowered by cation exchange, but chloride concentration in water may reach high values.

In semiarid and arid climates, there is an increasing salinity linked to *irrigation* of fields. Irrigation water evaporates in soil and there is build-up of concentrations of ions like Na and Cl because ions like Ca and Mg are incorporated to precipitated carbonates. Furthermore, precipitated minerals form salt crust at ground surface and they may be re-dissolved during precipitation period. Ground water discharges to surface water bodies and salinity in rivers increases in the direction of their flow. This process is enhanced by excessive withdrawal of river water for irrigation (for example, from Colorado River in the Southwest of USA).

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Chapter 3: Principles of Hydrogeochemistry

3.1 Basic Approaches

Dilution factor (DF): Ratio between final and initial concentration of a conservative ion like chloride, assuming that there was no input of the ion along flow path. The DF value can be used to evaluate the influence of physical processes like dispersion in transport of contaminants. An analogy of dilution factor is *concentration factor (CF),* which is used, for example, to evaluate a fraction of infiltrated precipitation after evapotranspiration. In that case, this is the ratio of chloride concentration in precipitation to chloride concentration in deep unsaturated zone water or in ground water.

Problem: In piezometer close to mining wastes, the concentrations of Cl^- and Al^{3+} were 100 mg/L and 40 mg/L, respectively. In piezometer located about 50 m downgradient the same concentrations were 60 mg/L and 10 mg/L. Which part of Al^{3+} concentration change was caused by geochemical processes?

Solution: The dilution factor DF for Cl^- is DF = 100/60 = 0.6. When we multiply initial concentration of Al^{3+} by DF we get 40×0.6 = 24 mg/L. This is expected concentration after physical processes. However, measured concentration was 10 mg/L. This means that 24 – 10 = 14 mg/L of the change was probably caused by chemical processes like precipitation of minerals as gibbsite, $Al(OH)_3$. We can check saturation index for gibbsite, which should have a value close to zero (see later).

Thermodynamic approach: There is assumption of very fast reaction rate with instantaneous equilibrium and no time factor is included. This assumption may be valid in the case of slow ground water flow and long residence time in ground water system.

Kinetic approach: Time factor plus other factors which have an impact on rate of reactions are included. Kinetic approach is much less used than thermodynamic approach because data on reaction kinetics are limited. However, some slow reactions like silicate weathering and redox reactions require kinetic description. One of the best known reaction kinetics is the kinetics of pyrite oxidation.

Mass balance approach: It is based on determination of concentration changes in different phases of an investigated system. It cannot be applied in some situations because solid phase composition changes may be difficult or even impossible to determine.

Problem: Calculate the volume of water with pH = 3.5 necessary to dissolve calcite in 1 m^3 of sand with 0.5 wt% of calcite. Specific weight of sand is 1 600 kg/m^3 and 1 mol of calcite is 100 g.

Solution:
- calculate number of moles of calcite in 1 m^3 of sand = (1 600 000 g × 0.005)/100 g = 80 mol
- calculate the volume of water to dissolve 80 mol of calcite: $V = 80 \text{ mol}/10^{-3.5} = 2.5\times10^5 \text{ L} = 2.5\times10^2 \text{ m}^3$

Master parameters (variables) are pH, redox potential Eh and ionic strength. They determine speciation (e.g., distribution of total concentrations among free ions and complexes) and behavior of dissolved species.

Macrocontaminants generally occur in high concentrations and influence master parameters of water. Examples are SO_4^{2-} and Fe^{2+} (only in acid mine drainage because in other environments Fe^{2+} generally has low concentration). The concentration of sulfate and Fe^{2+} in acid mine drainage, for example, has an impact on ionic strength (see later) and, thus, on activity coefficients, and Fe^{2+} concentration also has an impact on redox potential Eh. Macrocontaminants influence behavior of *microcontaminants* like Pb^{2+}, Zn^{2+} through ionic strength impact on activity coefficients and formation of complexes. When Pb^{2+} enters ground water, it has no influence on master parameters and macrocontaminants. On the other hand, formation of complexes like $PbSO_4^0$ has strong impact on lead behavior, but not on sulfate behavior because generally concentration of lead is negligible compared to the concentration of sulfate. When only contamination by microcontaminants takes place, we do not have to predict changes of master parameters like in the case of contamination by macrocontaminants. This means that modeling of behavior of contaminants is much simpler.

3.2 Thermodynamics

Common concentration units in hydrogeochemistry are *molarity M*, defined as mass in moles in 1 litr of solution and *molality m*, defined as mass in moles in 1 kilogram of solution. In dilute solution molarity is approximately equal to molality. Concentrations in miliequivalents per liter is concentration in milimoles per liter multiplied by charge of an ion.

Problem: Concentration of Ca in water is 65.1 mg/L. Calculate concentrations in mmol/L and meq/L. Atomic weight of Ca is 40.08.

Solution: Concentration in mmol/L is 65.1/40.08 = 1.62, concentration in meq/L is 1.62×2=3.24.

Activity a_i is "thermodynamic concentration" or the fraction of total concentration which participates in geochemical reactions. It is calculated as a product of *activity coefficient* γ_i and concentration m_i:

$$a_i = \gamma_i m_i \qquad 3.1$$

Activity coefficient is a function of *ionic strength I*, which is calculated as

$$I = \frac{1}{2}\sum m_i z_i^2 \qquad 3.2$$

where m_i is concentration and z_i is charge of ion *i*.

Problem: Calculate ionic strength of 0.2 mol solution of $NaSO_4$.

Solution:

$$I = \frac{1}{2}\left(m_{Na^+} z_{Na^+}^2 + m_{SO_4^{2-}} z_{SO_4^{2-}}^2\right)$$

$$I = \frac{1}{2}\left(0.2\times 1^2 + 0.2\times 2^2\right) = 0.5$$

Ionic strength is a measure of mineralization of a solution. When ionic strength increases, activity coefficient decreases (Fig. 3.1). In very diluted solutions activity coefficient is ≅ 1.0 and activity is equal to concentration. The decreasing trend is related to the "cage" of opposite charge particles around ions. There is reversal of the trend in extremely concentrated solutions (brines) because beyond of ionic strength of about 1.0 mol/L because there is an increase of activity coefficients with increasing ionic strength. This is related to decreasing amount of free water because most of water is already binded around particles. In the case of uncharged species like $H_2CO_3^0$, $H_4SiO_4^0$ or $H_3AsO_3^0$ only second effect takes place and their activity coefficients are always ≥ 1.0.

Activity coefficients are calculated using Debye-Hückel equation for ionic I < 0.1, Davies equation I < 0.5, and Pitzer's equations for very high ionic strength (Langmuir, 1997; Drever, 1997). However, Pitzer's parameters are generally available for 25°C only.

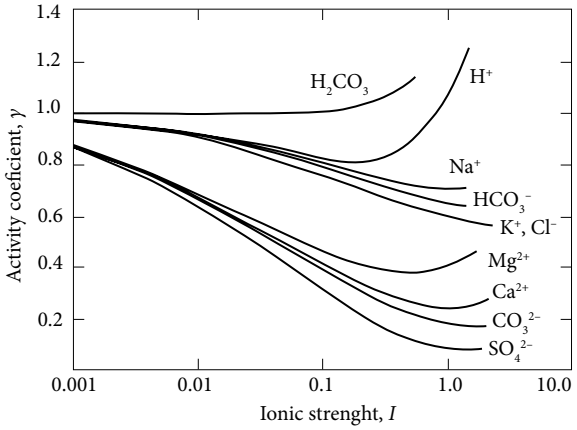


Fig. 3.1 Relation between ionic strength and activity coefficients (after Freeze and Cherry, 1979).

The Debye-Hückel equation in extended form is

$$\log\gamma_i = -Az_i^2\frac{\sqrt{I}}{1+Ba\sqrt{I}} \qquad 3.3$$

where γ_i is activity coefficient of ion *i*, z_i is its charge, *A*, *B* are temperature-dependent constant, and *a* is parameter corresponding to the size of an ion.

For higher ionic strength ($I > 0{,}1$), the Davies equation is used:

$$\log \gamma_i = \frac{-Az_i^2\sqrt{I}}{1+\sqrt{I}} + 0.2Az_i^2 I \qquad 3.4$$

where A is temperature-dependent constant, and the final term is purely empirical. Constants and ion sizes used in both equations can be found, for example, in Stumm and Morgan (1996) and in Langmuir (1997). Hand calculation of activity coefficients becomes complicated and tedious when more species are involved. Thus, the equations above are used in speciation programs like PHREEQC (Parkhurst, 1995) to calculate distribution of total concentrations among free ions and complexes.

Law of mass action (also called Guldberg-Waag Law): In reaction

$$a\,\mathrm{A} + b\,\mathrm{B} \longleftrightarrow c\,\mathrm{C} + d\,\mathrm{D} \qquad 3.5$$

where small letters indicate stechiometric coefficients and capital letters are concentrations, the Gibbs free energy, which is driving force of the reaction, is expressed as

$$\Delta G_R = \Delta G_R^0 + RT\ln\frac{a_\mathrm{C}^c a_\mathrm{D}^d}{a_\mathrm{A}^a a_\mathrm{B}^b [A]^a [B]^b} \qquad 3.6$$

where $\Delta G_R^{\,0}$ is standard Gibbs free energy of the reaction, R is universal gas constant, and T is temperature. For equilibrium applies that $\Delta G_R = 0$ and then

$$\Delta G_\mathrm{R}^0 = -\ RT\ \ln\ K \qquad 3.7$$

where K is equilibrium constant for the reaction. The standard Gibbs free energy is calculated as

$$\Delta G_R^0 = \Delta G_{f\ \text{products}}^0 - \Delta G_{f\ \text{reactants}}^0 \qquad 3.8$$

where G_f is Gibbs formation energy (from thermodynamic tables).

At equilibrium, there is no more change of reactants and products concentrations and $\Delta G_R = 0$. If $\Delta G_R < 0$, then a reaction proceeds from the left to the right, if $\Delta G_R > 0$, then a reaction proceeds from the right to the left.

Van't Hoff equation is used to correct a value of equilibrium constant generally available for 25°C. When the constant is K_{T1} for temperature T_1, its value for temperature T_2 is

$$\log K_{T_2} = \log K_{T_1} + \frac{\Delta H_R^0}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \qquad 3.9$$

where ΔH^0_R is enthalpy of reaction (from tables), and R is universal gas constant.

Solubility product K_{sp} is equilibrium constant for dissolution/precipitation of a mineral. Let us have dissolution of gypsum in water:

$$\mathrm{CaSO_4 \cdot 2H_2O}(s) = \mathrm{Ca^{2+}} + \mathrm{SO_4^{2-}} + \mathrm{2H_2O}$$

Mass action equation is

$$\frac{\left[\mathrm{Ca^{2+}}\right]\left[\mathrm{SO_4^{2-}}\right]\left[\mathrm{H_2O}\right]^2}{\left[\mathrm{CaSO_4 \times 2H_2O}\right]} = K_{equil}$$

where terms in brackets are activities. By definition, activities of pure solid phases and water (except for very mineralized solutions) are equal to 1.0, and we can write

$$[\mathrm{Ca^{2+}}]\ [\mathrm{SO_4^{2-}}] = K_{equil} = K_{sp} = 10^{-4.60} \qquad \text{for 25°C}$$

where K_{sp} is equilibrium constant called solubility product. This constant applies for the reaction as it is written, e.g., for dissolution. For precipitation its value is $1/10^{-4.60} = 10^{4.60}$.

Saturation index SI indicates the degree of saturation with respect to a given mineral. It is defined as

$$SI = \log\frac{IAP}{K_{sp}} \qquad 3.10$$

where IAP is ion activity product, for example in the case of gypsum dissolution it is

$$IAP = [\mathrm{Ca^{2+}}]\ [\mathrm{SO_4^{2-}}]$$

where brackets denote activities.

When $IAP = K_{sp}$, the SI value is 0 and water is at equilibrium with respect to a given mineral. If $SI > 0$, water is supersaturated and the mineral should precipitate, and if $SI < 0$, water is undersaturated and the mineral should dissolve (of course, if the mineral is present in solid phase in contact with water). It has to be emphasized that the SI value indicates direction, but does provide information about rate of a reaction. Furthermore, there are reactions which never attain equilibrium and reactants are gradually transformed into products. An example is the oxidation of organic matter:

$$CH_2O + O_2 \rightarrow CO_2 + H_2O$$

In this reaction, organic matter is consumed and even when concentration of products such as CO_2 increases, organic matter cannot be re-created. This means that this type of reactions requires kinetic description.

Only some minerals dissolve and precipitates relatively fast and they are called *reactive minerals*. In this case we can apply thermodynamic approach. Common reactive minerals are (adapted from Deutsch, 1997):

Carbonates:
- calcite, $CaCO_3$
- dolomite, $CaMg(CO_3)_2$
- siderite, $FeCO_3$
- rodochrozite, $MnCO_3$

Sulfates:
- gypsum, $CaSO_4.2H_2O$
- jarosite, $KFe_3(SO_4)_2(OH)_6$
- melanterite, $FeSO_4.7H_2O$
- alunite $KAl_3(SO_4)_2(OH)_6$(questionable)

Oxides and hydroxides:
- ferrihydrate, $Fe(OH)_3$
- goethite, FeOOH
- gibbsite, $Al(OH)_3$
- manganite, MnOOH
- amorphous silica, $SiO_2(am)$
- brucite, $Mg(OH)_2$

Congruent dissolution: when a mineral dissolves, the ratio between ions in solution is the same as in the mineral. For example, the ratio $Ca^{2+}:SO_4^{2-}$ is 1:1 in both gypsum and in water.

Incongruent dissolution: the ratio is different in dissolving mineral and in water. This is typical for dissolution of silicates, when secondary minerals are formed. An example is dissolution of anorthite with formation of kaolinite:

$$CaAl_2Si_2O_8 + H^+ + H_2O \rightarrow Al_2Si_2O_5(OH)_4 + Ca^{2+}$$

The ratio $Ca^{2+}:Al^{3+}:Si^{4+}$ is 1:2:2 in ortoclase, but 1:0:0 in water because all Al^{3+} and Si^{4+} are retained in secondary mineral kaolinite.

Stability diagrams for silicates: They are constructed for selected silicate minerals and with assumption of all aluminum conserved in solid phase. There is no guarantee that a water sample is at equilibrium with a mineral, when water samples fall into the field of the mineral. This behavior just indicates that the water is relatively closer to equilibrium with the mineral compared to other mineral phases used for construction of the diagram. An example of stability diagram for system with K_2O is in Fig. 3.2.

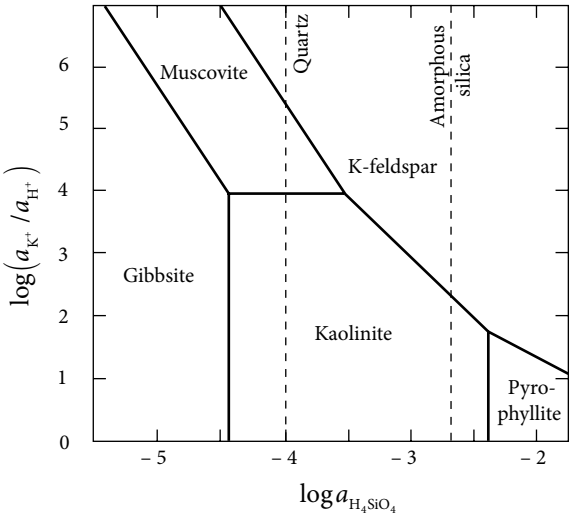


Fig. 3.2 Stability diagram for system with K_2O.

Influence of complexation: there is formation of *aquatic complexes* of ions, for example calcium can be in solution as free ion Ca^{2+} and in the form of complexes like $CaSO_4^0$, $CaHCO_3^+$ etc. These complexes increase solubility of calcium minerals, which would be lower if only Ca^{2+} would have been present in water.

Let us consider dissolution of anglesite,

$$PbSO_4(s) \longleftrightarrow Pb^{2+} + SO_4^{2-} \qquad K_{sp} = 10^{-7.79}$$

If there are Mg^{2+} and Cl^- already present in water, there is formation of complexes

$$Mg^{2+} + SO_4^{2-} \longleftrightarrow MgSO_4^0 \text{ and } Pb^{2+} + Cl^- \longleftrightarrow PbCl^+ \text{ (and also } PbSO_4^0)$$

and total dissolved lead concentration will be

$$[Pb]_{total} = (Pb^{2+}) + (PbSO_4^0) + (PbCl^+)$$

There also is an influence of ionic strength on dissolution of anglesite. In water with Mg^{2+} and Cl^-, the activity coefficients for Pb^{2+} and SO_4^{2-} are lower than in distilled water and more anglesite dissolves. In that case we can write that

$$\gamma_{Pb^{2+}} m_{Pb^{2+}} \gamma_{SO_4^{2-}} m_{SO_4^{2-}} = K_{\text{anglesite}}$$

The value of solubility product of $K_{\text{anglesite}}$ is a constant, and, thus, when values of activity coefficients γ are reduced as a consequence of high ionic strength, then values of concentrations *m* have to increase to compensate for the change.

Common ion effect: If water is at equilibrium with less soluble mineral and encounters more soluble mineral, which contains an ion from the first mineral already

dissolved in water, then the first mineral precipitates (Drever, 1997). An example is precipitation of calcite during dissolution of gypsum:

$$Ca^{2+} + HCO_3^- + CaSO_4 \cdot 2H_2O(s) \longleftrightarrow$$
$$\longleftrightarrow Ca^{2+} + SO_4^{2-} + CaCO_3(s) + H^+ + 2H_2O$$

Water of Ca-HCO_3 type at equilibrium with calcite encounters gypsum and resulting water is of Ca-SO_4 type. Calcite is less soluble than gypsum and dissolution of gypsum with input of large quantity of Ca^{2+} forces precipitation of calcite and reduction of bicarbonate concentration. Similarly, if the water dissolving anglesite in previous case contains SO_4^{2-} instead of Cl^-, there will be very limited dissolution of anglesite because sulfate is in both anglesite and in water.

Order of encounter refers to the order in which strata with different minerals are encountered by flowing ground water. Even when the same strata with the same mineral assemblage are encountered, resulting ground water chemistry at outflow will be different if the order of strata is different (Palmer and Cherry, 1984). For example, if first sequence contains shale layer with Na-montmorillonite, limestone layer, and gypsum layer and second sequence contains limestone layer, gypsum layer, and shale layer with Na-montmorillonite and organic matter, the water at the first sequence outflow will have high Ca^{2+} and SO_4^{2-}–concentrations and low Na^+ concentration, and the water at the second sequence outflow will have high Na^+, and low SO_4^{2-} Ca^{2+} concentrations. This is a consequence of common ion effect, cation exchange and sulfate reduction in different orders.

3.3 Kinetics

Kinetic approach includes time factor. Let us have dissolution of halite, NaCl. When we plot concentration of Na^+ *vs.* time (Fig. 3.3), concentration of Na^+ increases initially, but at time $t = t_2$ reaches a maximum, and then remains constant. Since time t_2, the concentration of Na^+ does not depend on time and is determined by the solubility product of halite.

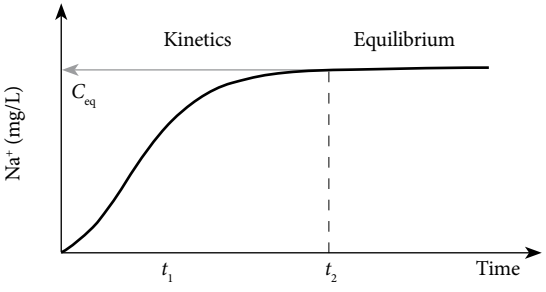


Fig. 3.3 Dissolution of halite (adapted from Appelo and Postma, 1999).

Behavior in the region where $t > t_2$ is described by thermodynamics, and behavior in region where $t < t_2$ is described by kinetics. The time t_2 necessary to attain equilibrium is different for different minerals. It is relatively short for reactive minerals like calcite and gypsum and long for non-reactive minerals like quartz. However, if a reaction is "fast" or "slow" also depends on the relation between velocity of ground water flow and reaction rate (the faster the flow is, the less probable is equilibrium) and on time scale of investigation (for example, predictions for radioactive disposal sites are up to more than 10,000 years).

Order of reaction kinetics: depends on exponent of independent variable, for example reaction

$$-\frac{dC}{dt} = k\ C \qquad 3.11$$

is of first order because the exponent of concentration C is one. In the reaction t is time and k is reaction constant linked to half-life $t_{1/2}$ as $k = ln\ 2 / t_{1/2}$. Solution of the equation obtained by integration for C_0 at t_0 is

$$C_t = C_0\ e^{-kt} \qquad 3.12$$

where C_0 and C_t are concentrations at time $t = 0$ (initial concentration) and at time t. Rate of reaction decreases with declining concentration and this reaction is used to describe radioactive decay of isotopes like ^{14}C and tritium and is also used for biodegradation of petroleum products like benzen and toluen and chlorinated solvents like PCE and TCE.

In the case of zero order kinetics, the reaction is

$$-\frac{dC}{dt} = k \qquad 3.13$$

and

$$C_t = C_0 - kt \qquad 3.14$$

Rate of zero order reaction is always the same and does not depend on concentration. In the case of 2nd order reaction concentration is squared,

$$-\frac{dC}{dt} = k\ C^2 \qquad 3.15$$

Example of second order reaction is oxidation of Fe^{2+} by oxygen,

$$-\frac{dm_{Fe^{2+}}}{dt} = k\ m_{Fe^{2+}} \left[OH^-\right]^2 p_{O_2} \qquad 3.16$$

This reaction is of 2nd order with respect to pH, but of first order with respect to Fe^{2+} concentration and partial pressure of O_2.

Homogeneous vs. *heterogeneous reaction:* Homogeneous reaction includes only one phase. Example is formation of $PbSO_4^0$ complex in solution. Heterogeneous reactions include more phases and an example is dissolution of CO_2 in water.

Relation between reaction constant and temperature is given by the *Arrhenius equation*,

$$k = A \exp \frac{-E_a}{RT} \qquad 3.17$$

where A is pre-exponential (Arrhenius) factor, E_a is activation energy, R is universal gas constant and T is temperature. If we know reaction constants for different temperatures, we can plot a graph $\log k = f(1/T)$ in order to determine activation energy from its slope equal to $-E_a/2.3\,R$ (Fig. 3.4).

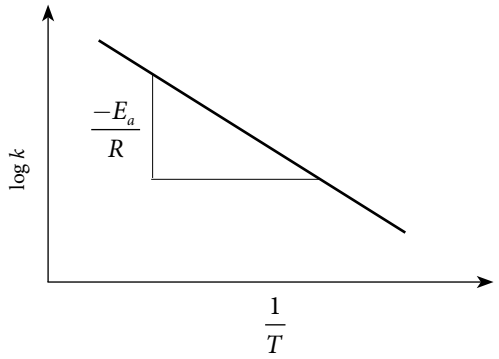


Fig. 3.4. Determination of activation energy.

3.4 Oxidation-reduction (redox) Reactions

In these reactions there is change of oxidation state of ions. Oxidation is a loss of electrons and reduction is a gain of electrons. Electrons cannot freely exist in solution, thus there is no oxidation without reduction and vice versa. Example is oxidation of Fe^{2+} combined with precipitation of ferric hydroxide:

$$Fe^{2+} + 0.25\ O_2 + 2.5\ H_2O \longleftrightarrow Fe(OH)_3(s) + 2\ H^+$$

In this reaction iron is oxidized from +2 state to +3 state and oxygen is reduced from 0 state to –2 state. On the other hand, dissolution of calcite,

$$CaCO_3(s) + CO_2 + H_2O \longleftrightarrow Ca^{2+} + 2HCO_3^-$$

is not redox reaction because oxidation numbers of calcium and carbon are always +2 and +4, respectively.

Each redox reaction can be written as a combination of two half-reactions, oxidation and reduction. For example, oxidation of Fe^0 by oxygen can be written as

$$Fe^0(s) \rightarrow Fe^{2+} + 2e^- \qquad \text{oxidation of } Fe^0 \text{ to } Fe^{2+}$$
$$0.5O_2 + 2H^+ + 2e^- \rightarrow H_2O \qquad \text{reduction of } O^0 \text{ to } O^{2-}$$

$$Fe^0(s) + 0.5\ O_2 + 2H^+ \rightarrow Fe^{2+} + H_2O \quad \text{complete reaction}$$

In this reaction, Fe^0 is oxidized and is donor of electrons and reducing agent, and oxygen is acceptor of electrons and oxidizing agent.

There are two basic types of redox notation:
First of them is *redox potential*, Eh [V], which is expressed with respect to hydrogen electrode. However, it is generally measured with respect to a different electrode (kalomel electrode etc.) and measured values have to be corrected for hydrogen electrode. The correction for kalomel electrode and temperature 25°C is about 0.245 V. The *Nernst equation* describes the relation between redox potential and activities of a redox couple. For example, for redox couple of iron the equation is

$$Eh = Eh^0 + \frac{RT}{nF} \ln \frac{[Fe^{3+}]}{[Fe^{2+}]} \qquad Eh^0 = 0.77\ V \qquad 3.18$$

where Eh^0 is standard potential (from tables), n is number of transferred electrons, F is Faraday constant and terms in squared brackets are activities. The Eh^0 values for other redox reactions are in Appelo and Postma (1993).

Second type of notation is the *activity of electrons*, p*e*, notation. This is expressed in analogy with pH as $pe = -\log[e^-]$. However, in contrast to H^+, electrons cannot exist separately in a solution. Equation for iron redox couple is in this notation

$$pe = pe^0 + \ln \frac{[Fe^{3+}]}{[Fe^{2+}]} \qquad pe^0 = 13.0 \qquad 3.19$$

In this case, the manipulation of equation is simpler than in the case of the Eh notation because the equation can be treated as an ordinary equilibrium equation. Conversion between both notations is

$$Eh[V] = 0.059\ pe \qquad \text{for } 25°C \qquad 3.20$$

Different forms of the same element with different oxidation number can have completely different behavior (soluble Fe^{2+} compared to insoluble Fe^{3+}) and toxicity (very toxic Cr^{6+} compared to Cr^{3+} with low toxicity).

Thus, information about oxidation number is necessary in investigation of contaminated sites.

Determination of oxidation number can be done:

(a) Directly, by analytical determination on perfectly preserved (filtered and acidified in the field) sample. This determination has a priority.

(b) By splitting of total concentration, for example Fe_{total}, on the basis of field Eh value and the Nernst equation. This determination is problematic because the Eh value may correspond to the strongest redox couple (which is often, but not always, iron couple) and other redox couples may not be with the strongest couple at equilibrium. Especially poor is match between Eh and O_2/H_2O couple.

(c) By calculating Eh value from one redox couple like Fe^{2+}/Fe^{3+} and using the calculated Eh or pe value to determine concentration of second redox couple (for example, Mn^{2+}/Mn^{4+}) by splitting of total concentration. This approach suffers of the same problem as the application of field Eh, e.g., there frequently is a lack of equilibrium between different redox couples. In geochemical programs like PHREEQC it is possible to choose between all options mentioned above.

The Eh-pH diagrams: they are used for interpretation of contaminants behavior. An example of the Eh-pH diagram for iron is in Fig. 3.5. Key points are:

- The diagrams are constructed for specified concentrations of metals and anions (for example, Pb_{total} = 10^{-6} mol/L, S_{total} = 10^{-3} mol/L etc.). If there is a significant difference between specified concentrations and concentrations at a studied site, then boundary in the diagram have to be recalculated.
- They is assumption of equilibrium.
- Boundaries between fields indicate equal concentrations for aqueous species. This means that, for example, Fe^{2+} can be present at lower concentration in the Fe^{3+} field.
- In solid phase fields, the aqueous ions are present at very low concentrations. In the contrary, there is no presence of solid phase in dissolved species fields. When total concentration of a metal increases, the size of solid phase field also increases.

Redox sequence (also redox ladder): There is a natural sequence of redox reactions during oxidation of organic matter. Dissolved oxygen is consumed first and methane is generated last, Fig. 3.6. The sequence is: $O_2 \rightarrow NO_3^- \rightarrow Mn^{4+} \rightarrow Fe^{3+} \rightarrow SO_4^{2-} \rightarrow CH_4$. The sequence is based on free energy released at each redox reaction, which decreases from consumption of oxygen to methanogenesis. There is the same sequence

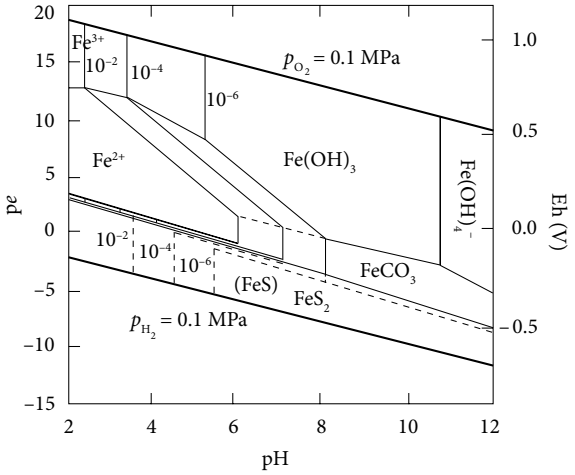


Fig. 3.5 The Eh-pH diagram for iron.

observed along a flow path in a pristine flow system, e.g., dissolved oxygen is generally found close to recharge area and methane, if present, at deep confined zone. When biodegradation of petroleum products occurs, electron acceptors are also consumed in the same order. In the case of sanitary landfills and dissolved petroleum products plumes, the sequence is reversed, e.g., methane is found close to (or directly in) a source zone (landfill or free phase zone) and dissolved oxygen is found at the periphery of a plume.

Problem: Ground water sample with pH about 7.0 has 5.0 mg/L of total iron and 160 mg/L of sulfate. Is there a possibility of significant concentrations of nitrate and methane?

Solution: Iron is present as Fe^{2+} at this pH range (Fe^{3+} precipitates as $Fe(OH)_3$), which is incompatible with nitrate. Iron comes from dissolution of $Fe(OH)_3$ after nitrate reduction. High sulfate concentration shows that there has not been a significant sulfate reduction. Thus, the sample does not already have nitrate and still does not have methane. There should be analysis for other metals (Pb, Zn etc.) generally adsorbed on $Fe(OH)_3$, which are generally released during reductive dissolution of $Fe(OH)_3$.

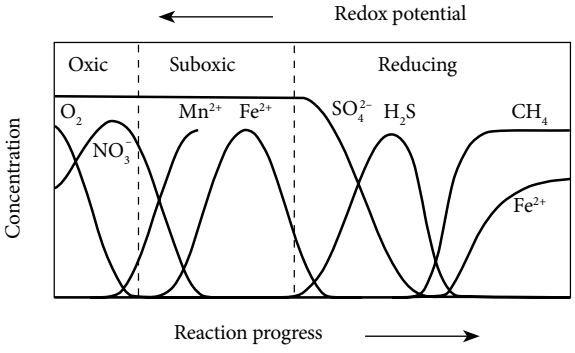


Fig. 3.6 Redox sequence of electron acceptors consumption.

3.5 Inorganic Adsorption

This section deals with adsorption of inorganic species. Adsorption of organics is treated in chapter about organic contamination. Adsorption refers to attachment of dissolved solids to surface of adsorbent (clay, hydroxide etc.), whereas absorption refers to penetration of dissolved solids into structure of an adsorbent. In many cases it is not possible to distinguish between both processes.

Clays have adsorption capacity relatively independent of pH. On the other hand, hydroxides and soil organic matter have adsorption capacity highly dependent on pH.

Clays have large specific surface, which generally has negative charge at close to neutral pH due to substitution of Si^{4+} and Al^{3+} in their crystal lattice by ions with lower valency.

Table 3.1 Properties of clay minerals (adapted from Deutsch, 1997).

Property/clay mineral	Montmorillonite	Illite	Kaolinite
Particle size [μm]	0.01–1.0	0.1–2.0	0.1–5.0
Ion substitution	high	intermediate	low
Surface [m^2/g]	600–800	100–120	5–20
CEC [meq/100g]	80–100	15–40	3–15

Cation exchange capacity (CEC): characterizes adsorption capacity for cations. It is determined by saturation of exchange sites by a cation (generally NH_4^+) and then by determination of its concentration after expulsion from exchange sites by other cation (Na^+ in concentrated solution of NaCl). Values of CEC are reported in meq/100 g of soil for specified pH (generally 7.0). Properties of clay minerals are in Table 3.1.

Montmorillonite has the largest specific surface and the highest CEC values, and kaolinite exhibits the lowest values. In the case of clays also occurs protonation of surface at low pH values and thus, adsorption capacity changes. However, bulk adsorption capacity of clay is pH-independent, for example, for montmorillonite it is about 90 % of total adsorption capacity.

Sand has low CEC values, generally less than 1 meq/100 g or less. However, even this value is by no means negligible.

Problem: Sand at Borden site in Ontario, Canada, has CEC equal to 0.5 meq/100 g. Calculate the amount of Na^+ which can be adsorbed, when grain density is 2.68 kg/dm^3 and porosity is 0.33.

Solution: 1 m^3 has 670 dm^3 of solids and 330 dm^3 of water, thus 1L of water is in contact with 670/330 = 2.03 dm^3 or 2.03 x 2.68 = 5.44 kg of solids, and this amount of solids can adsorb

54.4 x 0.5 = 27.2 meq of Na^+

which correspond to

27.2 x 22.99 = 625.33 mg/L

of Na^+ - this is more than usual Na^+ concentration in most ground waters.

Organic matter in solid phase (SOM-solid organic matter) plays an important role in adsorption of organic contaminants (see later), but also is important adsorbent for inorganic contaminants. This is related to deprotonation of carboxylic group –COOH and phenolic group –OH due to changes of pH, with resulting negative surface charge. Soil humus may have CEC up to 200 meq/100 g and can adsorb a significant fraction of metals like chromium (Nikolaidis et al., 1994). Appelo and Postma (1999) present an equation for calculation of CEC on the basis of both clay content and organic matter content:

$$\text{CEC[meq/100 g]} = 0.7\times(\%\ \text{clay}) + 3.5\times(\%\ \text{C})\ 3.21$$

The *ion exchange* comprises replacement of one species adsorbed on solid phase surface by another one present initially in solution. Cation exchange is generally much more important than anion exchange. Ions with higher charge are preferentially adsorbed, but ion exchange also depends on concentrations in solution. For example, Ca^{2+} has higher affinity for adsorption than Na^+ when dissolved concentrations are comparable, but Na^+ is more adsorbed than Ca^{2+} in sea water with much higher Na^+ concentrations. Adsorption affinity decreases in the sequence

$$Al^{3+} > Ca^{2+} > Mg^{2+} > K^+ > Na^+$$

When both charge and concentration of two ions are similar, then an ion with lower hydrated radius is preferred for adsorption. Hydrated radius is lower for ions with higher ion radius because in their case the ratio charge/ion radius is lower. Thus, Ca^{2+} has higher ion radius and lower hydrated radius than Mg^{2+} and is preferentially adsorbed.

There often are *colloids* (particles of size <1μm) in water. *Stern layer* with tightly held ions (generally cations) is close to surface of colloids and *Gouy layer* with mobile ions (cations still predominate) is further from surface, between Stern layer and bulk solution with the same concentrations of cations and anions. Stability of colloids depends on the thickness of the Gouy layer which in turn depends on ionic strength of solution.

When ionic strength increases, there is compression of the layer and flocculation of colloids (for example, during mixing of river water and sea water in estuaries).

In the case of Fe and Mn hydroxides the adsorption is strongly pH-dependent. When pH increases, there is de-protonation of surface,

$$\equiv SOH_2^+ \longleftrightarrow \equiv SOH^0 + H^+ \qquad 3.22$$

$$\equiv SOH^0 \longleftrightarrow \equiv SO^- + H^+ \qquad 3.23$$

and adsorbed ions also change surface charge of adsorbent, for example, in the case of Zn^{2+} adsorption we can write

$$\equiv SO^- + Zn^{2+} \longleftrightarrow \equiv SOZn^+ \qquad 3.24$$

In equations above, the sign ≡ indicates adsorption sites on solid phase and *S* indicates element in solid phase (in the case of ferric hydroxide it is Fe). When average charge at adsorbent surface is equal to zero, the numbers of positive and negative charge sites are equal and we can write that

$$\equiv SOH_2^+ \longleftrightarrow \equiv SO^- \qquad 3.25$$

Value of pH at the point is called pH_{ZPC} (pH of zero point of charge). Typical pH_{ZPC} values for different minerals are: clays 2.0 – 4.0, feldspars 2.0 – 2.5, $Fe(OH)_3$ 8.3, and calcite 8.4.

When pH of solution changes, there also is a change of electrostatic component of adsorption related to adsorption/desorption of H^+. This component of adsorption is expressed by coulombic (Boltzmann) term K_{coul},

$$K_{coul} = \exp\frac{-\Delta ZF\Psi}{RT} \qquad 3.26$$

where ΔZ is change of surface charge, *F* is Faraday constant, Ψ is surface potential, R is universal gas constant, and T is temperature. Bulk adsorption constant is a product of intrinsic (chemical) and coulombic constant:

$$K_{bulk} = K_{int} \times K_{coul} \qquad 3.27$$

At pH_{ZPC} the numbers of positively and negatively charged sites are identical, bulk surface charge is equal to zero, and, thus, $K_{bulk} = K_{int}$. When pH increases, negatively charged sites start to predominate, more cations are adsorbed and anions are desorbed (Fig. 3.7). This behavior is called *adsorption edge.*

However, it has to be emphasized that even at $pH < pH_{ZPC}$ some negatively charged sites exist, but they are less abundant than positively charges sites. Cations like Pb^{2+} are already adsorbed at pH much lower than pH_{ZPC} (for $Fe(OH)_3$ about 8.3), usually at $pH < 6.5$ because their concentrations in water are generally small and they have strong affinity for adsorption.

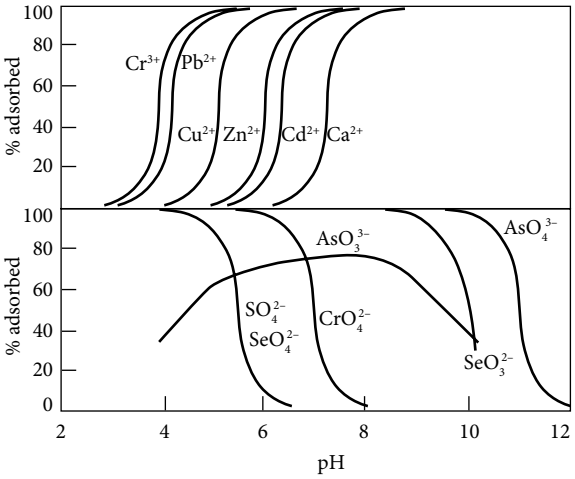


Fig. 3.7 Adsorption behavior of cations and anions (after Drever, 1997).

Modeling of adsorption

The most common approach is based on the application of adsorption isotherms. They are empirical (not true thermodynamic constants) determined from batch experiments. In batch experiment a flask with known quantity of water and solid phace is spiked with known concentration of contaminant and after equilibration (usually 24 hours) the partitioning between solid phase and water is determined. Adsorbed amount of contaminant (generally in mg/g) is plotted as a function of water concentration (usually in mg/L). Adsorbed amount is calculated as

$$S = \frac{\left(C_{equil} - C_{init}\right)V}{M} \qquad 3.28$$

where C_{equil} is equilibrium concentration, C_{init} is initial concentration, *V* is volume of water and *M* is mass of solid phase adsorbent.

Linear distribution coefficient K_d is determined as a slope in the graph $S = f(C)$.

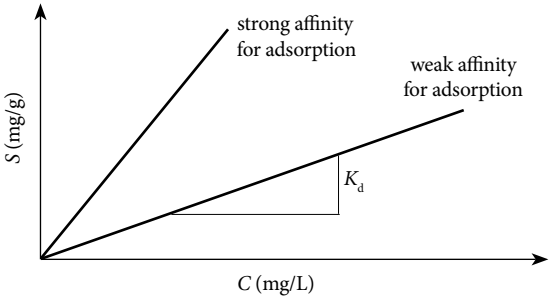


Fig. 3.8 Concept of linear adsorption isotherm K_d.

Principal problem of linear adsorption isotherm is related to the lack of limit for adsorption with increasing concentration in water. This is not correct because number of adsorption sites is limited and there is saturation of adsorption sites when concentration in water becomes too high.

Adsorption isotherm of Freundlich, expressed as

$$S = K_F \cdot C^N \qquad 3.29$$

takes into account decreasing adsorption with increasing concentration in water. The exponent N, which is generally < 1.0, changes the slope of straight line at higher concentrations in water. However, there is no maximum adsorption limit either. *Linear distribution coefficient* K_d is special case of the isotherm for $N = 1.0$.

Finally, *adsorption isotherm of Langmuir*, expressed as

$$S = \frac{S_{max} K_L C}{1 + K_L C} \qquad 3.30$$

where S_{max} is maximum amount of contaminant which can be adsorbed. When concentration in water is high, the product $K_L \times C >> 1$, we obtain $S = S_{max}$, which is asymptote of the graph $S = f(C)$ or adsorption limit.

Adsorption isotherms can be implemented into advection-dispersion equation (ADR) (see Chapter 7.7) and used to calculate *retardation factor* R (see section on transport), which is defined as

$$R = \frac{v_{water}}{v_{contam}} = 1 + \left(\frac{\rho_b}{n}\right)\frac{dS}{dC} \qquad 3.31$$

where v_{water} is velocity of ground water flow (or a conservative, non-adsorbed tracer migration) and $v_{contaminant}$ is velocity of adsorbed contaminant migration. Retardation factor for different isotherms is (Fetter, 1999):
a) linear isotherm:

$$R = 1 + \left(\frac{\rho_b}{n}\right) K_d \qquad 3.32$$

b) Freundlich isotherm

$$R = 1 + \left(\frac{\rho_b}{n}\right) K_F N C^{N-1} \qquad 3.33$$

c) Langmuir isotherm:

$$R = 1 + \left(\frac{\rho_b}{n}\right)\frac{K_L S_{max}}{(1 + K_L C)^2} \qquad 3.34$$

Note in the equations above that retardation factor R is constant for linear isotherm, but it is function of concentration for Freundlich and Langmuir isotherms! This behavior has very serious consequences for remediation of contaminated soils (see later).

We have discussed so far isotherms describing adsorption of only one ion on solid phase. *Selectivity coefficient* describes exchange between two ions in reaction expressed, for example, as

$$2\ \text{A-clay} + B^{2+} \longleftrightarrow \text{B-clay} + 2\ A^{+} \qquad 3.35$$

with selectivity coefficient (equilibrium constant) $K_{A\text{-}B}$. Selectivity coefficient $K_{A\text{-}B}$ just like adsorption isotherms is not a real thermodynamic constant because there is no thermodynamic description of adsorbed ions behavior. Values are also valid for specified pH and water chemistry.

Problem: Calculate fractions of adsorption sites occupied by Na^+ and Ca^{2+}, when concentrations in water are for both species 10^{-3} mol/L and $K_{Na\text{-}Ca}$ is equal to 1.0.

Solution: equation of reaction is

$$2\ \text{Na-clay} + Ca^{2+} = \text{Ca-clay} + 2Na^{+} \qquad K_{Na\text{-}Ca} = 1.0$$

then

$$\frac{X_{Ca\text{-clay}}}{X^2_{Na\text{-clay}}} = K_{Na\text{-}Ca}\frac{m_{Ca^{2+}}}{m^2_{Na^+}}$$

where X is molar fraction adsorbed on clay, for example

$$X_{Ca\text{-clay}} = \frac{\text{Ca-clay}}{\text{Ca-clay} + \text{Na-clay}}$$

and $X_{Ca\text{-clay}} + X_{Na\text{-clay}} = 1.0$, after substitution

$$\frac{1 - X_{Na\text{-clay}}}{X^2_{Na\text{-clay}}} = 1 \times \frac{10^{-3}}{10^{-6}}$$

which results in quadratic equation with solution $X_{Na\text{-clay}} = 0.03$, $X_{Ca\text{-clay}} = 0.97$.

In the problem above we can see that in the case of the same concentrations in water Ca^{2+} is preferentially adsorbed. However, in water with high Na^+ concentrations there is much more Na^+ adsorbed on solid phase than Ca^{2+}. Applications of selectivity coefficient are disscused in Appelo and Postma, (1999). In Table 3.2, there are selectivity coefficients for cation exchange with Na^+,

$$Na^+ + 1/i\ I\text{-}X_i = Na\text{-}X + 1/i\ I^{i+} \qquad 3.36$$

where X represents X fraction of ion I on adsorption sites, and i is charge of the ion.

The notation in the Equation 3.36. is called Gaines-Thomas notation. There are other types of notation (Gapon, Vanselow), discussed in Appelo and Postma, (1999).

Table 3.2 Selectivity coefficients (Appelo and Postma, 1999) .

Ion I^+	$K_{Na/I}$	Ion I^{2+}	$K_{Na/I}$
Li^+	1.2 (0.95–1.2)	Mg^{2+}	0.50 (0.4–0.6)
K^+	0.2 (0.15–0.25)	Ca^{2+}	0.40 (0.3–0.6)
NH_4^+	0.25 (0.2–0.3)	Sr^{2+}	0.35 (0.3–0.6)
Rb^+	0.10	Ba^{2+}	0.35 (0.3–0.6)
Cs^+	0.08	Fe^{2+}	0.6
		Cu^{2+}	0.5
		Zn^{2+}	0.4 (0.3–0.6)
Ion I^{3+}	$K_{Na/I}$	Cd^{2+}	0.4 (0.3–0.6)
Al^{3+}	0.6(0.5–0.9)	Pb^{2+}	0.3

Modeling of surface complexation, which takes into account changes in surface layer of adsorbent due to changes of pH and water chemistry, is beyond the scope of this text. We will mention briefly double diffuse layer (DDL) model as it is used in code MINTEQA2 (Allison et al., 1991). The model is based on adsorption on hydrous ferric hydroxide (HFO) with composition of goethite, molecular weight of 89 g/mol, surface area of 600 m^2/g, and number of adsorption sites 0.2mol/mol HFO. It is possible to change these parameters. In some cases (adsorption of trace metals) second type of adsorption sites with number of 0.005 mol/mol HFO is included.

The following procedure is used:

a) After water chemistry input open adsorption menu and choose diffuse double layer model. Enter concentration of Fe^{3+} converted to HFO as Fe^{3+} [g/L] × 1.589.
b) Enter specific surface in [m^2/g], which is 600 m^2/g for freshly precipitated HFO, but is lower for older precipitates.
c) Enter concentration of adsorption sites in [mol of sites/L], which is 0.2 mol sites/mol HFO × concentration of HFO [mol HFO/L].
d) Then append file feo-dlm.dbs, which is data base including chemical adsorption constants and run the program.

It is possible to use so called sweep option in MINTEQA2 with step-wise change of pH to determine adsorption edge for a metal.

Problem: (from Langmuir, 1997): Calculate using sweep option adsorption of zinc in pH interval 4.0–8.5 with step 0.5. Concentration of HFO is $C_s = 8.9\times10^{-2}$ g/L, concentration of zinc is 10^{-6} mol/L, surface area of HFO = 600 m^2/g, and adsorption sites density is $\Gamma = 2\times10^{-4}$ activ. sites/L.

Solution: See table of surface speciation and adsorption of Zn. It is evident that surface charge (second column) becomes negative between pH 8.0 and 8.5, but adsorption of zinc is already finished below pH of 7.0, where bulk surface charge is still positive.

Table 3.3 Surface speciation of HFO and adsorption of zinc (from Langmuir, 1997).

	ψ	σ	$(FeOH_2^+)$	(FeOH)	(FeO^-)	$(FeOZn^+)$	% Zn
pH	volts	C/m^2	M	M	M	M	adsorbed
4.0	0.184	0.212	–3.93	–4.10	–5.9	–8.43	0.4
4.5	0.169	0.158	–4.04	–3.97	–5.54	–7.56	2.8
5.0	0.152	0.112	–4.14	–3.90	–5.26	–6.76	17.5
5.5	0.132	0.0763	–4.30	–3.85	–5.05.	–6.21	61.4
6.0	0.110	0.0496	–4.41	–3.83	–4.90	–6.03	92.5
6.5	0.0865	0.0305	–4.49	–3.82	–4.79	–6.00	99.0
7.0	0.0609	0.0174	–4.56	–3.82	–4.72	–6.00	99.9
7.5	0.0341	0.0084	–4.60	–3.82	4.67	–6.00	100.0
8.0	0.00066	0.0015	–4.64	–3.82	–4.63	–6.00	100.0
8.5	–0.02100	–0.0049	–4.67	–3.82	–4.60	–6.00	100.0

Note: Listed are the surface potential (ψ) and surface charge (σ), and molar concentrations of surface species.

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Chapter 4: Carbonate System

4.1 Introduction

Water continually transforms the surface of the Earth, through interaction with the solid surface and transport of dissolved and suspended matter. One of the most important systems, which affect water quality, is carbonate system. Beyond that, carbonate system represents tight interconnection between inorganic and organic systems, and ensure the stable conditions for the latter. Aquatic carbonate geochemistry is therefore the principal concern of many geochemists and geologist.

In this chapter, the tools of thermodynamics will be applied to water carbonate systems. There will be developed methods for predicting the carbonate species present in water at equilibrium. Then there will be examined the interactions of solutions with solids through precipitation and dissolution.

Most reactions of carbonate system in aqueous solutions can be placed in one of the following categories:

- Acid-base reactions (e.g. dissociation of carbonic acid)

  $H_2CO_3 \longleftrightarrow H+ + HCO_3^-$
- Dissolution/Precipitation (e.g. dissolution of calcite)

  $CaCO_3(\text{calcite}) \longleftrightarrow Ca^{2+} + CO_3^{2-}$
- Adsorption/Desorption (e.g. adsorption of metal on a carbonate surface)

  $\equiv S + M^{2+} \longleftrightarrow =S–Mn$

  (where ≡S indicates the surface of the carbonate).
- Complexation (e.g. complexation of uranyl ion):

  $UO_2^{2+} + 2\ CO_3^{2-} \longleftrightarrow [UO_2(CO_3)_2]^{2-}$

In this chapter, we will consider the first two reactions in detail. Basic principles of adsorption/desorption were already introduced in Chapter 3.5.

4.2 Acid-base Reactions in Carbonate System

The hydrogen and hydroxide ions often participate in all the foregoing reactions. As a result, many of these reactions are pH dependent. In order to characterize the state of an aqueous solution, e.g., to determine how much $CaCO_3$ a solution will dissolve, the first step is usually to determine pH. On a larger scale, weathering of limestone and precipitation of carbonates in sediments depend critically on pH. Thus pH is sometimes called the master variable. While pH represents the hydrogen ion activity, or proton concentration, the hydroxide ion concentration can be easily calculated from pH since the proton and hydroxide concentrations are related by the dissociation constant for water, i.e., by:

$$H_2O \longleftrightarrow H^+ + OH^- \qquad K_W = a_H\, a_{OH} \qquad 4.1$$

The value of K_W, like all equilibrium constants, depends on temperature, but is about 10^{-14} at 25°C.

The strength of an acid or base is measured by its tendency to donate or accept protons. The dissociation constant for an acid or base is the quantitative measure of this tendency and thus is a good indication of its strength. For example, dissociation of HCl:

$$HCl \longleftrightarrow H^+ + Cl^-$$

has a dissociation constant

$$K_{HCl} = \frac{a_{H^+} a_{Cl^-}}{a_{HCl}} = 10^3$$

HCl is a strong acid because only about 3% of the HCl molecules added will remain undissociated. The equilibrium constant for dissociation of hydrogen sulfide:

$$H_2CO_3 \longleftrightarrow H^+ + HCO_3^-$$

is

$$K_{H_2CO_3} = \frac{a_{H^+} a_{HCO_3^-}}{a_{H_2CO_3}} = 10^{-6.35}$$

Thus H_2CO_3 is a weak acid because very few of the H_2CO_3 molecules actually dissociate except at high pH.

Most protons released by an acid will complex with water molecules to form hydronium ions, H_3O^+ or even $H_5O_2^+$. However, in almost all cases we need not concern ourselves with this and we can treat the H^+ ion as if it were a free species. Thus we will use $[H^+]$ to indicate the concentration of $H^+ + H_3O^+ + H_5O_2^+$.

4.2.1 Proton Accounting, Charge Balance, and Conservation Equations

4.2.1.1 Proton Accounting

Knowing the pH of an aqueous system is the key to understanding it and predicting its behavior. This requires a system of accounting for the H^+ and OH^- in the system. One approach is the Proton Balance Equation. In this system, both H^+ and OH^- are considered components of the system, and the proton balance equation is written such that the concentration of all species whose formation through reaction with water caused the production of OH^- are written on one side, and the concentration of all species whose formation through reactions with water caused the production of H^+ are written on the other side. Because water dissociates to form H^+ and OH^-, $[H^+]$ always appears on the left side (because one OH^- will have been produced for every H^+ produced by dissociation of water) and OH^- always appears on the right side of the proton balance equation (because one $H^+$is produced for every OH^- produced). The proton balance equation for pure water is thus:

$$[H^+] = [OH^-] \qquad 4.2$$

In pure water the concentrations of H^+ and OH^- are equal.

Now, consider the example of a carbonic acid solution. H^+ will be generated both by dissociation of water and dissociation of carbonic acid:

$$H_2CO_3 \longleftrightarrow H^+ + HCO_3^-$$

Since one HCO_3^- ion is generated for every H^+, and one CO_3^{2-} ion is generated for two H^+ ions, the proton balance equation becomes:

$$[H^+] = [OH^-] + [HCO_3^-] + 2\,[CO_3^{2-}] \qquad 4.3$$

An alternative approach to the proton balance equation is the TOT_H proton mole balance equation. In this system, H^+ and H_2O are always chosen as components of the system but OH^- is not. The species OH^- is the algebraic sum of H_2O less H^+:

$$[OH^-] = [H_2O] - [H^+] \qquad 4.4$$

Because aquatic chemistry almost always deals with dilute solutions, the concentration of H_2O may be considered fixed at a mole fraction of 1, or 55.4 M. Thus H_2O is made an implicit component, i.e., its presence is assumed by not written, so that equation 4.4 becomes:

$$[OH^-] = - [H^+] \qquad 4.5$$

The variable TOT_H is the total amount of component H^+, rather than the total of species H^+. Because we create the species OH^- by subtracting component H^+ from component H_2O, the total of component H^+ for pure water will be:

$$TOT_H = [H^+] - [OH^-]$$

The TOT_H in this case is the difference between the concentrations of H^+ and OH^-. Now consider the dissolution of CO_2 in water to form carbonic acid:

$$CO_2 + H_2O \longleftrightarrow H_2CO_3 \qquad 4.6$$

Under the normal conditions of pH, this carbonic acid will dissociate to form bicarbonate ion:

$$H_2CO_3 \longleftrightarrow H^+ + HCO_3^- \qquad 4.7$$

In our system of accounting, we would choose CO_2 as a component. The carbonic acid species would then be made from:

$$H_2CO_3 = H_2O + CO_2$$

The bicarbonate ion would be made from components CO_2, H_2O, and H^+:

$$HCO_3^- = CO_2 + H_2O - H^+$$

Thus in the proton mole balance equation, bicarbonate ion would count negatively, so TOT_H is:

$$TOT_H = [H^+] - [OH^-] - [HCO_3^-] \quad 4.8$$

We could have combined reactions 4.6 and 4.7 to write:

$$CO_2 + H_2O \longleftrightarrow H^+ + HCO_3^-$$

4.2.1.2 Charge Balance

Solutions are electrically neutral. This means that the number of positive and negative charges must balance:

$$\Sigma\, m_i z_i = 0 \quad 4.9$$

where m_i is the number of moles of ionic species *i* and z_i is the charge of species *i*. Equation 4.9 is known as the charge balance equation. This equation provides an important constraint on the composition of a system. In some cases, the proton balance and charge balance equations are identical.

For each acid-base reaction an equilibrium constant expression may be written. By manipulating these equilibrium constant expressions as well proton balance, charge balance, and mass balance equations, it is possible to predict the pH of any solution. In natural systems where there are many species present, however, solving these equations can be a complex task. An important step in their solution is to decide which reactions have an insignificant effect on pH and can be neglected.

4.2.1.3 Conservation Equations

A further constraint on the composition of a system is provided by mass balance. Acid-base reactions will not affect the total concentration of a substance. Regardless of reactions 4.6 and 4.7, and any other reactions, the total concentration of carbonate species remains constant. Thus we may write:

$$\Sigma\, c_T = [CO_2] + [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}] + ...$$

We can write one mass balance, or conservation, equation for each component in solution. Mass balance equations are useful for those components forming more than one species.

While the charge balance constraint is an absolute one and always holds, mass balance equations can be trickier because other processes, such a redox, precipitation, and adsorption, can affect the concentration of a species. We sometimes can get around this problem by writing the mass balance equation for an element, since an elemental concentration is not changed by redox processes. We might also define our system such that it is closed to get around the other problems. Despite these restrictions, mass balance often provides a useful additional constraint on a system.

Problem: Write the proton, proton mass balance, and charge balance, and carbonate conservation equations for a solution prepared by dissolving Na_2CO_3 in water. Assume that Na_2CO_3 dissociates completely and that the system is closed.

Answer: We begin with the proton balance equation. From the dissociation of water we have:

$$[H^+] = [OH^-]$$

In addition to this, hydroxide ions will also be generated by reaction between CO_3^{2-} and water:

$$CO_3^{2-} + H_2O \longleftrightarrow HCO_3^- + OH^-$$

$$HCO_3^- + H_2O \longleftrightarrow H_2CO_3 + OH^-$$

Since for each HCO_3^- formed, one OH^- must have formed and for each H_2CO_3 present two OH^- must have formed, the proton balance equation is:

$$[H^+] + [HCO_3^-] + 2[H_2CO_3] = [OH^-]$$

Choosing the carbonate and sodium ions as components (in addition to H^+ and H_2O), the bicarbonate and carbonic acid species are combinations of carbonate and one and two, respectively, protons, so that the proton mole balance equation is:

$$TOT_H = [H^+] + [HCO_3^-] + 2[H_2CO_3] - [OH^-]$$

Alternatively, we could chose CO_2 (in addition to H^+, H_2O and Na^+) as our forth component, rather than carbonate ion. In this case, the three carbonate species are made from components as follows:

$$H_2CO_3 = H_2O + CO_2$$
$$HCO_3^- = H_2O + CO_2 - H^+$$
$$CO_3^{2-} = H_2O + CO_2 - 2H^+$$

In this case, the proton mole balance equation is:

$$TOT_H = [H^+] - [HCO_3^-] - 2\,[CO_3^{2-}] - [OH^-]$$

Here we see that TOT_H depends on how we define our components. The charge balance equation is:

$$[H^+] + [Na^+] = [OH^-] + [HCO_3^-] + 2[CO_3^{2-}]$$

The conservation equation for carbonate species is:

$$\Sigma\, CO_3 = [CO_3^{2-}] + [HCO_3^-] + [H_2CO_3]$$

4.2.3 The Carbonate System

Water at the surface of the Earth inevitably contains dissolved CO_2, either as a result of equilibration with the atmosphere or because of respiration by organisms. CO_2 reacts with water to form carbonic acid:

$$CO_2 + H_2O \longleftrightarrow H_2CO_3 \qquad 4.10$$

Some of the carbonic acid dissociates to form bicarbonate and hydrogen ions:

$$H_2CO_3 \longleftrightarrow H^+ + HCO_3^- \qquad 4.11$$

Some of the bicarbonate will dissociate to an additional hydrogen ion and a carbonate ion:

$$HCO_3^- \longleftrightarrow H^+ + CO_3^{2-} \qquad 4.12$$

We can write three equilibrium constant expressions for these reactions:

$$K_{sp} = \frac{a_{H_2CO_3}}{p_{CO_2}} \qquad 4.13$$

$$K_1 = \frac{a_{H^+} a_{HCO_3^-}}{a_{H_2CO_3}} \qquad 4.14$$

$$K_2 = \frac{a_{H^+} a_{CO_3^{2-}}}{a_{HCO_3^-}} \qquad 4.14$$

The equilibrium constants for these reactions are given in Table 4.1 as a function of temperature.

In the above series of reactions, we have assumed that dissolved CO_2 reacts completely with water to form H_2CO_3. This is actually not the case, and much of the dissolved CO_2 will actually be present as distinct molecular species, $CO_2(aq)$. Thus reaction 4.10 actually consists of the two reactions:

$$CO_2(g) + H_2O \longleftrightarrow CO_2(aq) \qquad 4.10a$$

$$CO_2(aq) + H_2O \longleftrightarrow H_2CO_3 \qquad 4.10b$$

The equilibrium for the second reaction favors $CO_2(aq)$. However, it is analytically difficult to distinguish between the species $CO_2(aq)$ and H_2CO_3. For this reason, $CO_2(aq)$ is often combined with H_2CO_3 when representing the aqueous species. The combined total concentration of $CO_2(aq) + H_2CO_3$ is written as $H_2CO_3^*$. We will write it simply as H_2CO_3.

The importance of the carbonate system is that by dissociating and providing hydrogen ions to solution, or associating and taking up free hydrogen ions, it controls the pH of many natural waters. *Problem* shows that pure water in equilibrium with atmospheric

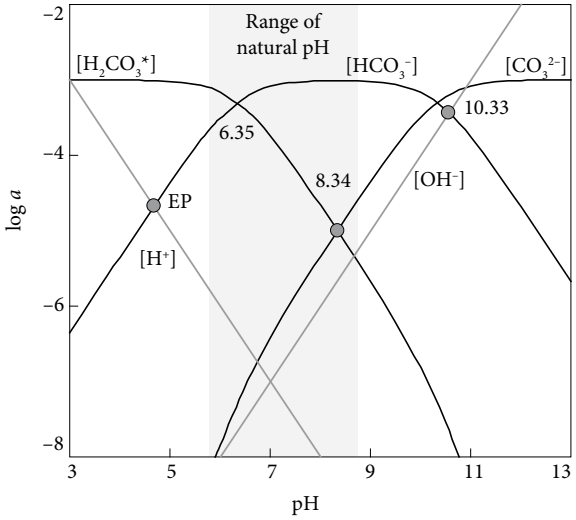


Figure 4.1. Activities of different species in the carbonate system as a function of pH assuming $\Sigma CO_2 = 10^{-3}$.

Table 4.1. Equilibrium constants for the carbonate system.

T (°C)	pK_{CO2}	pK_1	pK_2	pK_{cal}	pK_{arag}	$K_{CaHCO3+}$*	pK_{CaCO30}†
0	1.11	6.58	10.63	8.38	8.22	−0.82	−3.13
5	1.19	6.52	10.55	8.39	8.24	−0.90	−3.13
10	1.27	6.46	10.49	8.41	8.26	−0.97	−3.13
15	1.34	6.42	10.43	8.43	8.28	−1.02	−3.15
20	1.41	6.38	10.38	8.45	8.31	−1.07	−3.18
25	1.47	6.35	10.33	8.48	8.34	−1.11	−3.22
30	1.52	6.33	10.29	8.51	8.37	−1.14	−3.27
45	1.67	6.29	10.20	8.62	8.49	−1.19	−3.45
60	1.78	6.29	10.14	8.76	8.64	−1.23	−3.65
80	1.90	6.34	10.13	8.99	8.88	−1.28	−3.92
90	1.94	6.38	10.14	9.12	9.02	−1.31	−4.05

* $K_{CaHCO3+} = a_{CaHCO3+} / (a_{Ca2+}\, a_{HCO3-})$
† $K_{CaCO30} = a_{CaCO30} / (a_{Ca2+}\, a_{CO32-})$

CO_2 will be slightly acidic. The production of free H^+ ions as a result of the dissolution of CO_2 and dissociation of carbonic acid plays an extremely important role is weathering. Natural waters with a pH equal to or greater than 7 must contain cations other than H^+.

Problem: What is the pH of water in equilibrium with the atmospheric CO_2 at 25°C, assuming ideal behavior and no other dissolved solids or gases present? The partial pressure of CO_2 in the atmosphere is 3.5×10^{-4}.

Solution: In this case, the proton balance and charge balance equations are identical:

$$[H^+] = [OH^-] + [HCO_3^-] + [CO_3^{2-}]$$

We might guess that the pH of this solution will be less than 7 (i.e., $[H^+] \geq 10^{-7}$). Under those circumstances, the concentrations of the hydroxyl and carbonate ions will be much lower than that of the hydrogen and bicarbonate ions. Assuming we can neglect them, our equation then becomes simply:

$$[H^+] = [HCO_3^-]$$

We can combine equations 4.13 and 4.14 to obtain an expression for bicarbonate ion in terms of the partial pressure of CO_2:

$$[HCO_3^-] = K_1 K_{CO2} p_{CO2} / [H^+]$$

Substituting this into previous equation and rearranging, we have:

$$[H^+]^2 \longleftrightarrow K_1 K_2 K_{CO2} p_{CO2}$$

Taking the negative log of this expression and again rearranging, we obtain:

$$pH = (- \log K_1 - \log K_2 - \log p_{CO2}) / 2$$

Substituting values from Table 4.1, we calculate pH = 5.64. Looking at Figure 4.1, we can be assured that our assumption that carbonate and hydroxyl ion abundances are valid. Indeed, an exact solution using the Solver in Excel™ differs from the approximate one by less than 0.0001 pH units.

Ground water may not be in equilibrium with the atmosphere, but will nonetheless contain some dissolved CO_2. Because of respiration of organisms in soil (mainly plant roots and bacteria) through which they pass before penetrating deeper, ground water often contains more CO_2 than water in equilibrium with the atmosphere. In addition, calcite and other carbonates are common minerals in soils and in sedimentary, metamorphic, and altered igneous rocks. Ground water will tend to approach equilibrium with calcite by either dissolving it or precipitating it:

$$CaCO_3 \longleftrightarrow Ca^{2+} + CO_3^{2-} \qquad 4.16$$

Carbonate ions produced in this way will associate with hydrogen ions to form bicarbonate as in reaction 4.12, increasing the pH of the solution. Water containing high concentrations of calcium (and magnesium) carbonate is referred to as 'hard water'. Such waters are generally somewhat alkaline.

Now suppose we have a known activity of all carbonate species in solution, say for example 10^{-2}:

$$a_{H_2CO_3} + a_{HCO_3^-} + a_{CO_3^{2-}} = \sum CO_2 = 10^{-2} \qquad 4.17$$

From this, and the dissociation constants, we can calculate the amount of each species present as a function of pH and temperature. For example, we can use the equilibrium constant expressions to obtain substitutions for the carbonic acid and carbonate ion activities in equation 4.17 that are functions of bicarbonate ion activity and pH. We then solve Equation 4.17 to obtain an expression for the activity of the bicarbonate ion as a function of total CO_2 and hydrogen ion activity:

$$a_{HCO_3^-} = \frac{\sum CO_2}{\frac{a_{H^+}}{K_1} + 1 + \frac{K_2}{a_{H^+}}} \qquad 4.18$$

Similar equations may be found for carbonic acid and carbonate ion. Carrying out these calculations at various pH, we can construct the graph shown in Figure 4.1. In this figure, we see that carbonic acid is the dominant species at low pH, bicarbonate at intermediate pH, and carbonate at high pH.

Particularly simple relationships occur when the activities of two species are equal. For example, choosing pH to be 4.35 (at 25°C) we can rearrange equation 4.14 and substitute to obtain:

$$\frac{a_{H^+}}{K_1} = \frac{a_{H_2CO_3}}{a_{HCO_3^-}} = \frac{10^{-6.35}}{10^{-6.35}} = 1 \qquad 4.19$$

The activity of the carbonate ion will be very low at this pH. If we ignore it, equ. 4.17 becomes:

$$a_{H_2CO_3} + a_{HCO_3^-} \cong 10^{-2}$$

According to Equation 4.19, the activities of both species are equal, so each must be 5×10^{-3}.

Now consider the point where the hydrogen ion concentration equals the bicarbonate ion concentration. At this point, the concentration of the carbonate ion is extremely low, and there is exactly enough H^+ to convert all HCO_3^- to H_2CO_3. From the perspective of the proton balance then, the HCO_3^- concentration is equivalent to the same concentration of H_2CO_3. This point, labeled EP on Figure 4.1, is called the CO_2 equivalence point. In a similar way, the point where the carbonic acid and carbonate ion concentrations are equal is called the bicarbonate equivalence point, and that where bicarbonate and hydroxyl concentrations are equal is called the carbonate equivalence point. The pH of these equivalence points depends, among other things, on the $\Sigma\ CO_2$ concentration.

The exact concentrations of carbonate species depends on total carbonate concentration as well as the concentration of other ions in solution. Thus the distribution shown in Figure 4.1 is unique to the conditions specified ($c_T = 10^{-2}$, no other ions present). Nevertheless, the distribution will be qualitatively similar for other conditions.

Problem: A groundwater moving through soil into a deep aquifer acquires a total dissolved CO_2 concentration of 10^{-2} M. Assuming the water does not exchange with surrounding rock, ideal behavior and no other dissolved solids or gases, what is the pH of the water?

Solution: In this case, our charge and proton balance equations are the same as in Example 4.2, i.e., Equation 4.26. Since the solution does not exchange with surrounding rock, it can be considered a closed system and we can write the following mass balance equation:

$$\Sigma\ CO_2 = [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}] = 10^{-2}$$

Simultaneously solving the change balance and mass balance equations, and using equilibrium constant expressions to eliminate carbonate and OH^- species, we obtain:

$$[H^+]^4 + K_1\,[H^+]^3 + \{K_1 K_2 - K_W - K_1\,\Sigma\ CO_2\}[H^+]^2$$

$$- \{K_W + 2\,K_2\,\Sigma\ CO_2\}K_1\,[H^+] - K_1\,K_2\,K_W = 0$$

We might again guess that the concentration of the carbonate ion will be very low, and that we can therefore neglect all terms in which K_2 occurs. We might also guess that pH will be acidic so that $[H^+] \gg [OH^-]$, and therefore that we can neglect terms containing K_W. Our equation becomes:

$$K_1^{-1}[H^+]^2 + [H^+] = \Sigma\ CO_2$$

Solving this quadratic equation, we find that pH = 4.18.

4.2.4 Conservative and Non-Conservative Ions

We can divide dissolved ions into conservative and non-conservative ones. The conservative ions are those whose concentrations are not affected by changes in pH, temperature, and pressure, assuming no precipitation or dissolution. In natural waters, the principal conservative ions are Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, SO_4^{2-} and NO_3^-. These ions are conservative because they are fully dissociated from their conjugate acids and bases over the normal range of pH of natural waters. Non-conservative ions are those that will undergo association and dissociation reactions in this pH range. These include the proton, hydroxide ion, and carbonate species as well as many inorganic and organic anions. Variations in the concentrations of non-conservative ions result from reactions between them, and these reactions can occur in the absence of precipitation or dissolution. For example, reaction of the carbonate and hydrogen ion to form bicarbonate will affect the concentrations of all three ions. Of course, if the system is at equilibrium, this reaction will not occur in the absence of an external disturbance, such as a change in temperature.

4.2.5 Total Alkalinity and Carbonate Alkalinity

Alkalinity is a measure of acid-neutralizing capacity of a solution and is defined as the sum of the concentration (in equivalents) of bases that are titratable with strong acid. Mathematically, we define alkalinity as the negative of TOT_H when the components are the principal components of the solution at the CO_2 equivalence point. The acidity can be defined as the negative of alkalinity, and hence equal to TOT_H.

Let us consider a solution containing a fixed total dissolved concentration of $CaCO_3$. At the CO_2 equivalence point, H_2CO_3 (or $CO_2(aq)$) is the principal carbonate species, so we chose our components as H^+, H_2O, CO_2, and Ca^{2+}. Species HCO_3^- and CO_3^{2-} are made by combining these components as follows:

$$HCO_3^- = H_2O + CO_2 - H^+$$

$$CO_3^{2-} = H_2O + CO_2 - 2H^+$$

The proton mole balance equation is then:

$$TOT_H = [H^+] - [HCO_3^-] - 2[CO_3^{2-}] - [OH^-] \quad 4.20$$

The alkalinity is then:

$$Alk = -TOT_H = -[H^+] + [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] \quad 4.21$$

This sum, $-[H^+] + [HCO_3^-] + 2[CO_3^{2-}] - [OH^-]$, is called the carbonate alkalinity. In this example, carbonate alkalinity and alkalinity are equal since there are no other ions in solution. To avoid confusion with carbonate alkalinity, alkalinity is sometimes called total alkalinity.

Now let's consider a somewhat more complex example, a solution that contains $H_3SiO_4^-$, $B(OH)_4^-$, and HS^-, and phosphoric acid (H_3PO_4 and dissociated species). This solution is similar to seawater. The corresponding components, the species actually present at the CO_2 equivalence point, are H_4SiO_4, $B(OH)_3$, H_2S, and $H_2PO_4^-$. Our expression for alkalinity is then (assuming negligible concentrations of S^{2-} and PO_4^{3-}):

$$Alk = -[H^+] + [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] + [B(OH)_4^-]$$
$$+ [H_3SiO_4^-] + [HS^-] + [H_2PO_4^-] + 2[HPO_4^{2-}] \quad 4.22$$

An analytical definition of alkalinity is that it is the quantity of acid that must be added to the solution to bring the pH to the CO_2 equivalence point.

We can also express alkalinity in terms of conservative and non-conservative ions. The charge balance equation, equation 4.9, could be written as:

$$\Sigma \text{ cations (in equivalents)} - \Sigma \text{ anions (in equivalents)} = 0 \quad 4.23$$

This can the be expanded to:

$$\Sigma \text{ conserv.cat} - \Sigma \text{ conserv.an} + \Sigma \text{ non-conserv.cat} - \Sigma \text{ non-conserv.an} = 0$$

all in units of equivalents)*. Rearranging, we have:

$$\Sigma \text{ conserv.cat} - \Sigma \text{ conserv.an} = -\Sigma \text{ non-conserv.cat} + \Sigma \text{ non-conserv.an} \quad 4.24$$

The right hand side of equation 4.20 is equal to the alkalinity. Hence we may write:

$$Alk = \Sigma \text{ conserv.cat} - \Sigma \text{ conserv.an} = -\Sigma \text{ non-conserv.cat} + \Sigma \text{ non-conserv.an} \quad 4.25$$

* One equivalent of a species is defined as the number of moles multiplied by the charge of the species. Thus one equivalent of CO_3^{2-} is equal to 0.5 moles of CO_3^{2-}, but one equivalent of Cl^- is equal to 1 mole of Cl^-. For an acid or base, an equivalent is the number moles of the substance divided by the number of hydrogen or hydroxide ions that can be potentially produced by dissociation of the substance. Thus there are 2 equivalents per mole of H_2CO_3, but 1 equivalent per mole of Na(OH).

This equation emphasizes an important point. The difference of the sum of conservative anions and cations is clearly a conservative property, i.e., they cannot be changed except by the addition or removal of components. Since alkalinity is equal to this difference, alkalinity is also a conservative quantity (i.e., independent of pH, pressure and temperature). Thus total alkalinity is conservative, though concentrations of individual species are not.

Problem: Calculate the alkalinity of spring water from Thonon, France, whose analysis is given in table.

Anions	mM	Cations	mM
HCO_3^-	5.436	Ca^{2+}	2.475
SO_4^{2-}	0.146	Mg^{2+}	0.663
NO_3^-	0.226	K^+	0.036
Cl^-	0.231	Na^+	0.223

Solution: We can use equation 4.22 to calculate alkalinity. All the ions listed here are conservative with the exception of HCO_3^-. To calculate alkalinity, we first need to convert the molar concentrations to equivalents; we do so by multiplying the concentration of each species by its charge. We find the sum of conservative anion concentrations to be 0.749 meq (milliequivalents), and that of the conservative cation concentrations to be 6.535 meq. The alkalinity is the difference, 5.786 meq.

4.2.5.1 Alkalinity Determination and Titration Curves

If the concentrations of all major conservative ions in a solution are known, the alkalinity can be simply calculated from equation 4.23. It is often useful, however, to determine this independently. This is done, as the definition of alkalinity suggests, through titration. Titration is the process of progressively adding a strong acid or base to a solution until a specified pH, known as an endpoint, is reached. In the case of the determination of alkalinity, this end point is the CO_2 equivalence point.

Consider a solution containing a certain concentration of sodium bicarbonate (Na_2CO_3). Because the carbonate ion can act as a proton acceptor, $NaCO_3^-$ is a base. We can determine both the alkalinity and the total carbonate concentration of this solution by titrating with a strong acid, such as HCl.

For simple solution, we make several simplifying assumptions. First, we assume ideal behavior. Second,

we assume the system is closed, so that all components are conserved, except for $[H^+]$ and $[Cl^-]$, which we progressively add. Third, we assume that the volume of our Na_2CO_3 solution is sufficiently large and our HCl sufficiently concentrated that there is no significant dilution of the original solution. Finally, we assume both Na_2CO_3 and HCl dissociate completely.

The charge balance equation during the titration is:

$$[Na^+] + [H^+] = [Cl^-] + [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] \qquad 4.26$$

Since the Cl^- concentration is conservative, it will be equal to the total amount of HCl added. Into Equation 4.26, we can substitute the following:

$$\left[HCO_3^-\right] = \frac{K_1\left[H_2CO_3\right]}{\left[H^+\right]} \qquad 4.27a$$

$$\left[CO_3^{2-}\right] = \frac{K_2K_1\left[H_2CO_3\right]}{\left[H^+\right]^2} \qquad 4.27b$$

$$\left[OH^-\right] = \frac{K_W}{\left[H^+\right]} \qquad 4.27c$$

Doing so and rearranging yields:

$$\left[Cl^-\right] = \left[Na^+\right] + \left[H^+\right] - \frac{K_1\left[H_2CO_3\right]}{\left[H^+\right]} - \frac{K_2K_1\left[H_2CO_3\right]}{\left[H^+\right]^2} - \frac{K_W}{\left[H^+\right]} \qquad 4.28$$

We may also write a conservation equation for carbonate species, which is the same as last equation in first Chapter 4 problem. Substituting Equations 4.27a and 4.27b into

$$\Sigma\, CO_3 = [CO_3^{2-}] + [HCO_3^-] + [H_2CO_3]$$

and rearranging, we have:

$$\left[H_2CO_3\right] = \frac{\sum CO_2}{1 + \frac{K_1}{\left[H^+\right]} + \frac{K_1K_2}{\left[H^+\right]^2}} \qquad 4.29$$

Substituting this expression into 4.28, we obtain:

$$\left[Cl^-\right] = \left[Na^+\right] + \left[H^+\right] - \frac{\sum CO_2}{\left[H^+\right] + K_1 + \frac{K_1K_2}{\left[H^+\right]}}\left\{K_1 - \frac{K_1K_2}{\left[H^+\right]}\right\} - \frac{K_W}{\left[H^+\right]} \qquad 4.30$$

From stoichiometry, we also know that $\Sigma\, CO_2 = [Na^+]$. From this equation we can construct a plot showing how many moles of HCl we must add to achieve a certain pH. We can also use Equation 4.27 and similar ones expressing the bicarbonate and carbonate ions as functions of pH to plot the change in the carbonate speciation during the titration. Figure 4.2 shows such a plot for a 0.005 M Na_2CO_3 solution. There are two regions where pH changes rapidly with small additions of HCl. These are the two end-points of the titration. Comparing the titration curve with the speciation curves, we see that the two end-points correspond to the CO_2 and bicarbonate equivalence points.

An analytical definition of alkalinity is its acid neutralizing capacity when the end-point of the titration is the CO_2 equivalence point (Morel and Hering, 1993). We had previously defined alkalinity as the negative of TOT_H when the principal components are those at the CO_2 equivalence point. Now let's show that these definitions are equivalent.

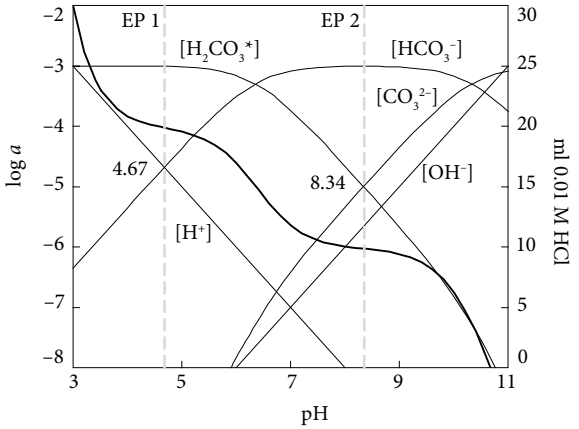


Figure 4.2. Titration curve (bold line) for 100 militer 0.001 M Na_2CO_3 solution titrated with 0.01 M HCl. Right axis shows the number of ml of HCl to be added to obtain a given pH. Also shown are the concentrations of carbonate species, H^+, and OH^- (thin lines, left axis gives scale).

Our TOT_H expression, written in terms of components at the CO_2 equivalence point, is identical to 4.20:

$$TOT_H = [H^+] - [HCO_3^-] - 2\,[CO_3^{2-}] - [OH^-] \qquad 4.20$$

and the charge balance equation (before any HCl is added) is:

$$[Na^+] + [H^+] = [HCO_3^-] + 2\,[CO_3^{2-}] + [OH^-] \qquad 4.9$$

Combining the two we have: $TOT_H = -[Na^+]$

Since the alkalinity is the negative of TOT_H, it follows that (before the addition of HCl):

$$Alk = [Na^+] \qquad 4.31$$

We obtain exactly the same result from Equation 4.25. It is easy to show that after titrating to the CO_2 equivalence point, the alkalinity is 0. The change in alkalinity is thus equal to the number of equivalents, or moles, of H^+ we have added to the solution.

Since at the end point, $[H^+] = [HCO_3^-]$ and the concentrations of CO_3^{2-} and OH^- are negligible, our charge balance equation, 4.26, reduces to:

$$[Na^+] = [Cl^-]$$

Comparing this with 4.29, we see that the alkalinity is equal to the amount of HCl added. In the example in Figure 4.2, the equivalence point occurs after the addition of 10 ml of 1M HCl, or a total of 0.01 moles of Cl^-. Notice that since at the end points, small additions of acid result in large changes in pH, we do not have to determine pH particularly accurately during the titration for an accurate determination of alkalinity. So the alkalinity is 0.01 equivalents. This is exactly the answer we obtain from 4.29 for 1 liter of 0.005 M Na_2CO_3 since there are 2 moles of Na^+ for each mole of Na_2CO_3.

By assuming that the concentration of H^+ contributes negligibly to charge balance, it is also easily shown (Example 4.2) that at the bicarbonate equivalence point:

$$\Sigma\, CO_2 = [Cl^-] + [OH^-] \qquad 4.32$$

Thus total carbonate is obtained by titrating to the bicarbonate equivalence point (knowing the pH of the end-point allows us to determine the $\Sigma\, CO_2$ exactly; however neglecting the $[OH^-]$ term in 4.30 results in only a 1% error in the example shown. In Figure 4.2, this occurs after the addition of 5 ml 1M HCl.

4.2.6 Buffer Intensity

The buffer intensity of a solution is defined as the inverse of change in pH per amount of strong base (or acid) added:

$$\beta = \frac{\mathrm{d}c_B}{\mathrm{d}\,\mathrm{pH}} = -\frac{\mathrm{d}c_A}{\mathrm{d}\,\mathrm{pH}} \qquad 4.33$$

where c_B and c_A are the concentrations, in equivalents, of strong base or acid respectively. The greater the buffer capacity of a solution, the less change in its pH as an acid or base is added. The buffer capacity of a solution can be calculated by differentiation of the equation relating base (or acid) concentration to pH, as is illustrated in following *Problem*.

In nature, a pH buffer acts to control pH within a narrow range as H^+ ions are added or removed from solution by other reactions. To understand how this works, imagine a solution containing carbonic acid, CO_3^{2-}, HCO_3^-, and H^+ ions in equilibrium concentrations. Now imagine that additional H^+ ions are added (for example, by addition of rain water containing HNO_3). In order for the right hand side of equation 4.19 to remain equal to K_1 despite an increase in the activity of H^+ (which it must at constant temperature and pressure), the bicarbonate activity must decrease and the carbonic acid activity increase. It is apparent then that reaction 4.11 must be driven to the left, taking free hydrogen ions from solution, hence driving the pH back toward its original value. Similarly, reaction 4.12, the dissociation of bicarbonate, will also be driven to the left, increasing the bicarbonate concentration and decreasing the hydrogen and carbonate ion concentrations.

The buffer capacity of the carbonate system depends strongly on pH and also on the concentration of the carbonate species and the concentration of other ions in solution. In pure water containing no other ions and only carbonate in amounts in equilibrium with the atmosphere, the buffering capacity is negligible near neutral pH, as is shown in Figure 4.4. Natural solutions, however, can have substantial buffering capacity. Figure 4.3 illustrates three examples of natural pH buffers. "Hard water" is an example of water with a substantial buffering capacity due to the presence of dissolved carbonates. How adversely lakes and streams are impacted by "acid rain" depends on their buffering intensity.

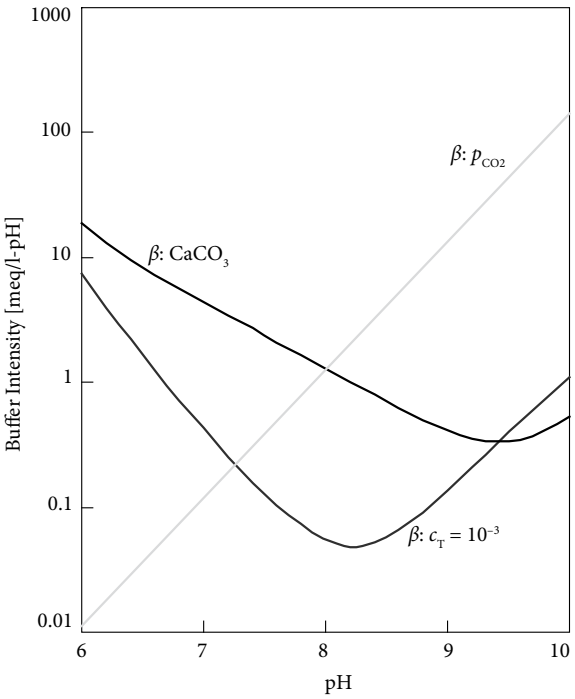


Figure 4.3. Buffer intensity as a function of pH for several ideal natural systems: β_{cT} fixed total dissolved CO_2, β_{pCO2} water in equilibrium with atmospheric CO_2, $\beta_{CaCO3(s)}$ water in equilibrium with calcite.

Problem: How will pH change for given addition of a strong base such as NaOH for a solution of pure water in equilibrium with atmospheric CO_2? Calculate the buffer intensity of this solution as a function of pH. Assume that NaOH completely dissociates and ideal behavior.

Solution: We want to begin with the charge balance equation in this case because it relates the two quantities of interest in this case, $[Na^+]$ and $[H^+]$. The charge balance equation is the same as in first Example:

$$[Na^+] + [H^+] = [OH^-] + [HCO_3^-] + 2[CO_3^{2-}]$$

Since Na^+ is a conservative ion, its concentration will depend only on the amount of NaOH added, so that $c_B = [Na^+]$. Substituting this into equation 4.9 and rearranging, we have:

$$c_B = [OH^-] + [HCO_3^-] + 2[CO_3^{2-}] - [H^+]$$

We can now use the equilibrium constant relations to substitute for the first three terms of the right hand side and obtain:

$$c_B = \frac{K_W + K_1 K_{sp} p_{CO_2}}{[H^+]} + 2\frac{K_2 K_1 K_{sp} p_{CO_2}}{[H^+]^2} - [H^+]$$

Using the relation pH = – log $[H^+]$ to replace $[H^+]$ in this equation with pH, we have:

$$c_B = \frac{K_W + K_1 K_{sp} p_{CO_2}}{10^{-pH}} + 2\frac{K_2 K_1 K_{sp} p_{CO_2}}{10^{-2pH}} - 10^{-pH}$$

Now differentiating with respect to pH, we obtain:

$$\frac{dc_B}{dpH} = \beta = \log\left\{\left(K_W + K_1 K_{sp} p_{CO_2}\right)\times 10^{pH} + \right.$$
$$\left. + 4K_2 K_1 K_{sp} p_{CO_2} 10^{2pH} + 10^{-pH}\right\}$$

Figure 4.4 shows a plot of this equation using the values in Table 4.1. Buffer intensity is negligible in neutral to slightly acidic conditions, but increases rapidly with pH.

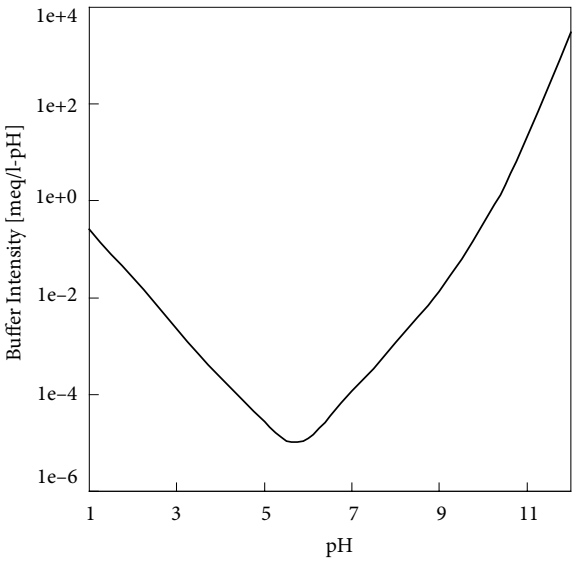


Figure 4.4. Buffer capacity of a carbonate solution in equilibrium with atmospheric CO_2.

4.3 Dissolution and Precipitation Reactions

4.3.1 Calcium Carbonate in Ground and Surface Waters

Calcium carbonate is a common component of sedimentary rocks and is found present in weathered igneous and metamorphic rocks. It is also a common constituent of many soils. Water passing through such soils and rocks will precipitate or dissolve calcite until equilibrium is achieved. This process has a strong influence on carbonate concentrations, hardness, and pH as well as dissolved calcium ion concentrations.

The solubility product of calcite is:

$$K_{sp\text{-}Cal} = a_{Ca^{2+}} a_{CO_3^{2-}} \qquad 4.34$$

This can be combined with Equations 4.13–15 to obtain the calcium concentration water in equilibrium with calcite as a function of p_{CO2}:

$$[Ca^{2+}] = p_{CO_2} \frac{K_1 K_{sp\text{-}Cal} K_{sp\text{-}CO_2}}{4K_2 \gamma_{Ca^{2+}} \gamma_{HCO_3^-}^2 [HCO_3^-]^2} \qquad 4.35$$

In a solution in equilibrium with calcite and a CO_2 gas phase and containing no other dissolved species, it is easy to modify equation 4.35 so that the calcium ion concentration is a function of p_{CO2} only. A glance at Figure 4.1 shows that we can neglect OH^-, H^+, and CO_3^{2-} if the final pH is less than about 9. The charge balance equation in this case reduces to:

$$2[Ca^{2+}] = [HCO_3^-] \qquad 4.36$$

Substituting this into 4.35, we obtain:

$$\left[Ca^{2+}\right] = p_{CO_2} \frac{K_1 K_{sp\text{-}Cal} K_{sp\text{-}CO_2}}{4K_2 \gamma_{Ca^{2+}} \gamma^2_{HCO_3^-} \left[Ca^{2+}\right]^2} \quad 4.37$$

or

$$\left[Ca^{2+}\right] = \left\{ p_{CO_2} \frac{K_1 K_{sp\text{-}Cal} K_{sp\text{-}CO_2}}{4K_2 \gamma_{Ca^{2+}} \gamma^2_{HCO_3^-}} \right\}^{1/3} \quad 4.38$$

There are two interesting aspects to this equation. First, the calcium ion concentration, and therefore calcite solubility, increases with increasing p_{CO2}. This might seem counter-intuitive at first, as one might think that increasing p_{CO2} should produce an increase the carbonate ion concentration and therefore drive the reaction toward precipitation. However, increasing p_{CO2} decreases pH, which decreases CO_3^{2-} concentration, and therefore drives the reaction towards dissolution. Second, calcium ion concentration varies with the one-third power of p_{CO2} (Figure 4.5). Because of this nonlinearity, mixing of two solutions, both of which are saturated in Ca^{2+} with respect to calcite, can result in the mixture being undersaturated with respect to Ca^{2+}. For example, consider the mixing of stream and ground water. Stream water is in equilibrium with the atmosphere for which p_{CO2} is $10^{-3.5}$. On the other hand, p_{CO2} in soils is often as high as 10^{-2}. So mixing between calcite-saturated groundwater and calcite-saturated surface water would produce a solution that is undersaturated with calcite.

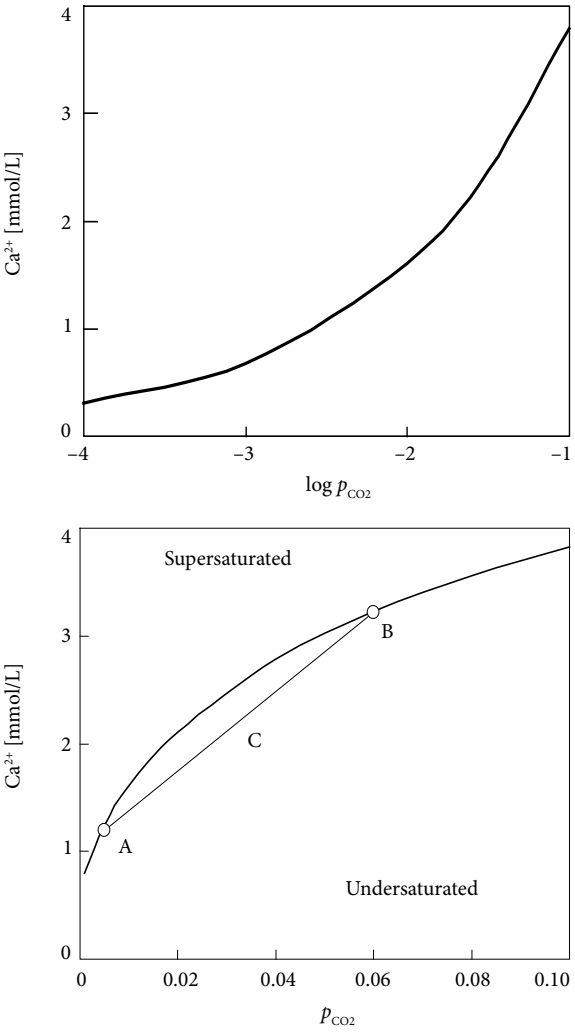


Figure 4.5. Concentration of calcium ion in equilibrium with calcite at 25°C and 1 atm as a function of p_{CO2}. After Drever (1988).

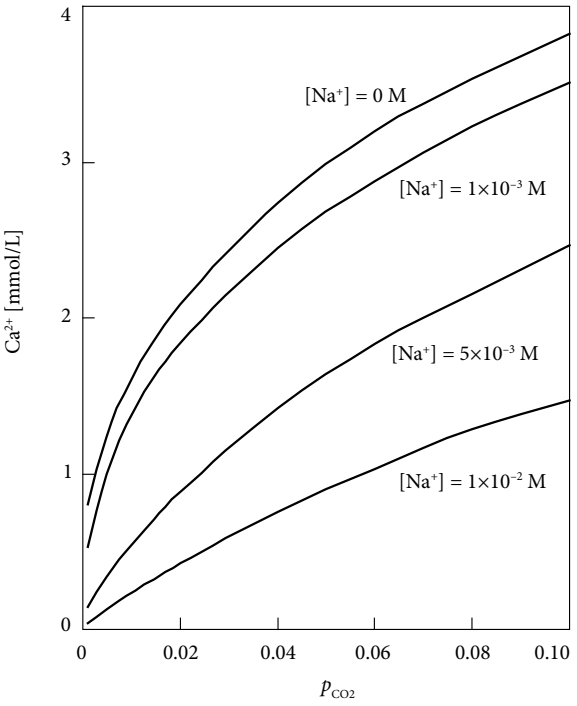


Figure 4.6. Concentration of calcium ion in a solution containing Na_2CO_3 in equilibrium with calcite at 25 °C and 0,1 MPa as a function of p_{CO2} and sodium concentration. After Drever (1988).

Calcite solubility is also affected by the presence of other ions in solution. Figure 4.6 illustrates the effect of sodium ion concentration on calcite solubility.

Equation 4.38 describes calcite solubility for a system open to exchange with gaseous CO_2. For a p_{CO2} of $10^{-3.5}$ (i.e., the atmosphere), this equation yields a calcium concentration of 1.39 mM. Water in pores and fractures in rocks does not exchange with a gas phase. Second *Problem* in this chapter shows that under those circumstances, less calcite will dissolve; in the case of $p_{CO2} = 10^{-2}$, calcite saturation is reached at only 0.33 mM, or about a fourth as much. The difference is illustrated in Figure 4.7, which is a plot of $[HCO_3^-]$ vs. pH. Systems in equilibrium with constant p_{CO2} (open systems) evolve along straight lines on this plot and ultimately reach calcite saturation at higher pH and lower $[HCO_3^-]$ (and $[Ca^{2+}]$) than closed systems that initially equilibrate with the same p_{CO2}.

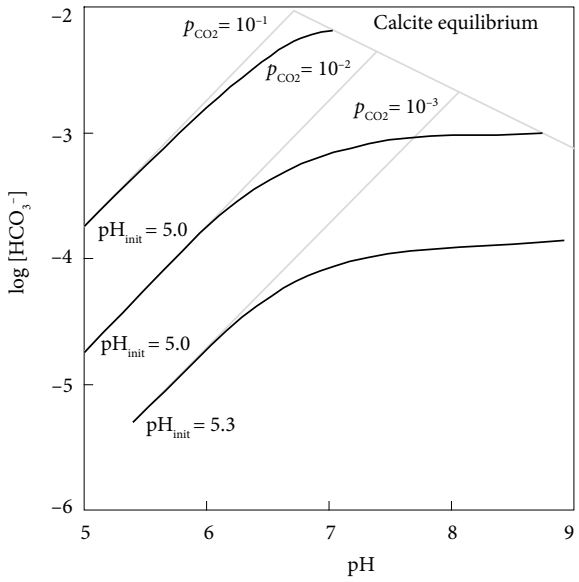


Figure 4.7. Comparison of the evolution of systems with constant p_{CO2} (open systems) with those closed to gas exchange. After Stumm and Morgan (1996) and Deines et al. (1974).

Problem: Using the water and stability constants given in the adjacent tables, calculate the activities of the major species in this water.

Analysis of Stream Water (mM):

Na^+	0.32	Cl^-	0.22
K^+	0. 06	SO_4^{2-}	0.12
Mg^{2+}	0.18	ΣCO_2	1.0
Ca^{2+}	0. 36	pH	8.0

Log of Stability Constants:

	OH^-	HCO_3^-	CO_3^{2-}	SO_4^{2-}	Cl^-
H^+	14	6.35	10.33	1.99	–
Na^+	–	–0.25	1.27	1.06	–
K^+	–	–	–	0.96	–
Mg^{2+}	2.56	1.16	3.4	2.36	–
Ca^{2+}	1.15	1.26	3.2	2.31	–

Solution: The first two problems we need to address are the nature of the carbonate species and activity coefficients. At this pH, we can see from Figure 4.1 that bicarbonate will be the dominant carbonate species. Making the initial assumption that all carbonate is bicarbonate, we can calculate ionic strength and activity coefficients using the Debye-Hückel Law. These are shown in the table below. Having the activity coefficients, we calculate the approximate abundance of the carbonate ion by assuming all carbonate is bicarbonate:

$$\left[CO_3^{2-}\right] = \frac{\gamma_{HCO_3^-} \sum CO_2}{\beta a_{H^+} \gamma_{CO_3^{2-}}}$$

where β is the stability constant for the complexation reaction:

$$CO_3^{2-} + H^+ \longleftrightarrow HCO_3^-$$

The "corrected" bicarbonate ion is then calculated as:

$$[HCO_3^-] = \Sigma\, CO_2 - [CO_3^{2-}]$$

The result confirms our initial first order assumption that all carbonate is present as bicarbonate. Using the concentrations and stability constants given as well as the activity coefficients we calculated, we can them make a first pass at calculating the concentrations of the complexes. For example, $MgCO_3$ is calculated as

$$a_{MgCO_3} = \beta_{MgCO_3}\, a_{Mg^{2+}} a_{CO_3^{2-}}$$

The results of this first iteration are shown in a matrix. Chlorine does not complex with any of the major ions to any significant degree, so we can neglect it in our calculations. We then correct the free ion activities by subtracting the activities of the complexes they form. Thus for example, the corrected free ion activity of Mg^{2+} is calculated as:

$$a^{corr}_{Mg^{2+}} = a^{init}_{Mg^{2+}} - a_{MgOH^+} - a_{MgHCO_3^+} - a_{MgCO_3} - a_{MgSO_4}$$

We then repeat the calculation of the activities of the complexes using these corrected free ion activities. A second matrix shows the results of this second iteration. In fresh waters such as this one, most of the metals are present as free ions, the alkaline earths being 5% complexed by sulfate and carbonate.

Ion Activities: Iteration 1

	free ion	OH^-	HCO_3^-	CO_3^{2-}	SO_4^{2-}
free ion		1×10–06	9.17×10–04	6.79×10–07	1.62×10–04
H^+	1×10–08	–	2.12×10–05	9.46×10–04	1.75×10–10
Na^+	3.03×10–04	–	1.62×10–07	2.51×10–08	6.27×10–07
K^+	5.69×10–05	–	–	–	9.33×10–08
Mg^{2+}	1.39×10–04	5.09×10–08	2.03×10–06	1.65×10–06	6.10×10–06
Ca^{2+}	2.77×10–04	4.29×10–09	5.08×10–06	2.07×10–06	1.08×10–05

Ion Activities: Iteration 2

	free ion	OH^-	HCO_3^-	CO_3^{2-}	SO_4^{2-}
free ion		1×10–06	9.12×10–0	41.1×10–06	1.65×10–04
H^+	1×10–08	–	2.06×10–05	9.12×10–04	1.58×10–10
Na^+	3.03×10–04	–	1.57×10–07	2.35×10–08	5.64×10–07
K^+	5.69×10–05	–	–	–	8.40×10–08
Mg^{2+}	1.40×10–04	5.03×10–08	1.84×10–06	1.45×10–06	5.14×10–06
Ca^{2+}	2.80×10–04	3.92×10–09	4.64×10–06	1.83×10–06	9.16×10–06

Problem: Suppose ground water initially equilibrates with a p_{CO2} of 10^{-2} and thereafter is closed to gas exchange, so that there is a fixed $\Sigma\ CO_2^{initial}$. The water then equilibrates with calcite until saturation is reached. What will be the final concentration of calcium in the water? Assume ideal behavior and an initial calcium concentration of 0.

Solution: Since the system is closed, a conservation equation is a good place to start. We can write the following conservation equation for total carbonate:

$$\Sigma\ CO_2 = \Sigma\ CO_2^{initial} + \Sigma\ CO_2^{from\ calcite}$$

Since dissolution of one mole of calcite adds one mole of Σ CO2 for each mole of Ca^{2+}, this equation may be rewritten as:

$$\Sigma\ CO_2 = \Sigma\ CO_2^{initial} + [Ca^{2+}]$$

Neglecting the contribution of the carbonate ion to total carbonate, this equation becomes:

$$[H_2CO_3] + [HCO_3^-] = ([H_2CO_3]^{initial}) + [Ca^{2+}]$$

where $([H_2CO_3]^{initial})$ denotes that amount of H_2CO_3 calculated from Equation E 4.1.1 for equilibrium with CO_2 gas; in this case a partial pressure of 10^{-2}. This can be rearranged to obtain:

$$([H_2CO_3]^{initial}) = [H_2CO_3] + [HCO_3^-] - [Ca^{2+}]$$

Further constraints are provided by the three carbonate equilibrium product expressions (E 4.1.1–4.1.3) as well as the solubility product for calcite (4.34), and the charge balance equation. We assume a final pH less than 9 and no other ions present, so the charge balance equation reduces to equation 4.36. From equation 4.13 and the value of K_{CO2} in Table 4.1, $[H_2CO_3]^{initial} = 10^{-2}\times10^{-1.47}$ M. Dividing equation 4.14 by 4.15 yields:

$$\frac{K_1}{K_2} = \frac{\left[HCO_3^-\right]^2}{\left[H_2CO_3\right]\left[CO_3^{2-}\right]}$$

Then substituting Equations 4.34 and 4.36 gives:

$$\frac{K_1}{K_2} = \frac{4\left[Ca^{2+}\right]^3}{K_{sp\text{-}Cal}\left\{\left[H_2CO_3\right]_{init} - \left[Ca^{2+}\right]\right\}}$$

Into this equation we substitute $p_{CO2}\,K_{CO2} = [H_2CO_3]$ and rearrange to obtain:

$$\left[Ca^{2+}\right]^3 + \frac{K_1K_{Cal}}{4K_2}\left[Ca^{2+}\right] - \frac{K_1K_{Cal}K_{CO_2}}{4K_2}\,p_{CO_2^{init}} = 0$$

This is a cubic that is readily solved for $[Ca^{2+}]$. For an initial p_{CO2} of 10^{-2}, we calculate a calcium concentration of 0.334 mM

4.3.2 Solubility of Mg

There are a number of compounds that can precipitate from Mg-bearing aqueous solutions, including brucite ($Mg(OH)_2$), magnesite ($MgCO_3$), dolomite ($CaMg(CO_3)_2$), as well as hydrated carbonates such as hydromagnesite ($MgCO_3(OH)_2\times3H_2O$). The stability of these compounds may be described by the following reactions:

$$Mg(OH)_2 \longleftrightarrow Mg^{2+} + 2OH^- \qquad K_{bru} = 10^{-11.6} \qquad 4.39$$

$$MgCO_3 \longleftrightarrow Mg^{2+} + CO_3^{2-} \qquad K_{mag} = 10^{-7.5} \qquad 4.40$$

$$CaMg(CO_3)_2 \longleftrightarrow Mg^{2+} + Ca^{2+} + 2CO_3^{2-} \qquad K_{dol} = 10^{-17\,\dagger} \qquad 4.41$$

†The solubility of dolomite is poorly known; values for this equilibrium constant vary between $10^{-16.5}$ and 10^{-20}.

We can use these reactions and their equilibrium constants, together with the reactions for the carbonate system (Equations 4.10–4.12) to construct predominance diagrams for Mg-bearing solutions in equilibrium with these phases. For example, for reaction 4.39 we may derive the following relationship (assuming ideal solution):

$$\log\frac{\left[Mg(OH)_2\right]}{\left[Mg^{2+}\right]} = \qquad 4.42$$

$$= pK_{Bru} + 2pK_W + 2pH = -16.4 + 2pH$$

where we use the notation $pK = -\log K$. For reaction 4.61, we can derive the following:

$$\log\frac{\left[MgCO_3\right]}{\left[Mg^{2+}\right]} = \qquad 4.43$$

$$= pK_{Mag} + \log\sum CO_2 + \frac{1}{\frac{\left[H^+\right]^2}{K_1K_2} + \frac{\left[H^+\right]}{K_2} + 1}$$

Assuming the solid is a pure phase, the term on the left of each equation is then just $-\log [Mg^{2+}]$. We can use these equations to construct stability, or predominance diagrams. For example, on a plot of $\log [Mg^{2+}]$ vs. pH, the predominance boundary between Mg^{2+}_{aq} and brucite plots as a line with a slope of –2 and an intercept of +16.4. Figure 4.8 shows two predominance diagrams derived from these equations. Brucite is the stable phase at high pH and low p_{CO2}.

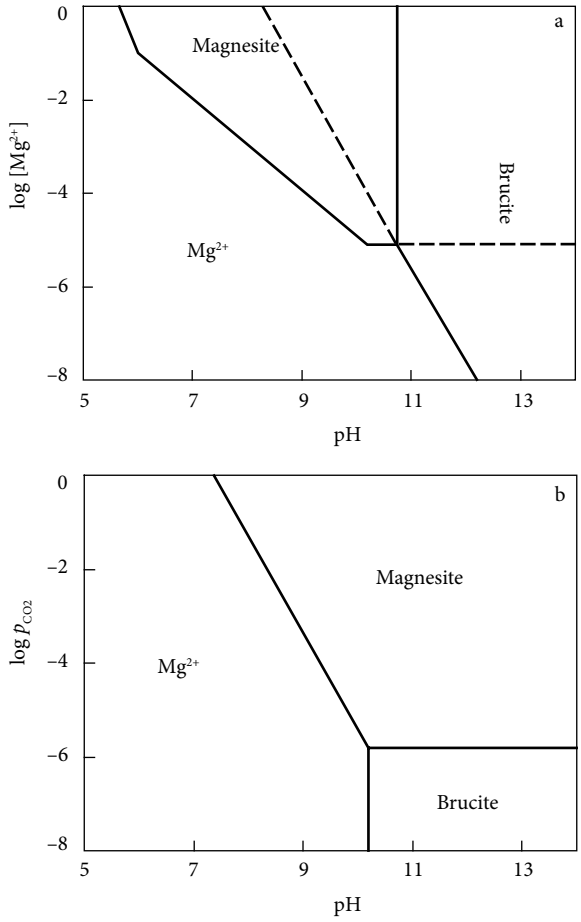


Figure 4.8. Predominance diagrams for Mg-bearing phases in equilibrium with aqueous solution. Total CO_2 is fixed at $10^{-2.5}$ M in 4.14a. The concentration of Mg^{2+} is fixed at 10^{-4} M in 4.14b. After Stumm and Morgan (1996).

Virtually all natural solutions will contain dissolved calcium as well as magnesium. This being the case, we must also consider the stability of dolomite. We can construct similar predominance diagrams for these systems but we must add an additional variable, namely the Ca^{2+} concentration. To describe the relative stability of dolomite and calcite, it is more convenient to express the solubility of dolomite as:

$$CaMg(CO_3)_2 + Ca^{2+} \longleftrightarrow Mg^{2+} + 2\,CaCO_3 \qquad 4.44$$

because the reaction contains calcite as well as dolomite. Since this reaction can be constructed by subtracting two times the calcite dissolution (Equation 4.34) from the dolomite dissolution (4.39), the equilibrium constant for this reaction can be calculated from:

$$K = \frac{K_{Dol}}{K_{Cal}^2} \qquad 4.45$$

Figure 4.9 illustrates the stability of magnesite, dolomite, brucite and calcite as a function of p_{CO2} and the Ca^{2+} / Mg^{2+} concentration ratio. Whether any of these phases are stable relative to a Mg^{2+}-bearing solution depends on the Mg^{2+} concentration, which is not specified in the graph.

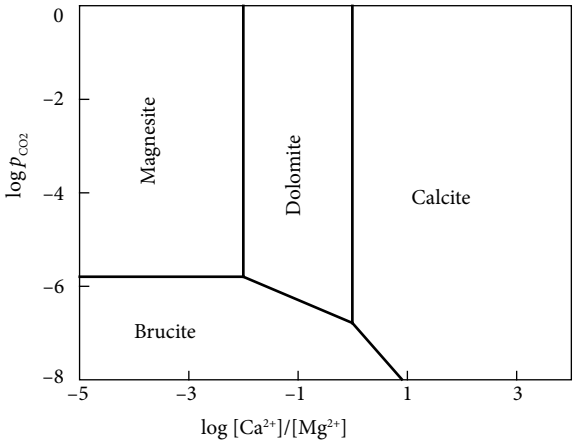


Figure 4.9. Stability of magnesite, dolomite, calcite, and brucite in equilibrium with a Mg- and Ca-bearing aqueous solution.

4.4 Regulation of Natural Waters pH by Carbonate System

The most important sources of acidity in the natural environment are: (1) Fossil-fuel combustion: Reduced sulfur contained in coal and oil is oxidized during burning to SO_2 gas which is released to the atmosphere. (2) Smelting of metal ores: Sulfide sulfur is again oxidized during ore roasting to SO_2. As a result SO_2 is dissolved in precipitation and oxidized to sulfuric acid which is deposited during rainfall. (3) Gasoline and diesel fuel combustion at temperatures when air nitrogen is oxidized to the mixture of nitrogen oxides usually denoted as NO_X. Their further oxidation in atmosphere and dissolution in rain produce nitric acid and acid rain. (4) Acid mine drainage: The waters draining from coal and ore mines are often acid because of pyrite oxidation. As will be presented in Chapter 9 the stoichiometry of this reaction can be written as

$$FeS_2 + 3.5\,O_2 + H_2O \rightarrow Fe^{2+} + 2\,SO_4^{2-} + 2\,H^+ \qquad 4.50$$

with production of acidity (presented reaction scheme does not express mechanism of this reaction). (5) Hydrolysis of Al^{3+} and Fe^{3+} released during rock weathering processes can produce quite large amount of H^+ ions according to reactions

$$Al^{3+} + H_2O \rightarrow Al(OH)_3(solid) + 3\,H^+ \qquad 4.51$$

$$Fe^{3+} + H_2O \rightarrow Fe(OH)_3(solid) + 3\,H^+ \qquad 4.52$$

(6) Decomposition of organic matter: This process produces organic acids, particularly humic/fulvic acids.

Serious environmental effects have been attributed to the acid production and acid deposition. Among others the most important damages are degradation and loss of soil (prevention of clay minerals formation), injury and death to trees, the disappearance of fish from dilute, soft-water lakes; deterioration of building stones and monuments. Probably the most serious consequence of acid rain and deposition is increased dissolution of carbonate minerals, the main component of limestone and the very important component of soil, sediment and bottom sediment of rivers, lakes and seas.

The carbonate system acts as the main regulation mechanism of natural water pH. When atmospheric carbon dioxide dissolves in rain, weak carbonic acid is formed according to equation

$$CO_2 + H_2O \longleftrightarrow H_2CO_3 \qquad 4.10$$

which dissociates and bicarbonate ion is formed.

$$H_2CO_3 \longleftrightarrow H^+ + HCO_3^- \qquad 4.11$$

The rain water in equilibrium atmospheric CO_2 contains about 1×10^{-5} M dissolved carbon dioxide and is always weakly acidic with pH value around 5.6. We can find this value as a point of intersection of $[H^+]$ and $[HCO_3^-]$ concentration lines in Figure 4.10. Dissociation of second proton from carbonic acid is negligible and according to the Equation 4.11 concentrations of protons and bicarbonate ions have to be equal.

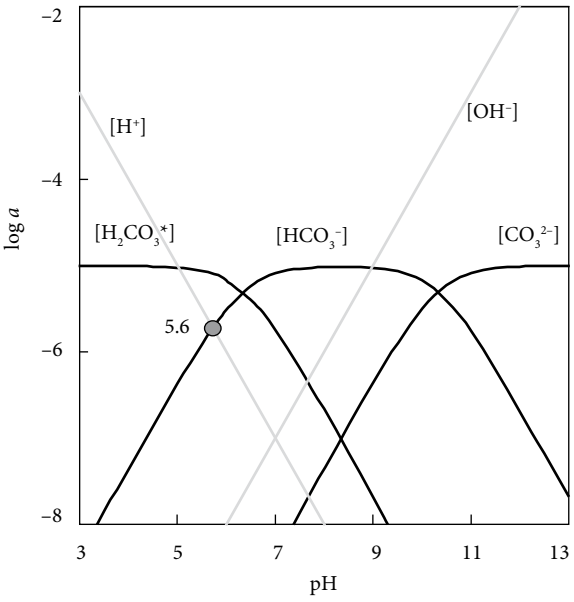


Figure 4.10 Activities of carbonate species in pure water in equilibrium with atmospheric carbon dioxide ($p_{CO2} = 10^{-3.5}$, $\Sigma\ CO_2(aq) \approx 10^{-5}$ M).Equilibrium pH is characterized by intersection of $[H^+]$ and $[HCO_3^-]$.

pH of natural water isolated from atmosphere and in contact with solid calcite can be estimated from the same diagram but for different concentration of dissolved carbonate species. Solubility product of calcite is

$$CaCO_3(Cal) \longleftrightarrow Ca^{2+} + CO_3^{2-} \qquad K_{sp\text{-}Cal} = 10^{-8.48} \qquad 4.53$$

According to the Equation 4.53 (neglecting further interactions of carbonate ion) the concentrations of Ca^{2+} and carbonate anion have to be equal and thus $[Ca^{2+}] = [CO_3^{2-}] = c_T$

$$K_{sp\text{-}Cal} = [Ca^{2+}]\,[CO_3^{2-}] = c_T^{\,2}$$

so

$$c_T = \sqrt{K_{sp\text{-}Cal}}$$

This system closed to the atmosphere (there are no additional strong acids or strong bases, $c_B - c_A = 0$) is characterized by intersection of $[OH^-]$ and $[Ca^{2+}] = c_T$. (Fig. 4.11, almost all of dissolved carbonate species is in the form of bicarbonate ion). Estimated pH value for water saturated with respect to calcite is 9.7 (exact calculation yields at 25 °C pH = 9.91).

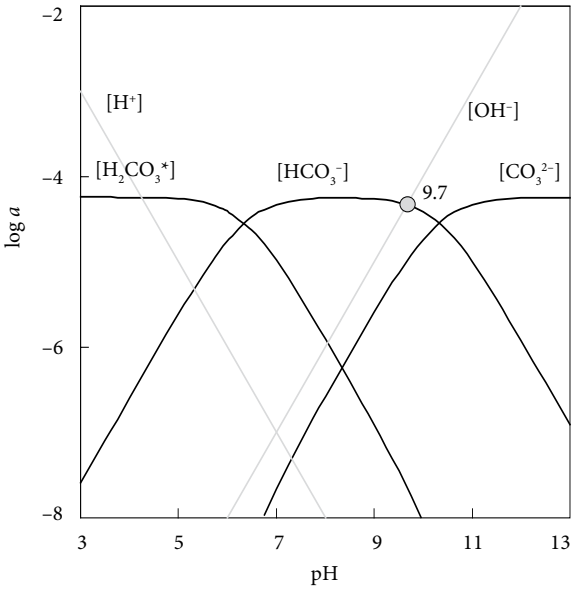


Figure 4.11 Activities of carbonate species in water in equilibrium with solid calcite. Equilibrium pH is characterized by intersection of $[OH^-]$ and $[Ca^{2+}] = c_T$. Almost all carbonate species are in the form of $[HCO_3^-]$ ($c_T \approx 6\times10^{-5}$ M).

Last system which we can usually find on surface is combination of the both previous – water in equilibrium with atmospheric carbon dioxide and solid carbonates, mostly calcite. The equilibrium composition is given by the electroneutrality condition 2 $[Ca^{2+}] \approx [HCO_3^-]$. This condition is indicated by a point on in-

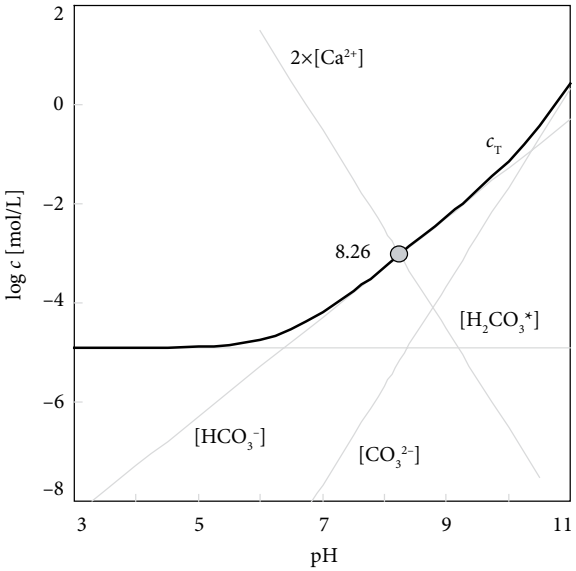


Figure 4.12 Activities of carbonate species in water in equilibrium with solid calcite and atmospheric carbon dioxide ($p_{CO2} = 10^{-3.5}$). Equilibrium pH is given by intersection of $2\times[Ca^{2+}]$ and $[HCO_3^-]$ lines. Almost all carbonate species are in the form of $[HCO_3^-]$ ($c_T \approx 6\times10^{-5}$ M). Thick curved line indicates overall concentration of dissolved carbonate species.

tersection of $2\times[Ca^{2+}]$ and $[HCO_3^-]$ lines and is reached at pH about 8.26 (Figure 4.12). The calcium concentration is determined by calcite solubility product.

Comparing this result with that of simple water equilibrium with calcite, we see that the influence of atmospheric CO_2 has depressed the pH markedly and that of $[Ca^{2+}]$ have been raised to values representative of those in natural waters. We can conclude that normal pH values of natural waters are kept by carbonate system in the range from about 5.5 (rain water, fresh water in small creeks and mountains – low amount of total dissolved species including carbonates because of short interaction time) to values about 8.3 which is characteristic for soils, waters in rivers, lakes, seas and oceans with fully developed equilibrium between water, carbon dioxide in atmosphere and solid carbonates. Note that carbonate system keeps pH values in narrow range around neutral conditions (pH ≈ 7) which is very favorable for biota.

Now we can check what will happen when some acidity enters water environment with carbonate equilibrium in the region of neutral pH. According to the Figure 4.1 the most of the carbonate species in water is in the form of bicarbonate ions. In principle, bicarbonate ions can accept proton and form carbonic acid or release proton and form carbonate ion. When some acidity enters system the protons are consumed during carbonic acid formation and thus removed from water. The pH value almost does not change. The amount of carbonic acid which is above equilibrium concentration splits to water molecule and dissolved carbon dioxide which is then released to the atmosphere. For long term functioning of this mechanism it is critically important that water is in contact and in equilibrium with solid carbonates in soils and bottom sediments of rivers and lakes.

On the other hand when some strong bases are released to water e.g. during silicate weathering when strong bases like Ca^{2+} and Mg^{2+} are released parallel with weak acids like H_4SiO_4 giving the net alkali reaction. Bicarbonate ions release proton which will react with hydroxyl anion forming neutral water molecule. Carbonate ions interact with metals in solution and are precipitated and deposited as solid carbonates. Consumed bicarbonate ions are replenished by dissolution of atmospheric carbon dioxide and carbonic acid formation. For this mechanism it is critically important that water is in contact with atmosphere.

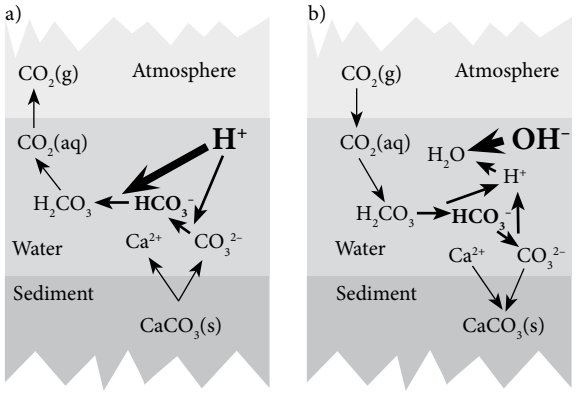


Figure 4.13 Regulation of pH in natural water by dissolved carbonate species. Addition of acidity or alkalinity is eliminated and pH value change of natural water is negligible. (a) Protons entering water system are consumed by bicarbonate ions and thus neutralized. (b) Hydroxyl ions entering water system are neutralized by protons released from bicarbonate ions.

These two mechanisms are responsible for very strong buffering action of carbonate species in natural waters. As we saw there is one important condition – in bottom sediments has to be solid carbonates present. They are normally formed during rock weathering (precipitation of solid carbonates keeps concentration of calcium and magnesium in the range of tens to hundreds milligrams per liter in fresh waters). When acid rains, acid deposition or other form of acidity enters natural waters the solid carbonates are dissolved and pH values are free to decrease. When pH decrease to values around 5, almost all carbonate species in solution are in the form of carbonic acid and no more protons can be removed by bicarbonate ions. The buffering action of carbonate species disappear and no more carbonates can be formed. At these conditions any small amount of acidity will cause large change in pH values.

There are some other not on the first sight visible consequences of carbonate system "degradation" by acid production and acid deposition. With environment

acidification: (1) no heavy metal carbonates are formed (most of heavy metal carbonates are insoluble and are deposited in bottom sediments) and (2) the capacity of clay minerals and other surface active solids to catch heavy metals is decreased and originally sorbed heavy metals are again released to the water environment (metals sorbed on solid surfaces are gradually replaced by protons).

We can conclude that keeping carbonate system at "healthy" state i.e. in pH range between 5 and 9 is extremely important for maintaining stable pH water conditions in nature.

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Chapter 5: Sampling of Water and Solids

5.1 Basic Considerations

A principal objective is to obtain a water sample with the same chemistry as those of water in its original environment (aquifer, surface water body etc.). When ground water is sampled in wells with long screen zone, then several redox zones may mix and irreversible chemical processes may occur. For example, when conditions close to water table are relatively oxic and dissolved oxygen is present, and conditions in deeper zone are reducing with dissolved iron, then there is mixing of ground water from both zones with resulting loss of both oxygen and iron in reaction like

$$Fe^{2+} + 0.25\ O_2(g) + 2.5\ H_2O = Fe(OH)_3(s) + 2H^+ \qquad 5.1$$

In that case, not only iron and oxygen are lost, but other metals like Zn and Pb may be lost too because they are adsorbed on precipitated ferric hydroxide.

However, even when no reactions occur, there still is reduction of concentration due to a conservative mixing. For example, when a plume of chloride considered as non-reactive tracer has thickness of about 4 m and thickness of screen zone is of about 10 m, then there will be lower concentration of chloride in water sample, which will not correspond to its concentration in aquifer. The only solution is the sampling with vertical resolution, using several piezometers with short screen zones open at different depths (Appelo and Postma, 1999). Piezometers are located in so called *piezometric nest.* Principal limitation is cost of such device, which is higher compared to a single well.

Another problem is related to de-gassing of CO_2. In many cases, partial pressure of CO_2 (P_{CO2}) dissolved in ground water is higher than atmospheric value of $10^{-3.5}$ atm. Thus, when a sample is equilibrated with atmosphere, the reaction

$$CaCO_3(s) + CO_2(g) + H_2O = Ca^{2+} + 2HCO_3 \qquad 5.2$$

goes to the left and calcite precipitates. Thus, a part of calcium and dissolved inorganic carbon (*DIC*) are lost. This process can be even accelerated as a consequence of increasing temperature of sample in the case of later measurement.

There is a controversy related to how many volumes of a well or piezometer should be evacuated prior to collection of sample(s). It is assumed that 3 volumes should be enough, but this requirement cannot be sometimes met in the case of large diameter domestic wells. Thus, it is recommended to pump water until parameters like pH and *EC* are stabilized and then start the sampling (Appelo and Postma, 1999). There also is requirement of low pumping rate (<1L/min) in the case of sampling of a contaminant plume because uncontaminated background water could dilute samples otherwise.

5.2 Field Parameters

Several parameters have to be measured in the field because their values based on later measurement in laboratory are almost meaningless.

Temperature: this parameter changes quickly and has an impact on other parameters such as pH and Eh. Furthermore, temperature is necessary for geochemical speciation calculation. In the ideal case, temperature should be measured directly in a well by a down-hole

probe. If it is impossible, then measurement should be performed in a flow-through cell, with minimized contact with atmosphere (Fig. 5.1). Flow-through cell is a plexi-glass cylinder with slots for insertion of measurement electrodes, which is connected to a pumping device.

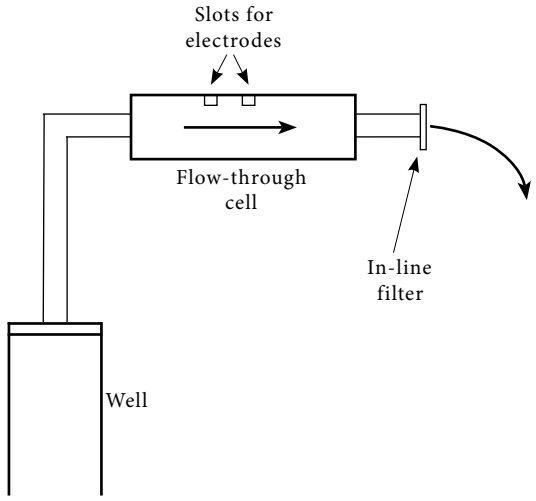


Figure 5.1 Flow though cell for measurement of temperature, pH, and Eh.

Hydrogen ion activity (pH): this is an essential parameter because most geochemical processes are pH-sensitive. The value of pH is generally determined by distribution of carbonate species in water and, thus, it is strongly affected by equilibration with atmosphere. There is de-gassing (Equation 5.2) and resulting pH is generally higher than its correct value. Thus, measurement without contact with atmosphere is required. The pH-meter has to be calibrated using standard buffers prior to measurement.

Redox potential(Eh): the Eh value is generally lower in ground water compared to surface conditions. Thus, the contact of a sample with atmosphere (log P_{O2} = –0.68 atm) causes changes in speciation such as oxidation of Fe(II) to Fe(III) (Equation 5.1). This means that any contact with atmosphere has to be avoided. Measurement is also performed in flow-through cell. The Eh value measured in field is measured with respect to Ag-AgCl or Hg-HgCl (kalomel) electrodes and the measured value has to be converted to a corresponding value for hydrogen electrode, E_{H2}:

$$E_{H2} = Eh_{field} + Eh_{correction} \quad 5.3$$

where $Eh_{correction}$ is electrode and temperature dependent and is indicated by manufacturer for different measurement electrodes. An alternative method to obtain $Eh_{correction}$ value is based on measurement of Eh in both field sample and Zobell solution with known E_{H2} value (Kehew, 2000).

Alkalinity: it is a measure of acid-neutralizing capacity of a solution. It is generally based on carbonate species, but there can be a contribution of other species:

$$\text{Alkalinity} = HCO_3^- + 2CO_3^{2-} + H_3SiO_4^- + H_3BO_2^- \ldots \text{etc.} \quad 5.4$$

Especially significant can be contribution of dissolved organic matter with de-protonated carboxylic acid groups, $R\text{-}COO^-$, in the proximity of sanitary landfills. In that case, the value of alkalinity cannot be used to calculate distribution of carbonate species without corrections (Deutsch, 1997). In an ideal case, alkalinity is determined in the field by titration with acid like HCl and is reported in units like mg/L of $CaCO_3$ or mg/L of HCO_3. When field determination is impossible, then there should be collection of a special sample for later determination of alkalinity in laboratory. When a sub-sample is taken from a bigger sample later, there can be loss of alkalinity due to precipitation of calcite (Equation 5.2). Fritz (1994) concluded that most positive charge-balance errors (e.g., missing anions) were caused by errors in the measurement of alkalinity.

Dissolved oxygen (DO): this is qualitative parameter only because O_2/H_2O redox pair cannot be used for quantitative calculations. Detectable values indicate oxic environment where, for example, dissolved nitrate should be stable and ferrous iron should be unstable. Measurements are often performed by oxygen electrode, but there are more precise methods like Winkler titration.

Electrical conductivity (EC): this is semi-quantitative parameter, which roughly corresponds to total dissolved solids (*TDS*) concentration. Thus, it can be used for delimitation of inorganic contaminants plumes, salt water intrusions etc. It is measured by conductivity meter in units such as μS cm^{-1}. According to Appelo and Postma (1999), the *EC* divided by 100 gives a good estimate of the sum of anions or cations (in meq/L):

$$\Sigma \text{ anions} = \Sigma \text{ cations (meq/L)} = EC/100 \ (\mu S\ cm^{-1}) \quad 5.5$$

This relation holds up to *EC* values of about 2000 μS cm^{-1}.

5.3 Collection and Preservation of Samples

There is a controversy related to the filtration of samples. Generally, filtration is recommended in the case of samples for cation and metal analysis. The filter used is

generally 0.45 μm, but filter 0.1 μm is more convenient in some cases because some colloids can pass through 0.45 μm filter. Filtering is also recommended for anion samples because organic matter and some bacteria which could participate in reactions after collection of sample like sulfate reduction are removed. Filter is generally located on the output pipe of flow-through cell (so called *on-line filter*). Samples for cation and metal analysis should be acidified by acid such as HCl to pH less than 2.0 to avoid precipitation of iron (Equation 5.1). Samples for anion analysis are unacidified, but filtration is recommended.

If we are interested in the presence of colloids, we take 2 samples: one sample filtered and acidified and second one unfiltered and acidified. In the case of the presence of colloids concentrations in second sample should be higher.

After collection, samples should be kept at low temperature (about 4°C) and analyzed as soon as possible. Conservation of samples is indicated in Table 5.1, based on Appelo and Postma (1999).

5.4 Sampling of Solids

The presence of reactive solids has a significant impact on concentration of some contaminants in water. Also, concentrations of some minerals are required in geochemical modeling.

As a general rule, contact with atmosphere should be avoided after collection of samples and samples should be deposited in tight barrels, and, if possible, in nitrogen atmosphere. For example, de-gassing of CO_2 could cause precipitation of calcite and, thus, concentration of calcite in a sample would be overestimated. There can also be oxidation of pyrite in a sample after its contact with atmospheric oxygen, with resulting precipitation of ferric hydroxide. Thus, reducing capacity of solids would be underestimated and adsorption capacity would be overestimated. Also, drying of samples should be prevented because secondary minerals previously not present in samples could be formed.

The following minerals are of interest:

Calcite: determines a neutralization capacity of a system and plays a significant role in migration of acid mine drainage. Its dissolution is generally fast. Determination is by X-ray diffraction (for content > 5.0 wt %) and by acid digestion in carbonate step of sequential extraction.

Dolomite: plays the same role as calcite, but its dissolution is slower and may be kinetically constrained. Determination is the same as for calcite.

Ferric oxides and hydroxides: they are significant adsorbents of metals and may play a role in neutralization of acid mine drainage at low pH values (above 3.0). Their adsorption capacity is strongly pH-dependent. They can be determined by X-ray diffraction or by oxalate step of sequential extraction. Ferric minerals and Mn(IV) minerals play a principal role in *oxidation capacity (OXC)* of solid phase. Methodology of the *OXC* determination is in Heron et al. (1994) and Christensen et al. (2000).

Pyrite: contributes to reducing capacity of aquifer solids and can be determined by X-ray diffraction and by SEM. Pyrite content together with organic matter content are basis for determination of *reduction capacity (RDC)* of sediments, see discussion in Christensen et al., 2000.

Organic matter: contributes to reducing capacity of aquifer solids. There is special importance of fraction of organic carbon f_{oc} in adsorption of organic contaminants (see later). Determination is based on burning of samples of solids and on detection of CO_2 released during combustion. However, there has to be removal of carbonates by acid digestion prior to analysis.

Table 5.1 Conservation of samples (based on Appelo and Postma, 1999).

Parameter	Conservation of sample
Ca, Mg, K, Na	Acidified to pH<2.0 in polyethylene
NH_4, Si, PO_4	
Heavy metals	Acidified to pH<2.0
SO_4, Cl	No conservation
NO_3, NO_2	Store at 4°C and add bactericide like thymol
H_2S	Zn-acetate conservation or spectrophotometric field measurement
TIC	Dilute sample to TIC<0.4 mmol/L to prevent CO_2 escape
Alkalinity	Field titration using Gran method
Fe^{2+}	Spectrophotometric measurement on acidified sample
pH, T, Eh, O_2	Field measurement

Clays (kaolinite, smectite): contribute to adsorption capacity of solid phase and generally represent pH-independent component of adsorption (especially smectites). They are determined by X-ray diffraction or by differential thermal analysis (DTA).

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Chapter 6: Principles of Geochemical Modeling

6.1 Introduction

In this text we discuss geochemical models, which consider chemical reactions in the migration of contaminants. However, more sophisticated coupled transport and geochemistry models are being developed. Transport processes are discussed in Chapter 7 and there is brief discussion about coupled models at the end of this chapter.

There are geochemical equilibrium models, based on assumption of thermodynamic equilibrium reached in relatively short time (no time factor is included) and geochemical kinetic models, which include time factor. Basic division of equilibrium models is into: (a) speciation models, (b) mass balance models (also called inverse models), and (c) forward models (also called reaction path models). One of principal weaknesses of the equilibrium models is the assumption of chemical equilibrium. However, models including chemical kinetics are not common in environmental geochemistry and there still is a lack of kinetic data for many geochemical processes. There are some exceptions like the oxidation of pyrite, which has been studied extensively. Recent codes like PHREEQC-2 (Parkhurst, Appelo, 1999) include several reaction kinetics. In this text only equilibrium models are discussed.

It must be emphasized that the application of geochemical models is based on the assumption of known flow pattern. If sampling points used for the interpretation of geochemical evolution of ground water are not hydraulically connected, then the geochemical interpretation is in troubles. This means that generally we have to solve flow model prior to geochemical model. Let us look at the influence of water sampling locations on the interpretation of geochemical evolution of ground water (Fig. 6.1). This is a plan view of a simple flow system with recharge area represented by point A. From point A ground water flow is diverted in 2 directions: towards river – points B and C, and in the opposite direction, towards lake – point D. When we investigate geochemical evolution of water, we can compare points A and B (and also C), but comparison of C and D does not make much sense from the viewpoint of geochemical evolution of ground water.

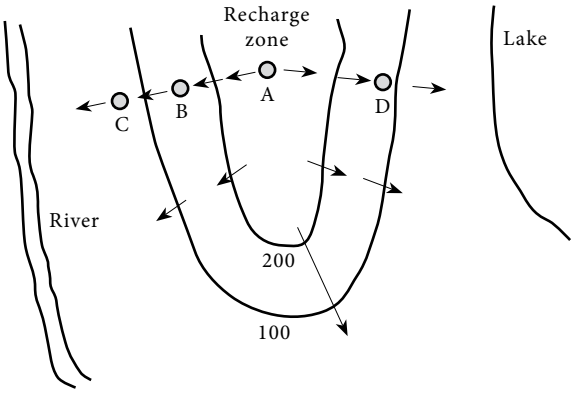


Figure 6.1 Geochemical sampling of a hypothetical flow system (adapted from Chapelle, 1993).

6.2 Speciation Models

They represent the most simple example of equilibrium models. We know chemistry of water from one sampling point (for example, from a well or piezometer) and speciation program calculates distribution of dissolved species between free ions and aqueous complexes and also saturation indexes for different minerals. Lead, for example, can be present in water as free ion Pb^{2+}, and also in the form of complexes with anions:

$$[Pb]_{total} = [Pb^{2+}] + [PbSO_4^0] + [PbCl^+] + [PbCO_3^0] \quad \text{etc.}$$

where $[Pb]_{total}$ is total lead concentration from laboratory chemical analysis.

Information about distribution of dissolved species is important for risk assessment of contamination by metals because toxicity of metals depends on their speciation in solution. Carbonate complexes of metals, for example, are less toxic than their free ions.

We will demonstrate the significance of saturation index on the example of dissolution of gypsum. The dissolution is expressed as

$$CaSO_4 \cdot 2H_2O(s) = Ca^{2+} + SO_4^{2-} + 2H_2O \qquad K_{sp} = 10^{-4.60} \text{ for } 25°C$$

where K_{sp} is solubility product, which is equilibrium constant for this reaction from available from thermodynamic database. The value of K_{sp} is valid for a given temperature and for the reaction as it is written, e.g., for dissolution. In the case of precipitation of gypsum, the value of K_{sp} is $1/10^{-4.60}$. Ion activity product (*IAP*) for the reaction is

$$IAP = [Ca^{2+}]\,[SO_4^{2-}]$$

where terms in brackets are activities calculated by speciation program applying the Debye-Hückel or Davies equation for calculation of activity coefficients (Drever, 1997, Langmuir, 1997). The activity α_i is equal to the product of activity coefficient γ_i and concentration m_i:

$$\alpha_i = \gamma_i\, m_i \qquad 6.1$$

We can write, for example, for Ca^{2+} that $\alpha_{Ca2+} = \gamma_{Ca2+}\, m_{Ca2+}$. Activity coefficients are a function of ionic strength of solution I, $\gamma_i = f(I)$. When ionic strength of a solution is higher than about 0.5, then the ions interaction approach based on the Pitzer's equations has to be used instead (Langmuir, 1997). Saturation index *SI* is defined as

$$SI = \log (IAP/K_{sp}) \qquad 6.2$$

When $[Ca^{2+}]\,[SO_4^{2-}] = K_{sp}$ for gypsum, then $SI = 0$ and water is at equilibrium with gypsum and gypsum in contact with the water neither dissolves nor precipitates. When $SI>0$, gypsum precipitates from the water and when $SI<0$, gypsum dissolves in contact with the water, if it is present in solid phase. Field data necessary for input of speciation program are temperature, pH, alkalinity, and results of laboratory chemical analysis. If behavior of redox-sensitive species (for example, Fe, As, U, etc.) is modeled, then field Eh value can be entered to split total concentrations on the basis of the Nernst equation. Redox couple concentrations (for example, Fe^{2+}/Fe^{3+}) can also be determined analytically or a total concentration can be split on the basis of the Eh value calculated from other redox couple (for example, As_{total} split on the basis of the Eh value calculated from the Fe^{2+}/Fe^{3+} couple). However, analytical determination of redox species has priority because redox equilibrium is rarely observed (Langmuir, 1997). Thus, the redox speciation based on Eh values and on other redox couples is just a rough estimate.

An example of typical speciation model output is shown in Fig. 6.2.

Common problems solved using speciation programs are: (a) there is a sample with high concentration of dissolved aluminum and we need to know distribution of aluminum between Al^{3+} and different complexes

Figure 6.2 Output of speciation in program SIMUL (Reardon, 1992).

Species	Conc	log Conc mmol/kg	Gamma mol/kg
H+	3.023E-05	-7.5196	0.5310
OH-	4.911E-04	-5.3089	0.8103
Ca2+	4.17	-2.3798	0.4452
Mg2+	1.32	-2.8794	0.4455
MgOH+	4.414E-05	-7.3552	0.8254
Na+	11.7	-1.9318	0.8365
Fe3+	1.238E-12	-14.9073	0.1796
FeOH2+	1.343E-07	-9.8721	0.4454
Fe(OH)2+	2.872E-05	-7.5418	0.8284
F e(OH)30	2.844E-04	0.5451	1.0054
Fe(OH)4-	1.969E-02	-4.1058	0.8546
Cl-	0.157	-3.8053	0.8497
SO42-	5.49	-2.2504	0.4322
HSO4-	6.660E-06	-8.1765	0.8547
CO2aq	0.531	-3.2750	1.0054
HCO3-	11.4	-1.9425	0.8503
CO32-	5.410E-02	-4.2668	0.3255

Phase	Log SI	
PCO2	-1.79	
Brucite	-5.15	
Portlandite	-10.34	
Calcite	0.93	NOTE: Supersalurated
Aragonite	0.74	NOTE: Supersaturaled
Valerile	0.42	NOTE: Supersalurated
Gypsum	-0.78	
Bassanite	-1.65	
Nesquehonite	-2.88	
Mg-oxychloride	-13.57	
Ca-oxychloride	-41.83	
Ca~monochlorid	-24.55	
Halite	-7,46	
Nahcolite	-3.52	
Dolomite	1.62	NOTE: Supersaturated
Fe{OH)3	5.38	NOTE: Supersaturated

(for example, $Al(OH)_4^-$, $AlSO_4^+$ etc.) because different forms of aluminum have different toxicity, (b) there are ground water samples from contaminant plume downgradient from mine tailing impoundment and we want to verify the possibility of precipitation of minerals like gypsum, $CaSO_4.2H_2O$, and jarosite, $KFe_3(SO_4)_2(OH)_6$. An example of speciation program is WATEQ4F (Plummer et al., 1976). However, more advanced programs like PHREEQC (Parkhurst, 1995) also include speciation modul. There are countless examples of speciation modeling applications in geochemical and hydrogeological literature (for example, Blowes, Jambor, 1990, Robertson et al., 1991, etc.).

Principal difficulties related to the application of speciation models are:

(1) Calculations are based on assumption of thermodynamic equilibrium and do not include a time factor. This means that the *SI* values just determine the direction of a reaction, but not how long time it takes to complete the reaction. There are so called reactive minerals with fast dissolution/precipitation rate (however, expressions "fast" and "slow" depend on the velocity of ground water flow and on time scale of investigation). Examples of reactive minerals are (Deutsch, 1997): Carbonates: calcite $CaCO_3$, dolomite, $CaMg(CO_3)_2$, siderite, $FeCO_3$, rodochozite, $MnCO_3$; Sulfates: gypsum, $CaSO_4.2H_2O$, jarosite, $KFe_3(SO_4)_2(OH)_6$, melanterite, $FeSO_4.7H_2O$, basaluminite, $AlOHSO_4$; Oxides and hydroxides: ferrihydrite, $Fe(OH)_3$, goethite, FeOOH, gibbsite, $Al(OH)_3$, manganite, MnOOH, and amorphous silica, SiO_2(am).

On the other hand, dissolution of silicates like feldspares is slow and can be made even slower by the formation of secondary products layers on their surfaces. This type of reactions requires kinetic descriptions with a time factor. There are other reactions which never reach equilibrium, and in which reactants are gradually transformed into products. An example is the oxidation of organic matter by oxygen. Another example is the oxidation of pyrite because pyrite does not precipitate in oxidizing environment even when concentrations of Fe^{2+} and SO_4^{2-} increase.

(2) Equilibrium constants are defined for pure mineral phases, which seldom occur in nature. For example, there can be a gradual transition between K-jarosite $KFe_3(SO_4)_2(OH)_6$ and natro-jarosit $NaFe_3(SO_4)_2(OH)_6$ with changing value of equilibrium constant. A notorious example is ferric hydroxide because the value of equilibrium constant for the mineral phase changes several orders of magnitude depending on the degree of crystallization (Langmuir, 1997).

(3) Complexation with organic matter can highly increase concentrations of dissolved metals. In ground water without organic matter metals would precipitate as minerals. Most of modeling codes do not have data base of equilibrium constants for complexation with organic matter. Furthermore, the characterization of organic matter composition is complicated and expensive problem. Terms like humic and fulvic acids describe groups of organic acids with several hundred of members and only for some of them equilibrium constants are available.

6.3 Mass Balance Models

This type of models (also called inverse models) is used in cases, when we already know chemistry of ground water and solid phase composition, and we want to determine which reactions have already happened between hydraulically connected sampling points. There are two types of the mass balance modeling: evolution of ground water chemistry between 2 sampling points and mixing problem. In the case of chemical evolution, the input includes ground water chemistry of 2 samples located on the same flowline and composition of solid phase in the aquifer between these 2 points. In the case of mixing problem, the required input are 3 (or more) samples, which represent chemistry of 2 waters prior to mixing and chemistry of final water after mixing and completion of geochemical reactions. Typical model of the type is NETPATH (Plummer et al., 1994). Program is based on mass balance equation:

$$\Delta m_{T,k} = \Sigma \alpha_p b_{p,k} \qquad k = 1, j \tag{6.3}$$

where $\Delta m_{T,k}$ is change of total dissolved concentration of k^{th} component between sampling points, α_p is the quantity of component p (for example, in mol/kg of water) which dissolved or precipitated and $b_{p,k}$ is stechiometric coefficient of k^{th} component in p^{th} mineral. For example, for dissolved inorganic carbon change along flowpath with reacting phases including calcite, dolomite and CO_2(g), we can write

$$\Delta m_{T,C} = \alpha_{calcite} + 2\alpha_{dolomite} + \alpha_{CO2} \tag{6.4}$$

Then the program solves a set of equations for specified components and the goal is to calculate mass transfer coefficient α for each phase. Similar equations are solved for mass balance of electrons and isotopes.

The output has the following form:

$$\text{Water A + Reactants = Water B + Products} \tag{6.5}$$

Example of mass balance model output is the interpretation of water chemistry in the Madison Aquifer in Wisconsin, USA (Plummer et al., 1984):

Recharge water +2 0.15 gypsum + 3.54 dolomite + 0.87 CH_2O +15.31 NaCl + 2.52 KCl + 0.09FeOOH+8.28 Na_2-X = Mysse water + 5.33 calcite + 0.09 pyrite + 8.28 Ca-X

where mass transfer coefficients are in mmol/L and X indicates exchange sites on clays. The type of model is often used for the interpretation of regional water chemistry evolution, but it has also been used for interpretation of reactions in contaminated aquifers. An example of contaminated site data interpretation is the interpretation of geochemical reaction in a shallow aquifer contaminated by crude oil near Bemidji, Minnesota, USA (Baedecker et al., 1993). Selected ground water chemistry data are in Table 6.1. Site B, far from the oil plume, is located about 40 m downgradient from Site A, at the margin of the plum with free phase.

The interpreted geochemical reactions related to the degradation of dissolved organic carbon released from the oil spill were: - methanogenesis of DOC, degassing of CO_2 and CH_4 from the water table into the unsaturated zone, - dissolution of calcite, MnO_2, and goethite in solid phase, and precipitation Ca-siderite with 20 % of Ca. Values of $\delta^{13}C$ for carbon species in liquid and solid phases were also used for interpretation. Elements (constraints) used in modeling were: C, Ca, Fe, Mn, N, Redox (includes electron mass balance in redox reactions).

Table 6.1 Water chemistry at the Bemidji site [in mmol/L, unless stated otherwise].

Property or constituent	Site A (upgradient)	Site B (downgradient)
Temperature [°C]	10	9
pH	6.78	6.93
Eh [V]	-0.15	-0.09
Dissolved O_2	0	0
Ca	3.322	3.046
Mg	1.77	1.366
Na	0.135	0.091
K	0.169	0.036
Fe	1.055	0.079
Mn	0.016	0.127
Cl	0.09	0.01
SO_4	0.005	0.012
H_2S	<0.0006	<0.0006
TDIC	17.165	10.572
DOC	4.171	1.515
CH_4(aq)	1.353	0.386
NH_4^+	0.028	0.005
SiO_2	1.018	0.508
$\delta^{13}C_{TDIC}$ [per mil]	-5.80	-5.95
$\delta^{13}C_{CH4}$ [per mil]	-56.1	-53.6

Minerals (phases) used in model were: MnO_2, goethite, siderite, adsorption of NH_4^+, mixture CO_2-CH_4 with CO_2 fraction 0.14, and calcite (Plummer et al., 1994). Resulting ground water evolution model was

Water A + 0.111 MnO_2 + 6.488 goethite + NH_4^+-X = Water B + 7.464 siderite + 2.476 CO_2-CH_4 + 0.276 calcite

The calculated isotopic values of $\delta^{13}C$ were relatively close to the values of samples from the field.

Difficulties related to the application of mass balance models are: (1) results are non-unique and the same water chemistry evolution can be explained by several models, (2) there are no thermodynamic constraints in mass balance models and program may suggest impossible reactions. This means that the type of models has to be used in conjunction with speciation model. If, for example, the mass balance model suggests dissolution of gypsum as a possible reaction, then saturation index SI_{gypsum} has to be less than 0 and gypsum has to be present in solid phase. However, principal proof of dissolution/precipitation of a mineral is its mineralogical evidence using methods like X-ray diffraction and scanning electron microscope (SEM). (3) There is a problem related to the definition of solid phase composition because in the case of silicates their composition may be quite complex.

6.4 Forward Models

This type of models, also called reaction path models, is used for prediction of water chemistry evolution along a flowline. In this case, initial water chemistry is known and we try to predict water chemistry at some downgradient point along flowpath. We have to stipulate reacting mineral phases which dissolve and also mineral phases which precipitate when their SI values are more than 0. The input of model is the initial water and reacting mineral phases. This type of model also can equilibrate a water sample with a gas with specified partial pressure (for example, with P_{CO2}). The output is similar to the output of speciation model (e.g., list of dissolved species and saturation indexes), but the amount of dissolved or precipitated minerals during equilibration is also indicated (for example, 0.05 mol $Fe(OH)_3$ per 1 L of water). The concept of modeling is

Initial water + Reacting phases =
= Predicted water + Products 6.6

Let us assume dissolution of halite, NaCl, and barite, $BaSO_4$, in an initial water. Both minerals can be includ-

ed in input as "infinite phase" (which means that their amount in solid phase is large and is not influenced very much by their dissolution) and "finite phase" (in this case we stipulate their amount in contact with 1L of water). The code will dissolve in each reaction step

$$\Delta NaCl + \Delta BaSO_4$$

where Δ is mass transfer coefficient in mol/L, which is a small number. In each step, the program adds into water ΔNa^+, ΔCl^-, ΔBa^{2+}, ΔSO_4^{2-}, and then there is speciation calculation. If saturation index for a dissolving phase is still negative, then dissolution continues. The transfer coefficient is kept small to avoid sudden supersaturation of water and conversion of reactants into products. In the meantime, other pre-determined reactive minerals can be precipitated if their saturation indexes values become positive.

Examples of this type of models are MINTEQA2 (Allison et al., 1991) and PHREEQC (Parkhurst, 1995). Both models include adsorption modeling using adsorption isotherms and surface complexation (Langmuir, 1997). However, in MINTEQA2 we can not mix and titrate different waters like in PHREEQC. Both codes can be used in "batch mode", e.g., there is equilibration of water with given phases in a closed batch. The program PHREEQC can also be used in "column mode", e.g., water flows through a column and is equilibrated with minerals and adsorbing phases in the column. Mass balance models and forward models are complementary because when we want to determine downgradient evolution of water chemistry, then we need to know which processes influenced water chemistry upgradient.

Typical problems solved by forward modeling are: (a) Reactions of contaminated water with aquifer solids like calcite and $Fe(OH)_3$. (b) Determination of water chemistry after mixing with water in the stream, equilibration with gases with specified partial pressures and after completion of chemical reaction. (c) Evaporation of contaminated water in discharge area with precipitation of minerals etc. Toran, (1994), used forward geochemical modeling for interpretation of data from zinc-lead mines in Schullsburg, Wisconsin, USA. Acid mine drainage produced by the oxidation of PbS and ZnS was neutralized by dissolution of calcite and dolomite and concentration of iron was lowered by precipitation of siderite and ferrihydrite. Sulfate concentration was influenced by dilution during flooding of mines, but precipitation of gypsum did not play a significant role.

Let us consider a hypothetical example of forward modeling of acid mine drainage (AMD) evolution. Ground water from mine tailings after the oxidation of pyrite with low pH, high Fe^{2+}, Fe^{3+}, and sulfate concentrations (Table 6.2) enters an aquifer with porosity 0.3, bulk density 1.8 kg/m^3, and 1.0 wt % calcite in solid phase (e.g., 0.6 mol of calcite in contact with 1 L of water). After neutralization with calcite several minerals like gypsum, siderite, and $Fe(OH)_3$ may precipitate. Finally, there is discharge of ground water to a local creek with neutral pH water (Table 6.2), where water in the creek mixes with discharging ground water in ratio 60 : 40. After the mixing, there is equilibration with atmospheric CO_2 and O_2, and there may be precipitation of calcite and $Fe(OH)_3$.

We calculate ground water chemistry (Water 2) after reaction of Water 1 with calcite in solid phase and precipitation of gypsum, siderite, and $Fe(OH)_3$ (if ground water is supersaturated with respect to them). Then water chemistry in the creek is calculated as Water 4 after mixing of original creek water (Water 3) with ground water (Water 2) in ratio 60 : 40, and after equilibration with $P_{CO2} = 10^{-3.5}$ atm, and precipitation of calcite, and $Fe(OH)_3$ (water becomes supersaturated with respect to them). Results of modeling steps are in Table 6.2. Supersaturation with respect to gypsum has never been reached and thus, there was zero amount of precipitated gypsum. Supersaturation with respect to siderite was reached only after neutralization of acid ground water by calcite, when concentration of Fe^{2+} was still high (Water 2). Concentrations of both Fe^{2+}

Table 6.2 Results of forward modeling, concentrations in mol/L (see text).

Parameter/ sample	Water 1 (acid mine drainage)	Water 2 (neutralized water)	Water 3 (original creek water)	Water 4 (mixed and equilibrated with air)
Ca	2.99×10^{-3}	2.46×10^{-2}	1.05×10^{-4}	8.75×10^{-3}
Mg	9.87×10^{-4}	9.87×10^{-4}	8.23×10^{-5}	4.44×10^{-4}
Na	2.00×10^{-3}	2.00×10^{-3}	1.44×10^{-4}	8.86×10^{-4}
C_{total}	9.83×10^{-2}	1.27×10^{-2}	2.56×10^{-4}	3.70×10^{-4}
SO_4	1.04×10^{-2}	1.04×10^{-2}	1.05×10^{-4}	4.26×10^{-3}
Fe(II)	1.00×10^{-2}	1.11×10^{-4}	-	9.91×10^{-19}
Fe(III)	5.01×10^{-3}	9.81×10^{-8}	-	2.19×10^{-8}
Cl	1.01×10^{-3}	1.01×10^{-3}	1.01×10^{-4}	4.67×10^{-4}
pH	2.7	6.26	7.6	7.77
T [°C]	22.0	22.0	25.0	23.8
$SI_{calcite}$	-8.77	0.0	-3.09	0.0
$SI_{Fe(OH)3(a)}$	-0.67	0.0	-	0.0
$SI_{siderite}$	-5.82	0.0	-	-13.54
SI_{gypsum}	-1.01	-0.05	-3.51	-0.58
log P_{CO2} [atm]	-1.57	-0.78	-3.43	-3.50
log P_{O2} [atm]	-	-	-	-0.69
Δcalcite	-	-2.16×10^{-2}	-	$+1.15\times10^{-3}$
$\Delta Fe(OH)_3(a)$	-	$+5.01\times10^{-3}$	-	$+4.43\times10^{-5}$
Δsiderite	-	$+9.92\times10^{-3}$	-	-

and Fe^{3+} after mixing of acid mine drainage with water in creek dropped to almost zero because iron precipitated as ferric hydroxide (Water 4).

This reaction generated acidity and thus, resulting pH after equilibration with atmospheric CO_2 would be even higher than calculated value of 7.77 if there would have not been precipitation of dissolved iron.

There are similar problems related to the applications of forward models like in the case of speciation models. Furthermore, we have to choose reactive mineral phases which are allowed to dissolve or precipitate in the case of corresponding values of saturation index. After equilibration of water with these minerals, their SI values will be equal to zero (see, for example, $SI_{calcite}$ in Table 6.2. for Water 4).

6.5 Coupled Transport and Geochemical Models

We have discussed so far purely geochemical models, which do not include physical processes. Now we will mention coupled models briefly. Coupled transport/chemistry models are being developed and are not available as common commercial codes so far. In this type of models, transport and chemical steps are generally separated. The advection-dispersion equation (ADE) in 1-D with chemical reactions is

$$\frac{D}{R}\frac{\partial^2 C}{\partial x^2} - \frac{v}{R}\frac{\partial C}{\partial x} - \lambda C \pm W = \frac{\partial C}{\partial t} \qquad 6.7$$

where D is hydrodynamic dispersion ($D = \alpha v + D_e$, where α is longitudinal dispersivity and D_e is effective diffusion coefficient), v is average linear velocity, R is retardation coefficient based on an adsorption isotherm like adsorption isotherm K_d, λ is 1st order decay constant, x is distance from source, t is time, and W is chemical term, which includes chemical reactions. In an iterative mode, the code solves in transport step the ADE for each of dissolved species, and then in chemical step a set of chemical reactions based on forward modeling takes place (formation of complexes, precipitation of pre-determined minerals etc.). In sequential mode the code uses the same transport parameters for all species in transport step. Some coupled codes use common forward modeling codes, for example, the code MINTRAN (Walter et al., 1994) uses MINTEQA2 (Allison et al., 1991) in its geochemical module.

We can also use transport and geochemical models separately (de-coupled approach). Migration of a conservative contaminant like chlorides can be modeled by a transport code. On the basis of transport model output we can determine the mixing factor for other, non-conservative species, and calculate concentrations of these species using mixing option in a forward geochemical model. Similar approach was used by Stollenwerk, (1994), for modeling of evolution of water chemistry in an aquifer contaminated by acid mine drainage near Globe, Arizona, USA.

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Chapter 7: Introduction to Transport Processes

7.1 Importance of Transport Processes

Our text places emphasis on geochemical processes, but a brief introduction to transport processes is also included in this chapter. The principal reason is related to the fact that all processes are coupled and there is no clear boundary between transport and geochemical processes.

In general, there is transfer of mass, but no transformation of contaminants during transport processes. Principal transport processes are diffusion, advection, dispersion, adsorption resulting in retardation, and decay.

Sources of contamination can be broadly divided on temporal basis into continuous sources (input continues for long time) and instantaneous sources (input lasts for very limited time and then stops) or on spatial basis into point sources (landfills, mine tailings and other relatively small sources), diffuse sources (there are no clear limits of a source, for example, nitrate contamination from agriculture pollution, acidification from acid deposition), and linear sources (pipelines for petrol, pollution from road salts).

7.2 Diffusion

Diffusion is transport of a contaminant based on concentration gradient. This process may take place also in stagnating water (velocity of flow $v = 0$) or even against the direction of flow. The process is described by First Fick's Law for steady-state diffusion (e.g., concentration gradient does not change in time):

$$J_D = -D_e \, \partial C/\partial x \qquad 7.1$$

where J_D is diffusive flux (kg m^2 s^{-1}), D_e (m^2 s^{-1}) is effective diffusion coefficient for porous media, C is concentration, and x is distance of transport from source of contamination. The concentration gradient $\partial C/\partial x$ can be determined relatively easily. In contrast, the value of D_e is more problematic. Generally, values of diffusion coefficient D_w for free water are in literature (they decrease with increasing molecular weight of a compound) for different ions (Table 7.1) and they have to be converted to values of D_e for porous media. There are several equations for conversion available, one of them is

$$D_e = (n/\tau) \, D_w \qquad 7.2$$

where n is porosity (or volume fraction of water in unsaturated zone) and τ is tortuosity (defined as ratio between real transport distance and straight distance in porous media, value > 1.0 is taken from literature).

When diffusion is transient, 2nd Fick's Law applies:

$$\partial C/\partial t = D_e \, \partial^2 C/\partial x^2 \qquad 7.3$$

This equation can be used, for example, to calculate diffusive flux across a clay liner for a certain period.

Table 7.1 Values of diffusion coefficient D_w for free water (from Domenico and Schwartz, 1998).

Cation	D_w [10^{-10} m^2.s^{-1}]	Anion	D_w [10^{-10} m^2.s^{-1}]
H^+	93.1	OH^-	52.7
Na^+	13.3	F^-	14.6
K^+	19.6	Cl^-	20.3
Rb^+	20.6	Br^-	20.1
Cs^+	20.7	HS^-	17.3
Mg^{2+}	7.05	HCO_3^-	11.8
Ca^{2+}	7.93	CO_3^{2-}	9.55
Sr^{2+}	7.94	SO_4^{2-}	10.7
Ba^{2+}	8.48		
Ra^{2+}	8.89		
Mn^{2+}	6.88		
Fe^{2+}	7.19		
Cr^{3+}	5.94		
Fe^{3+}	6.07		

7.3 Advection

Advection is transport with bulk motion of flowing water. Driving force of advective transport is hydraulic gradient. There are several expressions for water movement based on Darcy's Law:

Volumetric flux $Q = k\,I\,A$ (m^3 s^{-1}) 7.4

where k is hydraulic conductivity, I is hydraulic gradient, and A is flow cross section.

Specific discharge $q = k\,I$ (m s^{-1}) 7.5

e.g., this is flux across a unit cross section.

Average linear velocity $v = q/n_e = (k\,I)/n_e$ (m s^{-1}) 7.6

where n_e is effective porosity (e.g., volume of interconnected pores transmitting flow divided by total volume).

The average linear velocity is velocity of advection because advective transport takes place only within pores and not across complete profile.

Advective flux is expressed as

$J_A = v\,n\,C = q\,C$ (kg m^{-2} s^{-1}) 7.7

Units for diffusive flux and advective flux are consistent because both fluxes have to be additive. Advection just moves contaminated zone downgradient and if there would not have been any other process, the interface between contaminated and uncontaminated zones would have been abrupt. Obviously, this is not a real situation and, thus, other processes are also operating.

7.4 Dispersion

Dispersion is process of contaminant spreading based on velocity variations at several scales (Fig. 7.1):

- Pore scale, where velocity is larger in the middle of a pore and zero close to contact with grains. There also is branching of particle trajectories based on different sizes of pores.
- Layer scale, where particle move larger distance in layers of higher permeability.
- Aquifer scale, where larger heterogeneity change particle trajectories.

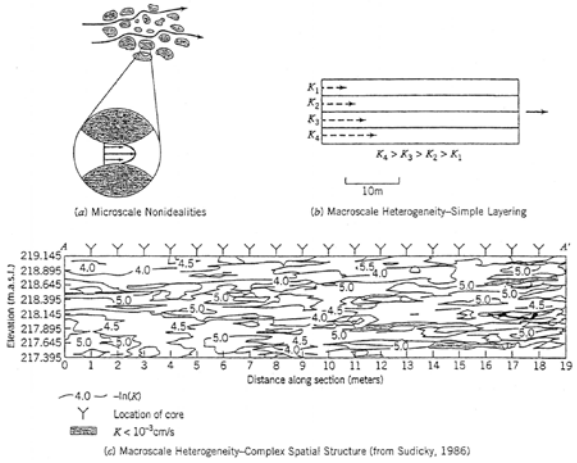


Figure 7.1 Different scales of dispersion (from Domenico and Schwartz, 1998).

Dispersion depends on advection and when advective velocity $v = 0$, there is no dispersion. Dispersion is characterized by a parameter called *dispersivity* (also characteristic length), α (m). In 3-D world, there are 3 parameters of dispersivity:

- *longitudinal dispersivity* α_L, acting in the direction of flow,
- *transverse dispersivity* α_T acting in the direction perpendicular to flow, and
- *vertical dispersivity* α_V acting in vertical direction.

In most cases, it holds that $\alpha_L > \alpha_T > \alpha_V$, e.g., longitudinal dispersivity has values in m, transverse dispersivity in dm, and vertical dispersivity in mm.

The values of effective diffusion coefficient and dispersivity are combined in parameter called hydrodynamic dispersion, D. In the direction of flow it is

$D_L = \alpha_L\,v + D_e$ 7.8

All parameters have already been defined. When advective velocity $v \rightarrow 0$ (for example, in clay sediments of low permeability), we obtain $D_L = D_e$, e.g., hydrodynamic dispersion is equal to diffusion coefficient.

Unfortunately, the value of dispersivity is not constant. The values obtained on column tests in laboratory are generally much smaller than those obtained from field tracer tests or from calibration based on large scale contaminant plume. This is related to a higher degree of heterogeneity in the field. When a tracer fills a larger volume of an aquifer, encounters more heterogeneities and value of dispersivity increases. When a sufficient volume of an aquifer is filled, dispersivity may attain a constant value. Several empirical formulas relating dispersivity to migration distance exist. Probably the most common is the formula of Xu and Eckstein (Fetter, 1999):

$$\alpha_L = 0.83 \, (\log L_s)^{2.414} \qquad 7.9$$

where L_s is migration distance.

7.5 Adsorption

Adsorption is process of attachment of particles of a contaminant to the surface of solid phase. When concentration of a contaminant in water decreases, these particles are released in process called *desorption.* In classical concept, adsorption is considered fast compared to the velocity of flow and reversible.

The most common is the concept of linear adsorption isotherm K_d, defined as

$$K_d = \mathrm{d}S/\mathrm{d}C \ \ (\mathrm{L/kg}) \qquad 7.10$$

where S is amount of contaminant adsorbed on solid phase (mg/kg) and C is concentration of contaminant in water. The value of K_d is generally obtained from *batch test* based on addition of different amounts of contaminant into a batch with water and solid phase from investigated site. Then equilibrium concentrations of contaminant in water and in solid phase are determined and K_d is calculated as a slope of straight line in graph $S = f(C)$. There are other types of adsorption isotherms like the Freundlich isotherm and the Langmuir isotherm (see Chapter 3.5). Also, the value of K_d for organic contaminants is often determined from value of octanol-water partition coefficient K_{ow} (Chapter 11.3).

Adsorbed contaminant is retarded compared to advective flow velocity. The measure of the retardation is retardation coefficient R, linked to the K_d by equation

$$R = v_w/v_c = 1 + (\rho_b/n) \, K_d \qquad 7.11$$

where v_c and v_w are velocities of contaminant transport and water flow, respectively, ρ_b is bulk density of solids, and n is porosity. The term (ρ_b/n) for bulk density in kg/dm^3 indicates kg of solid phase in contact with 1 L of water. When bulk density and K_d are in consistent units, the value of R is dimensionless. For example, when R = 4.0, velocity of a contaminant transport is four times slower than velocity of water flow.

Problem: The hydraulic conductivity of an aquifer is 1×10^{-4} m/s, hydraulic gradient is 0.001 and effective porosity is 0.25. Calculate migration distance during 1 year for Cd^{2+} with K_d value of 0.3 L/kg. Bulk density of solid phase is 1.8 kg/dm^3 and total porosity is 0.3.

Solution: Advective velocity is
$v = (k\times I)/n_e = (1\times10^{-4})/0.25 = 4 \times 10^{-7}$ m/s,
water flow distance for 1 year is
$L_w = 4 \times 10^{-7} \times 86400 \times 365 = 12.61$ m.
Retardation factor for Cd^{2+}
$R = 1 + (\rho_b/n) = 1 + (1.8/0.3)\times0.3 = 2.8.$
Thus, migration distance of Cd^{2+} is
$L_{Cd2+} = 12.61/2.8 = 4.5$ m/year.

7.6 Decay

Decay is decomposition of a contaminant, generally accompanied with formation of daughter products. The most common description of the process is by 1st order kinetics, where decay rate depends on concentration:

$$\mathrm{d}C/\mathrm{d}t = -k\,C \qquad 7.12$$

where C is concentration and t is time, and k is decay konstant (day^{-1}). By integration of the equation 12 we obtain

$$C_t = C_0 \, e^{-kt} \qquad 7.13$$

where C_t is concentration at time t and C_0 is initial concentration. The kinetic constant can be easily converted to half-life $t_{1/2}$,

$$t_{1/2} = 0.693/k \qquad 7.14$$

Half-life, $t_{1/2}$, (s) is the time necessary for decay of 50 % of initial concentration.

Examples of 1st order kinetics processes are radioactive decay and decay of petroleum products like ben-

zene. However, when concentrations of benzene and other organics are too high, then 0. order kinetics with decay rate independent of concentration applies:

$$dC/dt = -k \quad 7.15$$

where the value of decay constant is in $kg\,m^{-3}\,day^{-1}$. By integration of equation 7.15 we obtain

$$C_t = C_0 - k\,t \quad 7.16$$

When kinetic data are taken from literature, caution has to be used because the meanings of kinetic constant and half-life are completely opposite, e.g., large value of kinetic constant means fast decay and large value of half-life means slow decay.

7.7 Equations of Transport and their Solutions

Basic transport equation in 1-D is called the advection-dispersion equation (ADE). Its form for transport in saturated zone along *x*-axis is

$$D_x\,\partial^2C/\partial x^2 - v_x\,\partial C/\partial x = \partial C/\partial t \quad 7.17$$

where D_x is hydrodynamic dispersion, C is concentration, v_x is advection velocity and t is time. 1st term is dispersion term, 2nd term is advection term, and 3rd term is concentration term.
When adsorption/retardation are included, D_x and v_x are divided by retardation coefficient R:

$$(D_x/R)\,\partial^2C/\partial x^2 - (v_x/R)\,\partial C/\partial x = \partial C/\partial t \quad 7.18$$

Finally, when decay of 1st order decay is included, the ADE has the following form:

$$(D_x/R)\,\partial^2C/\partial x^2 - (v_x/R)\,\partial C/\partial x - kC = \partial C/\partial t \quad 7.19$$

where k is 1st order decay constant.

A common solution of ADE in 1-D is the solution Ogata-Banks:

$$C(x,t) = (C_0/2)\,(\mathrm{erfc}[(x-v_x\,t))/2(D\,t)^{1/2}] + \\ + \exp(v_x\,x/D)\mathrm{erfc}[(x+v_x\,t))/2(D\,t)^{1/2}] \quad 7.20$$

Short form of the equation applicable a long distance from source is

$$C(x,t) = (C_0/2)\,(\mathrm{erfc}[(x-v_x\,t))/2(D\,t)^{1/2}] \quad 7.21$$

where C_0 is source concentration, x is distance from the source, t is time, v is advection velocity, D_x is hydrodynamic dispersion, and erfc is the complementary error function (Table 7.2). The calculations of erfc are also implemented in the spreadsheet function of Excel program. Boundary and initial conditions for semi-infinite column are $C(0, t) = C_0$ and $C(\infty, t) = 0$ for $t>0$, and $C(x, 0) = 0$. The equation 7.21. applies in farther distance from source, in the proximity of source complete version of Ogata-Banks solution (equation 7.20) has to be used (Fetter, 1999). Solution for adsorption/retardation problem is obtained by dividing D and v by retardation factor R.

When decay is implemented, the equation becomes (Domenico and Schwartz, 1998)

$$C(x,t) = (C_0/2)\,\exp((x/2\alpha_x)(1-(1+(4\lambda\alpha_x/v_x)^{1/2})) \times \\ \times \mathrm{erfc}((x-v_x\,t(1+4\lambda\alpha_x/v_x)^{1/2})/2(\alpha_x\,v_x\,t)^{1/2}) \quad 7.22$$

where λ is 1st order decay constant, and α_x longitudinal dispersivity (molecular diffusion is considered negligible). For steady state (e.g., $t\rightarrow\infty$) we obtain

$$C(x,t) = C_0\,\exp((x/2\alpha_x)(1-(1+(4\lambda\alpha_x/v_x)^{1/2})) \quad 7.23$$

The equation is used for evaluation of biodegradation in an investigation of natural attenuation.

Solution for transient diffusion equation (Second Fick's Law, Equation 7.3) is

$$C(x,\,t) = C_0[\mathrm{erfc}(x/(2(D_e\,t)^{1/2})] \quad 7.24$$

where D_e is effective diffusion coefficient. Also diffusing contaminant can be adsorbed and solution with adsorption/retardation is obtained by dividing D_e by R.

Other solutions including 3-D solution and solutions with decay are presented in Bear (1979), Fetter (1999), and Domenico and Schwartz (1998). In that case, the shape and size of source has to be known. For example, in the case of 3-D solution it can be a plane perpendicular to ground water flow (patch source). Solution in 3-D with decay is implemented in natural attenuation codes BIOSCREEN and BIOCHLOR (Chapter 11).

Problem: Source concentration of a contaminant is 100 mg/L, flow velocity is 90 m/year, and longitudinal dispersivity is 1.0 m. Calculate concentration after 1 year at a distance of a) 92 m, and b) 85 m from source.

Solution: We use 1-D equation Ogata-Banks, assuming that molecular diffusion is negligible, e.g., $D = \alpha_L\,v$:

a) $C = (C_0/2)\,\mathrm{erfc}[(x - v\,t))/2(\alpha_L\,v\,t)^{1/2}] = (100/2)\,\mathrm{erfc}[(92-90.1)/2\,(1.90)^{1/2}$ we obtain erfc[0.1053] = 0.8815 (erfc is available in Excel spreadsheet) and $C = C_0/2 \times 0.8815 = 50.8815 = 44.1$ mg/L

b) in this case, we are behind advection front and erfc[−0.26344], substitution erfc[$-\beta$] = 1 + erf[β] is used, then $C = C_0/2 \times 1.2904 = 64.52$ mg/L

Table 7.2 Values of complementary error function erfc [erfc($-\beta$) = 1 + erf(β)].

β	erf (β)	erfc (β)
0	0	1.0
0.05	0.056372	0.943628
0.1	0.112463	0.887537
0.15	0.167996	0.832004
0.2	0.222703	0.777297
0.25	0.276326	0.723674
0.3	0.328627	0.671373
0.35	0.379382	0.620618
0.4	0.428392	0.571608
0.45	0.475482	0.524518
0.5	0.520500	0.479500
0.55	0.563323	0.436677
0.6	0.603856	0.396144
0.65	0.642029	0.357971
0.7	0.677801	0.322199
0.75	0.711156	0.288844
0.8	0.742101	0.257899
0.85	0.770668	0.229332
0.9	0.796908	0.203092
0.95	0.820891	0.179109
1.0	0.842701	0.157299
1.1	0.880205	0.119795
1.2	0.910314	0.089686
1.3	0.934008	0.065992
1.4	0.952285	0.047715
1.5	0.966105	0.033895
1.6	0.976348	0.023652
1.7	0.983790	0.016210
1.8	0.989091	0.010909
1.9	0.992790	0.007210
2.0	0.995322	0.004678
2.1	0.997021	0.002979
2.2	0.998137	0.001863
2.3	0.998857	0.001143
2.4	0.999311	0.000689
2.5	0.999593	0.000407
2.6	0.999764	0.000236
2.7	0.999866	0.000134
2.8	0.999925	0.000075
2.9	0.999959	0.000041
3.0	0.99978	0.000022

7.8 Breakthrough Curve and Tracer Tests

When a tracer is injected into 1-D column in laboratory, the curve $C/C_0 = f(t)$ for the outlet of column is called the breakthrough curve (Fig. 7.2).

The time $t_{0.5}$ of arrival of normalized concentration $C/C_0 = 0.5$ can be used to calculate advection velocity as $v = L/t_{0.5}$, where L is length of column. When both conservative (non-adsorbed) tracer and adsorbed tracer are used, the retardation coefficient R can be calculated as

$$R = (t_{0.5})_{ads}/(t_{0.5})_{cons} \qquad 7.25$$

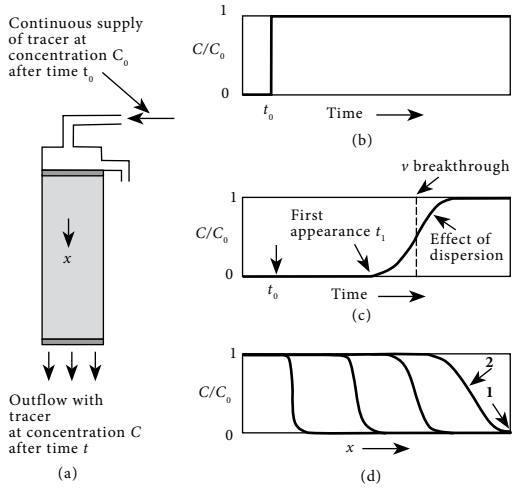


Figure 7.2 Breakthrough curve for 1-D column (after Freeze and Cherry, 1979).

The breakthrough curve can be also used to calculate longitudinal dispersivity α_L by inverse application of the Ogata-Banks solution (equation 7.21), but as we stated earlier, the dispersivity values obtained at laboratory scale have limited use at field scale. The column study can also be used to derive decay rate constant. In that case, several sampling ports across a column have to be installed and profile $C = f(x)$ in column is obtained. The concentration vs. distance curve is related to concentration vs. time curve using known velocity value:

$$C = C_0 \exp[-\lambda\,(x/v)] \qquad 7.26$$

Then the decay constant λ can be calculated easily by multiplying of slope in $\ln(C/C_0)$ vs. x graph, which is equal to $-\lambda/v$, by advective velocity of flow v. In that case, the influence of dispersion is included in decay constant and dispersion is considered as negligible.

Tracer tests in the field are performed by injection of tracer into ground water, followed by monitoring of

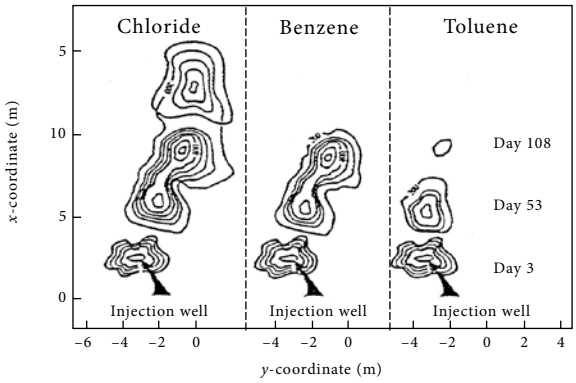


Figure 7.3 Instantaneous injection natural gradient tracer test (after Barker et al., 1987). Chloride represents conservative tracer, benzene decaying and retarded tracer and toluene represents fast--decaying tracer, which almost disappeared before last sampling campaign.

its migration in time. Mode of injection can be both instantaneous or continuous. The best data provides natural gradient test, when tracer(s) is injected into natural flow field. Results are used to calculate dispersivity values, and when comparison with a conservative tracer (chloride, bromide etc.) is available, values of retardation coefficient and decay constant can also be obtained (Mackay et al., 1986). Results of instantaneous injection, natural gradient test performed by Barker et al. (1987) are in Fig. 7.3. Forced gradient test is based on injection of tracer into injection well and its recovery from pumped well. In this case, flow field is influenced by pumping and results are less reliable than in previous case. Finally, one well tracer test is based on injection tracer into a well and recovery of tracer from the same well (Fetter, 1999). A variant of the test called push-pull test is based on injection of decaying and non-decaying tracers. It is used for determination of natural attenuation decay constant.

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Chapter 8: Contamination by Metals

8.1 Behavior of Metals in Water

Metals generally occur in ground water in low concentrations, less than 1 mg/L. However, it is often more than MCL (maximum contaminant level). Some metals dissolved in ground water have only one oxidation number, for example Pb^{2+}, Zn^{2+} , and Cd^{2+}. Other metals have several oxidation numbers, for example Fe^{2+} and Fe^{3+}, Mn^{2+} and Mn^{4+}, and Cr^{3+} and Cr^{6+}. Information about the oxidation state of a metal is essential for its speciation because different forms of a metal have different mobility in ground water (for example, Fe^{2+} is quite mobile and Fe^{3+} is immobile at neutral pH region), for determination of its toxicity (for example, Cr^{6+} is more toxic than Cr^{3+}), and for determination of its affinity to adsorption (for example, As^{5+} is more adsorbed than As^{3+}).

Compared to organic contaminants, there is no decay of metals during there transport and the total amount of a metal in an aquifer remains the same (of course, if there is no pumping of contaminated ground water). Metals can only change their form, for example, Cr^{6+} is reduced to Cr^{3+}, which then precipitates as $Cr(OH)_3(s)$. Total concentration of Cr in an aquifer remains the same, but Cr is immobilized in solid phase as $Cr(OH)_3(s)$. However, this solid phase may re-dissolve in future if pH and Eh change.

Concentration of metals can be limited by precipitation of their mineral phases like carbonates (for example, cerussite, $PbCO_3$, and smithsonite, $ZnCO_3$), sulfates (melanterite, $FeSO_4 \cdot 7H_2O$, chalkanthite, $CuSO_4 \cdot 5H_2O$, and anglesite, $PbSO_4$), and sulfides (secondary pyrite, FeS_2, and orpiment, As_2S_3). This means that for evaluation of the possibility of precipitation we have to determine concentrations of principal ions and not only concentrations of contaminating metals. The influence of principal ions is three-fold: 1) They contribute to ionic strength of solution, and thus, they influence activity coefficients γ_i of metals because activity coefficients are function of ionic strength I, $\gamma_i = f(I)$. 2) They increase total dissolved concentrations of metals by formation of complexes like $PbSO_4^0$. 3) They may participate in precipitation of minerals of metals. For example, precipitation of anglesite is expressed as

$$Pb^{2+} + SO_4^{2-} = PbSO_4(s) \qquad \log K_{sp} = -7.79 \text{ at } 25°C$$

where K_{sp} is the solubility product from thermodynamic database. Then ion activity product, *IAP*, is

$$[Pb^{2+}]\,[SO_4^{2-}] = IAP$$

where squared brackets indicate activities based on analytical concentrations corrected by geochemical modeling code for the influence of complexes (for example, lead in $PbSO_4^0$ is not included in Pb^{2+}) and calculated as products of activity coefficients and concentrations. Saturation index SI is defined as

$$SI = \log(IAP/K_{sp}) \qquad 8.1$$

When $IAP = K_{sp}$, ground water is at equilibrium with anglesite. When $IAP < K_{sp}$, the $SI < 0$ and anglesite should dissolve, if present in solid phase. If $IAP > K_{sp}$, the $SI > 0$ and anglesite should precipitate.

However, in many cases saturation with respect to contaminant minerals is not reached and the most

important factor which controls concentrations of dissolved metals is their adsorption on oxides and hydroxides in solid phase like $Fe(OH)_3$ and MnOOH. These phases are unstable when pH and Eh conditions change and they may release adsorbed metals back to solution. Adsorption behavior of metals is a function of pH. Metals in cationic form (for example, Zn^{2+}) are more adsorbed when pH increases, and, on the other hand, metals in anionic form (for example, CrO_4^{2-}) are desorbed when pH increases (see Chapter 3). This phenomena is called adsorption edge and is related to deprotonation of adsorbent surface as a consequence of increasing pH (Langmuir, 1997). The surface charge of an adsorbent becomes more negative at higher pH values, with resulting attraction of cations and repulsion of anions. Organic matter in both solid and dissolved phase plays an important role in adsorption and complexation of metals. However, the characterization of organic matter composition is complicated and costly.

The hydroxides and organic matter play an important role in preservation of samples. If a sample has colloidal $Fe(OH)_3$ or organic matter, then there will be a significant difference in metal concentrations between filtered and unfiltered samples. Furthermore, if there is Fe^{2+} in a sample, then acidification of the sample to pH about 2.0 will prevent oxidation of Fe^{2+} to Fe^{3+} followed by precipitation of $Fe(OH)_3$, and adsorption of dissolved metals. The overall reaction is expressed as

$$Fe^{2+} + 0.25O_2(g) + 2.5H_2O + Me^{2+} \rightarrow \rightarrow Fe(OH)_3(s) \equiv Me^{2+} + 2H^+ \quad 8.2$$

where Me^{2+} is a metal and ≡ indicates adsorption on surface of ferric hydroxide.

This means that we have to filter and acidify samples in the field, to prevent removal of metals by adsorption before analysis.

There are three redox zones of conceptual model of migration of metals (Fig. 8.1). In the Zone 1, oxidized zone with O_2 dissolved in ground water, ferric hydroxide is stable and metals are adsorbed. In the Zone 2, intermediate zone, there is no more dissolved oxygen and $Fe(OH)_3$ becomes unstable. Its dissolution produces dissolved metals in ground water. Their is no factor controlling metal concentrations in ground water, except for precipitation of carbonate minerals like siderite, $FeCO_3$, as a sink for Fe^{2+} in some cases. However, conditions in Zone 2 are not reducing enough for sulfate reduction. In the Zone 3, reduced zone, there is reduction of sulfate and incorporation of metals in secondary sulfides like FeS, and PbS:

$$2CH_2O + SO_4^{2-} \rightarrow H_2S + 2HCO_3^- \quad 8.2$$

$$Me^{2+} + H_2S \rightarrow MeS + 2H^+ \quad 8.3$$

where Me^{2+} represents a metal. Reactions in Zone 3 are also a basis for remediation of contamination by metals in permeable reactive barriers (*PRB*), filled with organic matter (Chapter 12).

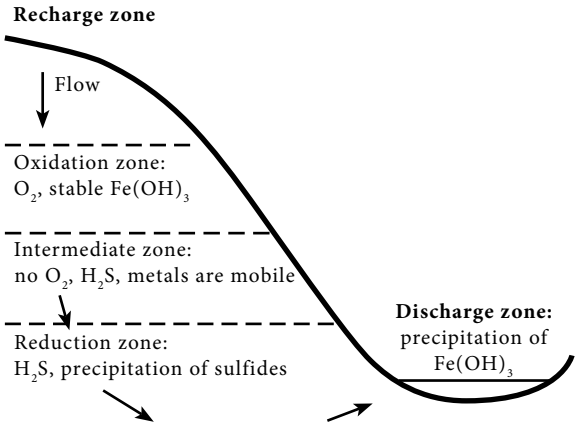


Figure 8.1 Conceptual model of redox zones in transport of metals.

In a graph of concentration in solid phase vs. concentration in water (Fig. 8.2) we can also distinguish 3 zones. In the zone A, concentration is not sufficiently high for precipitation of a mineral and concentration in water increases depending on adsorption on solid phase. The key parameter is the linear adsorption coefficient K_d (see Chapter 3.5).

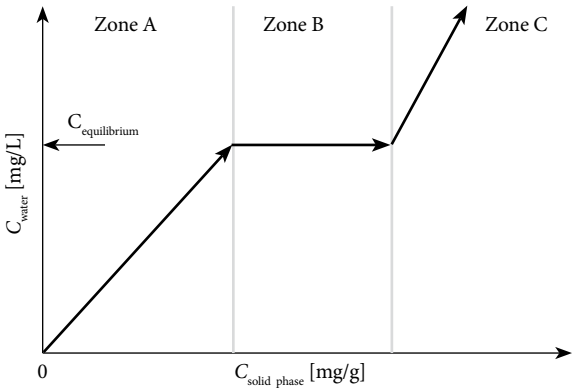


Figure 8.2 Behavior of a metal (see explanation in text).

The higher is K_d, the lower is the slope of line in Zone A of the graph.

When concentration reaches the value necessary for precipitation of a mineral of contaminant (for example, anglesite in the case of lead), then there is concentration plateau (Zone B) at equilibrium concentration because all contaminant entering water is implemented

into the mineral. If the concentration of other specie(s) forming the mineral is not high enough, then there is no more limiting factor after addition of more contaminant and concentration increases without any limitation (Zone C).

8.2 Examples of Contaminants

Examples of lead, chromium and arsenic are presented in the following text.

8.2.1 Lead

Lead occurs in ground water only in one oxidation state, as Pb^{2+}. However, it can form complexes with carbonates, sulfates, and chlorides. In this case total lead concentration is

$$[Pb]_{total} = [Pb^{2+}] + [PbSO_4^0] + [PbHCO_3^+] + [PbCO_3^0] + + [PbCl^+] \quad \text{etc.} \quad 8.4$$

In oxidized and moderately reducing environment, lead is dissolved, but can precipitate as cerussite at higher pH and dissolved inorganic carbon (*DIC*) values. Principal limiting factor for migration of lead in oxidized environment is its adsorption on $Fe(OH)_3$ and MnOOH. Adsorption begins at pH about 4.0 and adsorption intensity increases with increasing pH. At pH about 6.0, all lead is completely adsorbed. Adsorption may be prevented or shifted towards higher pH values by complexation of lead with anions like sulfate or with organic matter. In this case, there can be high concentration of lead in solution even at neutral pH region.

When an environment is reduced and sulfate reduction occurs, lead can precipitate as secondary galena, PbS. In oxidized environment with high concentrations of sulfate like acid mine drainage (*AMD*) sites, there can be precipitation of anglesite, $PbSO_4$. Inorganic speciation of lead is in Fig. 8.3.

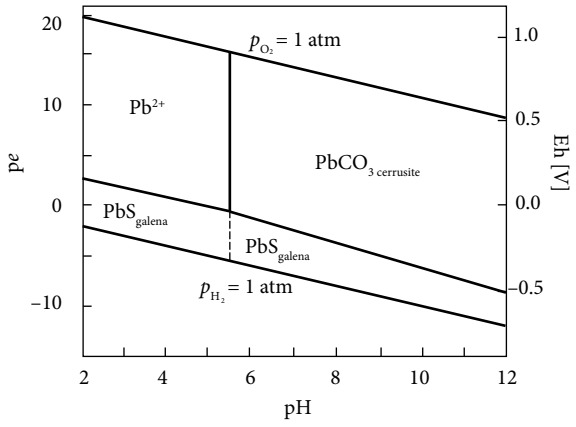


Figure 8.3 Speciation of lead as a function of Eh and pH, for Pb = 10^{-6}, $P_{CO2} = 10^{-2}$ atm, $S_{total} = 10^{-2}$, (from Drever, 1997).

8.2.2 Arsenic

Arsenic is metalloid and occurs in ground water in 3+ and 5+ forms. Oxidized arsenic (arsenate) is present as $H_2AsO_4^-$ at lower pH values and as $HAsO_4^{2-}$ at higher pH values (Fig. 8.4).

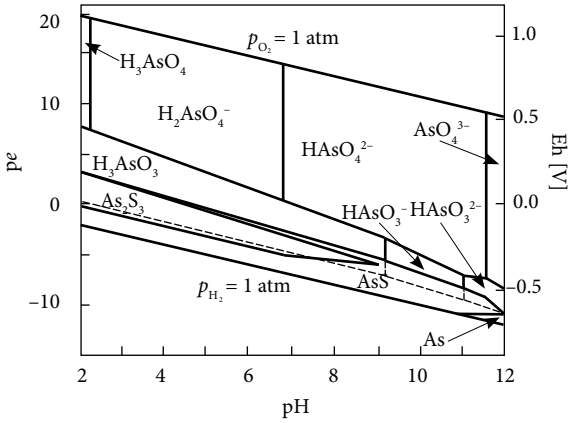


Figure 8.4 Speciation of arsenic as a function of Eh and pH, As=10^{-6}, $S_{total}=10^{-2}$, (from Drever, 1997).

Reduced arsenic (arsenite) is present as $H_3AsO_3^0$ at wide range of pH values, and only at pH above 9.0 there is formation of $H_2AsO_3^-$. The most important mineral, which can control arsenate concentration in water, is scorodite, $FeAsO_4.2H_2O$. However, the mineral is stable only at pH about 4.5, and its precipitation requires very high concentrations of dissolved As^{5+} and Fe^{3+}. Less soluble Fe(III) oxide and hydroxides generally exert more significant control on dissolved arsenic concentration. Both forms of arsenic are adsorbed on Fe(III) oxide and hydroxides, but As^{5+} has a stronger affinity for adsorption than As^{3+} (Pierce and Moore, 1982).

Adsorption of As^{5+} decreases with increasing pH due to the de-protonation of Fe(III) oxide and hydroxides surface and adsorption maximum is at pH about 4.0. Adsorption maximum for As^{3+} is at pH about 7.0, but the adsorption intensity is always lower than for As^{5+}. Some Fe(III) minerals like $Fe(OH)_3$ are unstable mineral phases, and they can dissolve when Eh and pH decrease with resulting release of adsorbed arsenic. When amorphous $Fe(OH)_3$ is aging and transformed to goethite, its specific surface decreases and this effect can also contribute to the release of adsorbed arsenic (Deutsch, 1997). Another factor, which can cause desorption of arsenic is its replacement from adsorption sites by an anion with stronger affinity for adsorption such as phosphate (Welch and Lico, 1998). This means

that an application of phosphate fertilizers may cause contamination of ground water by arsenic. When an environment is strongly reduced and sulfate reduction occurs, secondary sulfides like As-pyrite and orpiment, As_2S_3, may incorporate arsenic.

8.2.3 Chromium

Chromium has 3+ and 6+ forms in ground water, and both forms have different properties and behavior. Chromium 6+ is in anionic form like $HCrO_4^-$ or CrO_4^{2-}, depending on pH (Fig. 8.5). This means that its adsorption also depends on pH, and adsorption intensity decreases with increasing pH. Reported values of distribution coefficient K_d are in the range from 0.24 to 52 mL/g (Calder 1988, in: Henderson 1995).

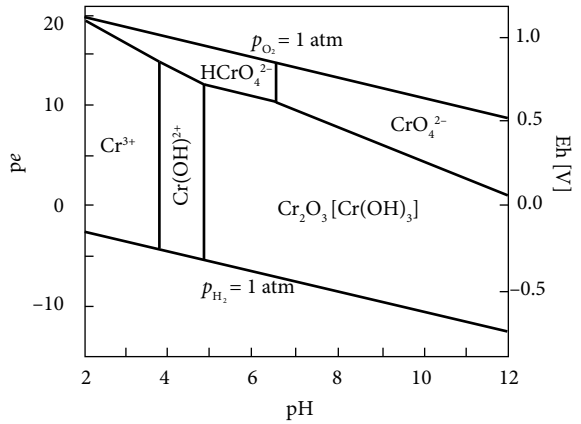


Figure 8.5 Speciation of chromium as a function of Eh and pH, $Cr_{total} = 10^{-6}$ (from Drever, 1997).

Reduced Cr^{3+} has cationic form except for pH > 12.0, where can be present as $Cr(OH)_4^-$. In the pH range from 6.0 to 12.0 (depending on concentration of Cr_{total}), Cr^{3+} precipitates as insoluble $Cr(OH)_3$. However, Cr^{6+} must be reduced to Cr^{3+} before precipitation of $Cr(OH)_3$ can take place. Reducing agents can be organic matter (both dissolved and in solid phase, but solid organic matter pool is generally much larger), and Fe^{2+} in reaction like

$$3Fe^{2+} + CrO_4^{2-} + 7H_2O = 3Fe(OH)_3 + Cr(OH)_2^+ + 3H^+ \quad 8.6$$

In many cases Cr^{3+} co-precipitates together with Fe^{3+} in the form of $(Cr_xFe_{1.0-x})(OH)_3$ mineral.

Kinetics of Cr^{6+} to Cr^{3+} reduction is slow at neutral pH region and increases at acidic pH region. Half-life for Cr^{6+} reduction at pH 7.0 was determined as 2.5 years (Henderson, 1995). The chromium reduction and $Cr(OH)_3$ precipitation is a basis for decontamination in reactive permeable walls (PRB) filled by Fe^0 or organic matter (Chapter 12).

8.3 Investigation of Sites Contaminated by Metals

Solubility of mineral phases, which contain metals as their components, generally represent the upper limit for metal concentrations (Drever, 1997). High concentrations of metals are often related to formation of complexes with organic matter. Principal factor controlling dissolved metals concentration is their adsorption on ferric and manganese oxides and hydroxides. Intensity of adsorption increases with increasing pH for cations and decreases for anions.

The following approach can be used:

1) Determine the oxidation number of a metal, how: by analytical determination on perfectly preserved sample (preferred) or by splitting of total concentration of a metal on the basis of field Eh and the Nernst equation or on the basis of Eh calculated from other redox couple determined analytically and total concentration (questionable). These operations are implemented in geochemical programs like WATEQ4F and PHREEQC (Chapter 6).
2) Determine, if their is possibility of precipitation of a mineral containing the metal. We can use speciation program with input including temperature, pH, Eh, alkalinity, and concentration of principal ions. Negative SI value excludes precipitation of a mineral, but positive SI value does not prove precipitation! In an ideal case, precipitation of a mineral is proved by mineralogical methods such as scanning electron microscope (SEM with mocroprobe. Sequential extraction can be used to deduce a type of mineral (Tessier et al., 1996).
3) Determine, if there is a possibility of sulfate reduction, how: - from decreasing sulfate concentration and increasing alkalinity in the direction of flow, - from the absence of species which are reduced before sulfate like dissolved O_2, and NO_3^-, - from the presence of reduced sulfur species like H_2S and HS^- (warning: samples must be preserved in the field by Zn-acetate because reduced sulfur can be lost), and - from enrichment of residual sulfate in isotope ^{34}S.
4) If we can exclude the sulfate reduction, then adsorption is probable mechanism controlling dissolved metals concentrations. Determine, if there is colloidal hydroxide present (how: by comparison of filtered, acidified samples and unfiltered, acidified samples-difference is contributed to colloids), and if Fe(III) oxide and hydroxides are stable (by speciation program and redox indicators). Then determine K_d for a metal in batch experiment. If there is a significant pH change during migration, then we have to use surface

complexation modeling instead of the K_d approach. If data on metal concentration in solid phase are available, then we can calculate expected adsorbed amount $M_{adsorbed}$ [mg/in contact with 1 mL of water] using formula

$$M_{adsorbed} = (\rho_b/n)K_dC_w \quad 8.7$$

where ρ_b is bulk density of solid phase [g/dm^3], n is porosity, K_d is linear distribution coefficient [L/g], and C_w is concentration in ground water [mg/L]. Then we compare it with M_{total} in solid phase sample. If the concentration in solid phase is higher then expected adsorbed concentration, then we have probably overlooked precipitation of a mineral. If dissolved concentration of metal is high even when water is supersaturated with respect to a reactive mineral of the metal, then there probably is complexation of the metal with organic matter.

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Chapter 9: Acid Mine Drainage

9.1 Formation of Acid Mine Drainage

Term acid waters is used for waters with zero carbonate alkalinity (pH < 4.5) and with free ions of strong acid such as H_2SO_4. In some cases, pH is even lower than 2.0. Principal (but not the only one) source of acid waters are mining residuals and the mechanism responsible for generation of acidity is the oxidation of sulfides like pyrite, FeS_2. In the absence of mining, acid waters are not common because the oxygen supply is insufficient to oxidize enough pyrite and to produce acidity higher than alkalinity of ground water. Water generally contains less than 10 mg/L (0.33 mmol/L) of dissolved O_2.

Situation changes dramatically when mining residuals with high concentration of pyrite are dumped. There are two principal types of mining residuals. First of them is waste rock, which was removed to access ore-bearing rocks. This material is deposited in waste rock piles, generally located in the proximity of a mine. Typical feature of waste rock is very heterogeneous size of particles, from clay fraction up to large blocks. The situation results in high permeability of waste rock and water table located close to the base of a pile. Second type of mining residuals are mine tailings. They are final by-products of ore-bearing rock extraction by technologies like flotation or application of cyanides. This material is crushed and milled prior to the treatment and resulting grain size is relatively small, corresponding to silt fraction. Mine tailings are located in depressions and water table is generally close to their surface as a consequence of their low permeability.

The oxidation of sulfides like pyrite is responsible for acid generation in both environments. Conceptual model of pyrite oxidation is shown in Fig. 9.1. At the beginning, pyrite is oxidized by oxygen in the presence of water and ferrous iron, Fe^{2+}, sulfate and H^+ ions are produced:.

$$FeS_2 + 7/2O_2 + H_2O = Fe^{2+} + 2SO_4^{2-} + 2H^+ \qquad 9.1$$

Ferrous iron is then oxidized to ferric iron, Fe^{3+},

$$Fe^{2+} + 1/4O_2 + H^+ = Fe^{3+} + 1/2H_2O \qquad 9.2$$

in a relatively slow reaction which can be catalyzed by bacteria *Thiobacillus Ferooxidans*. This reaction is the principal rate-limiting step of acid drainage formation (Stumm and Morgan, 1981). Further development depends on pH of water. If pH is higher than 3.0, then there is precipitation of ferric hydroxide, $Fe(OH)_3$, in reaction described as

$$Fe^{3+} + 3H_2O = Fe(OH)_3 + 3H^+ \qquad 9.3$$

Precipitated ferric hydroxide forms typical reddish layer at the bottom of streams draining mining wastes. This layer plays an important role in adsorption of metals like Pb^{2+}, Zn^{2+} etc. On the other hand, if pH is less than 3.0 and Fe^{3+} is in contact with unoxidized pyrite, the Fe^{3+} is consumed by pyrite oxidation because Fe^{3+} ion is strong oxidant:

$$FeS_2 + 14Fe^{3+} + 8H_2O = 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \qquad 9.4$$

This means that oxygen is only necessary to start the oxidation of pyrite and to recycle Fe^{2+} to Fe^{3+}. However, if an accumulation of mining residuals contains high quantity of dissolved Fe^{3+} from the previous oxidation period, then the oxidation of pyrite will continue for

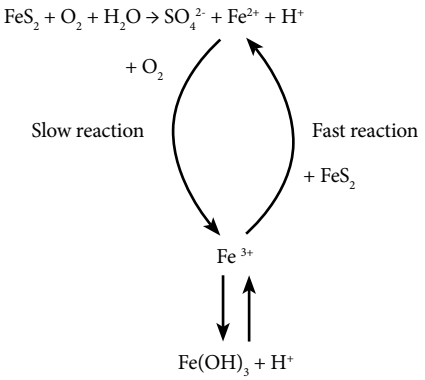


Figure 9.1 Conceptual model of oxidation of pyrite (adapted from Stumm and Morgan, 1981). Stoichiometrically balanced equations are in text.

long time even when there is no more oxygen supply. When both oxidation of ferrous iron and precipitation of ferric hydroxide take place, the coupled reaction is

$$Fe^{2+} + 1/4O_2 + 5/2H_2O = Fe(OH)_3 + 2H^+ \qquad 9.5$$

This means that there is generation of acidity in surface water bodies by the oxidation of Fe^{2+} and precipitation of ferric hydroxide even when discharging ground water originally has a neutral pH value.

9.2 Supply of Oxygen

All pyrite oxidation steps can take place in both waste rock and mine tailings. The principal difference between these two environments is in mechanism of oxygen supply and in the rate of acid generation. In fine grained mine tailings, the oxidation of pyrite takes place in relatively narrow zone (generally 0.5–5.0 m) between the surface of mine tailings and water table. The principal mechanism of the oxygen supply is diffusion in partially water filled porous media. The oxygen diffusion flux is expressed by First Fick's Law as the product of the effective diffusion coefficient for oxygen and the oxygen concentration gradient,

$$J_D = -D_{O2}\, dC_{O2}/dx \qquad 9.6$$

where J_D is diffusive oxygen flux, D_{O2} is effective coefficient of diffusion for oxygen and dC_{O2}/dx is oxygen concentration gradient in porous media. The principal problem is determination of D_{O2}, which is a function of water saturation and temperature. The following expression is applied (Reardon and Moddle, 1985)

$$D_{O2} = 3.9810^{-5}\, (\varepsilon - 0.05/0.95)^{1.7}\, T^{3.2} \qquad 9.7$$

where ε is porosity filled by air (= $n_{total} - n_{satur}$) and T is temperature.

In Fig. 9.2, we can see that D_{O2} decreases relatively slowly up to water saturation of about 60 % and then there is a sharp change about 5 orders of magnitude. The principal problem is the determination of the effective diffusion coefficient for oxygen because it decreases rapidly with increasing saturation of pore space by water.

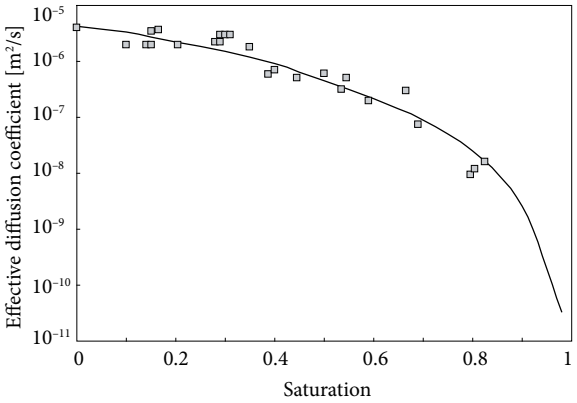


Figure 9.2 Relation between D_{O2} and water saturation (from Elberling, Nicholson, 1996).

There are 3 principal methods of *pyrite oxidation rate* (*POR*) determination:

1. Direct application of diffusive flux equation (Equation 9.6): Concentrations of O_2 are measured at different depth and then we can determine gradient of oxygen concentration. Then we need to know water saturation to determine D_{O2}. The simplest approach is to collect undisturbed mine tailings samples in vadose zone, and then calculate water saturation from weight difference before and after drying. The method is tedious and other methods from soil science like neutron probe and time-domain reflectometry can be used. However, these methods require calibration. Then the D_{O2} value is determined from water saturation-D_{O2} graph (Fig. 9.1). Under steady-state conditions, the diffusive flux of oxygen J_D can be directly converted to pyrite oxidation rate.

2. Oxygen consumption method: The method is described in detail in Elberling, Nicholson, (1996), and only brief principle is presented here. Closed vessel is located on the surface of mine tailings and oxygen concentration is measured in the headspace between surface of mine tailings and the vessel. The oxygen concentration decreases because O_2 diffuses into mine tailings. Diffusive flux is calculated as

$$J_D = C_0\, (k\, D_{O2})^{1.2} \qquad 9.8$$

where $k \times D_{O2}$ is the slope of the graph $\ln(C/C_0)$ vs. t divided by A/V, C_0 is initial oxygen concentration in

the vessel and C is oxygen concentration in time t, A is cross-section of the vessel, V is volume of the vessel above mine tailings interface, and k is kinetic constant of pyrite oxidation.

3. Sulfate mass balance: Sulfate concentration in pore water are determined, for example using samples from suction lysimeters installed at different depth in unsaturated mine tailings. Regardless of pyrite oxidation mechanism, 1 mol of oxidized pyrite produces 2 moles of sulfate, and sulfate produced during a certain period is converted to the amount of oxidized pyrite. However, precipitation of secondary sulfate minerals like gypsum and jarosite decreases sulfate concentration in water, and the pyrite oxidation rate is underestimated.

In summary, the pyrite oxidation rate in mine tailings is relatively slow and generally takes place in the time scale of tens of years. On the other hand, very permeable waste rock material has very high effective diffusion coefficient for oxygen and the pyrite oxidation rate is very high. The oxidation of pyrite is exotermic reaction and strong temperature gradients can develop within a waste rock pile. Temperature close to the slope of waste rock pile at Mine Doyon site, Québec, Canada, reaches 67°C. In this case, strong temperature gradients result in pressure gradients and the air with oxygen is sucked into the pile (Sracek et al., 2004). This process, called convection, takes place close to the slope and in the upper part of a waste rock pile and can increase the pyrite oxidation rate significantly. Thus, the oxidation of pyrite in waste rock is often very fast and concentrations of species like sulfate, Fe^{2+} , and H^+ in discharging water often reach extreme values.

9.3 Neutralization of Acid Mine Drainage

In either case, there is generally acid plume with high concentrations of dissolved species in mine tailings and in later period in an aquifer, moving in the direction of hydraulic gradient towards local surface water bodies. Regardless of the acid drainage generation mechanism, several common processes take place. If solids in mine tailings and in the aquifer contain high concentrations of carbonates like calcite, $CaCO_3$, and dolomite, $CaMg(CO_3)_2$, then H^+ ions in the acid plume are consumed in relatively fast neutralization reactions taking place during dissolution of these minerals. Dissolution of calcite is expressed as

$$CaCO_3 + H^+ = Ca^{2+} + HCO_3^- \quad 9.9$$

or at pH below 6.3 as

$$CaCO_3 + 2H^+ = Ca^{2+} + H_2CO_3^0 \quad 9.10$$

In this case, pH in the aquifer is maintained at close to neutral region (pH 6.0–7.0). However, $H_2CO_3^0$ which forms during neutralization, can prevent later pH increase due to de-protonation of H^+ in formation of HCO_3^-. This means that the reactions above are efficient when de-gassing of CO_2 is possible, e.g. in unsaturated zone or close to water table (Webb and Sasowsky, 1994).

Movement of the acid plume is slower compared to the movement of Fe^{2+} and sulfate plumes. The movement of Fe^{2+} can also be slowed down by the formation of siderite, $FeCO_3$,

$$Fe^{2+} + CO_3^{2-} = FeCO_3 \quad 9.11$$

If mining residuals have high content of carbonates, the acid drainage can be neutralized directly within them and low pH plume does not penetrate to the aquifer in their vicinity. After consumption of fast neutralization minerals like carbonates, several other reactions contribute to the buffering of acid drainage. Typical reactions are dissolution of previously formed siderite (pH around 5.0) and hydroxides like $Al(OH)_3$ (can maintain pH at about 4.5),

$$Al(OH)_3 + 3H^+ = Al^{3+} + 3H_2O \quad 9.12$$

and $Fe(OH)_3$ (pH at about 3.0),

$$Fe(OH)_3 + 3H^+ = Fe^{3+} + 3H_2O \quad 9.13$$

These buffers are generally formed during earlier, carbonate stage of the AMD buffering, and after their depletion principal buffering is related to the dissolution of silicates like muscovite and feldspars. However, kinetically constrained dissolution of silicates is slow, cannot maintain pH at neutral region, and also contributes harmful components like aluminum to water.

Concept of buffering plateaus is shown in Fig. 9.3. We can see that different types of buffering can occur in different zones of a contaminant plume. Even relatively low calcite content in solid phase (below 1.0 wt %) can slow down migration of acid plume. The retardation factor R for H^+ is calculated as

$$R = 1 + (m_{calcite}/m_{H+}) \quad 9.14$$

where $m_{calcite}$ is the amount of calcite in contact with 1 L of water and m_{H+} is molar concentration of H^+ (e.g., 10^{-pH}).

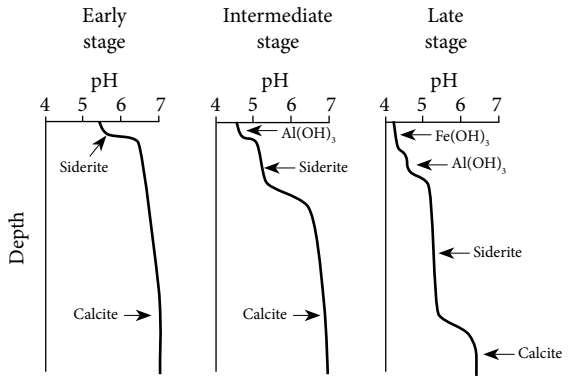


Figure 9.3 Buffering zones in the AMD plume (based on Blowes and Ptacek, 1994).

Problem: Velocity of ground water flow in an aquifer between mine tailings and a lake is 5m/day, porosity is 0.4, and bulk density of solid phase is 2.65 g/cm^3. The distance between mine tailings and lake is 100 m, pH of leachate is 2.4 and there is 1.5 wt % of calcite in solid phase. Calculate the time of acid plume migration to reach the lake.

Solution: 1m^3 of aquifer contains 600 dm^3 of solid phase and 400 dm^3 of water, thus 1 L of water is in contact with 600/400 = 1.5 dm^3 of solid phase, or with 1.5×2.65 = 4.05 kg of solid phase, which contains 4050×0.015 = 60.75 g = 0.6075 mol of calcite

1 mol of calcite neutralizes 1 mol of H^+

pH = 2.4 → $H^+ = 10^{-2.4} = 3.98\times10^{-3}$ mol

$R = [1 + (0.6075)/(3.98\times10^{-3})] = 154$

Water flows to the lake 100 m/(5 m/day) = 20 days

H^+ migration takes 20×154 = 3080 days = 8.44 years

During neutralization of AMD by carbonates there often is formation of gypsum, $CaSO_4.2H_2O$:

$$Ca^{2+} + SO_4^{2-} + 2H_2O = CaSO_4.2H_2O \qquad 9.15$$

This reaction can slow down the migration of sulfate, but to less extent than is the retardation of H^+.

After dissolution of $Fe(OH)_3$ there is dissolution of silicates. An example is dissolution of chlorite,

$$(Mg_4FeAl)(AlSi_3)O_{10}(OH)_8 + 16H^+ = \\ = 2Al^{3+} + Fe^{2+} + 4Mg^{2+} + 3H_4SiO_4 + 6H_2O \qquad 9.16$$

The reaction is kinetically constrained, and also contributes toxic aluminum to water. In this stage, there can be precipitation of jarosite,

$$K^+ + 3Fe^{3+} + 2SO_4^{2-} + 6H_2O = KFe_3(SO_4)_2(OH)_6 + 6H^+ \qquad 9.17$$

which can incorporate a large amount of dissolved sulfate.

We can summarize that if there are fast-acting neutralization minerals like carbonates in aquifer matrix, then the acid drainage can be neutralized completely. However, even if the water has neutral pH and contains high concentrations of dissolved iron and aluminum, then there is generation of acidity in surface streams during precipitation of aluminum and ferric hydroxides. The acidity in H^+ form can be only a smaller part of total potential acidity expressed as

$$\text{Potential acidity} = m_{H+} + 3m_{Al3+} + 2m_{Fe2+} + 3m_{Fe3+} \qquad 9.18$$

Coefficients are based on equations 9.12., 9.5 and 9.13 and m indicates concentrations in mol/L.

Problem: Determine total potential acidity of water sample with pH=2.4, Al^{3+} =400 mg/L, Fe^{2+} = 500 mg/L, and Fe^{3+} = 250 mg/L. Use equation 9.18.

Solution: Use equation 19. For pH = 2.4 concentration of $H^+ = 10^{-2.4} = 0.00398$ mol/L

Al^{3+} = 400 mg/L = 0.01483 mol/L×3 = 0.04449 mol/L

Fe^{2+} = 500 mg/L = 0.00895 mol/L×2 = 0.0179 mol/L

Fe^{3+} = 250 mg/L = 0.00448 mol/L×3 = 0.01344 mol/L

Total potential acidity is 0.07981 mol/L, and H^+ acidity is only of about 5 % of this value.

If there are no fast-acting neutralization minerals in an aquifer matrix and minerals like quartz and silicates predominate, then the migration of acid plume can be almost as fast as water flow.

9.4 Hydrogeology of Mining Wastes

Velocity of flow in mine tailings is generally low, of about 1 – 2 m/year. This is related to their small grain size and resulting low permeability. This means that residence period of water in mine tailings is in order of tens of years. We can use common programs for ground water flow modeling to determine flow pattern.

On the other hand, porous media in waste rock piles represents extremely heterogeneous unsaturated environment with multiple porosity, and strong temperature gradients. Furthermore, there are extremely high dissolved solids concentrations in pore water and density of water is often higher than 1.0 g/cm^3. Permeability of waste rock material is often high, with saturated hydraulic conductivity more than 10^{-3} m/s. Dur-

ing a rainfall event, a part of infiltrated water passes through a pile and emerges at its base in hours after the beginning of rain. However, a part of water in partially decomposed rock blocks is almost immobile. Fractures between large blocks are preferential flow zones during recharge period. During dry period, they drain first and then become barriers for water flow, which takes place mostly in fine grained material around fractures.

9.5 Prevention and Remediation of Acid Mine Drainage.

Acid drainage represents challenging problem for prevention and remediation. If mining residuals are responsible for its generation, several control and remediation options are available. Classical option is collection and treatment of leachate, but this is relatively costly. Other methods are based on the oxygen transport control.

The penetration of oxygen to mining residuals can be prevented by installation of fine-grained layer on the surface of mining residuals (Elberling, Nicholson, 1996). In this case, the effective diffusion coefficient for oxygen D_{O2} in the fine-grained material is low and so is the pyrite oxidation rate. It is related to rapid reduction of D_{O2} with increasing water saturation in fine grained material (see Fig. 9.2).

Another method is based on the application of organic material layer on the surface, in which the oxygen is consumed before its penetration to mining residuals in reaction like

$$CH_2O + O_2 \rightarrow CO_2 + H_2O \qquad 9.19$$

Potential problems are related to the formation of toxic methylated metal species under very reducing (methanogenic) conditions. The implementation of organic material cover has to be done immediately after closure of mine tailings. If the material in mine tailings is already partially oxidized, and there is large amount of $Fe(OH)_3$ in solid phase, then the implementation of organic cover could cause dissolution of $Fe(OH)_3$, and release of adsorbed metals. In some cases, mine tailings can be flooded completely to prevent contact with atmospheric oxygen. However, the flooding can decrease stability of mine tailings dams and may not be applicable in some cases.

When acid plume is already migrating in an aquifer, the situation becomes more complex. In this case, classical remediation and control technology is pump and treatment of acid water. In some situations, the volume of pumped and treated water is too large and application of this method can be inefficient. The injection of water with dissolved carbonates can be a plausible option. However, solubility of calcite under normal atmospheric pressure conditions is low and resulting bicarbonate concentration is only about 1 mmol/L (61 mg/L) with pH about 8.3. Furthermore, if water contains a significant quantity of iron, then the interaction of oxygenated alkaline water with the plume would results in precipitation of $Fe(OH)_3$ and in plugging of infiltration wells in short time period.

There are some new promising technologies for remediation of acid drainage plumes being developed. One of them is the installation of permeable reactive barrier (PRB) with crushed calcite and reducing material such as organic matter in the direction of acid plume migration. The barrier is located in the direction of the acid plume migration and must have higher permeability than the surrounding aquifer because in the opposite case it would be by-passed by the plume. There is neutralization of acid plume and reduction of sulfate within the PRB, followed by the precipitation of iron and other metals in secondary sulfides. The principal limitation of the method is the residence time requirement of 1 – 2 days within the wall to complete chemical reactions. Assuming the economically acceptable thickness of the wall of about 1 m, the maximum velocity of ground water flow for application of the method is 0.5 – 1.0 m/day.

9.6 Investigation of Acid Mine Drainage Sites

The investigation of mine tailings can be divided into investigation of unsaturated zone and saturated zone.

Common method of unsaturated zone investigation is the determination of O_2 and CO_2 concentration in pore space gas. This is done by inserting hollow needles connected to gas sensor on the ground surface. The result are O_2 and CO_2 profiles with depth, with decreasing and increasing concentrations, respectively. The O_2 profile can be used for calculation of pyrite oxidation rate. We can also use the O_2 profile to evaluate the performance of oxygen barriers. If there is high water saturation of fine grained material, then there is low O_2 concentration below the barrier (less than 2 vol %) with resulting low pyrite oxidation rate. There also is low O_2 concentration below organic matter layer.

Another important parameter is water saturation. High degree of water saturation is desirable because in this case diffusion coefficient for oxygen is low. The

most common method for determination of water saturation is based on the difference of weight of sample before and after drying. The method is tedious and can be used only once with a particular sample. Other methods are the application of time domain reflectometry (TDR) and neutron probe. Both methods require calibration and are costly. Thus, the oxygen profiles are the most common method for monitoring of unsaturated zone in mine tailings. Pore water in unsaturated zone can be collected by suction lysimeters.

Piezometers located at different depth are necessary to collect water in saturated zone of mine tailings because there generally is a significant vertical zonality of water chemistry. Another important parameter gained from piezometers are hydraulic heads. There generally are strong vertical gradients in the central part of mine tailings and flow becomes more horizontal in their periphery. Piezometers are also used to run slug or bail test and resulting values of K with values of hydraulic heads are used for modeling of flow in saturated zone of mine tailings. Monitoring of chemistry should be focused on index parameters (usually pH, total iron, aluminum etc.) determined in the initial stage of project.

Problems related to the sampling of acid mine drainage are discussed in Deutsch (1997). One of advantages is that the value of redox potential Eh corresponds well to the value based on Fe^{2+}/Fe^{3+} couple. Geochemical programs such as WATEQ4F (Plummer et al., 1976) can be used to predict which minerals could control concentrations of dissolved species in ground water. Solid phase composition is generally necessary for interpretation of data (Blowes and Jambor, 1990). The most important parameter is concentration of buffers like calcite and dolomite. Interpretation of water chemistry data can be improved by the determination of quantity of secondary sulfate minerals gypsum and jarosite in solid phase.

Situation in the case of waste rock piles is more complicated. Principal method is installation of thermistors and gas sampling ports at different depth (Lefebvre et al., 1993). Zones with high pyrite oxidation rate show positive temperature anomalies and high oxygen concentrations. These zones are generally located close to slopes and at the upper boundary of a waste rock pile (Sracek et al. 2004). It is possible to sample pore water in unsaturated zone of a pile by suction lysimeters (down to depth of about 15 m), but the method is complicated and rarely used. Much more common is the monitoring of the outflow from the saturated zone at the base of waste rock pile (Ritchie, 1994). However, water chemistry of the outflow represents mixing of water from different zones of the waste rock pile and interpretation of geochemical processes on the basis of the data is complicated.

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Chapter 10: Behavior of Radionuclides

10.1 Introduction

Lord Kelvin estimated the age of the solar system to be about 100 million years, based on the assumption that the energy of Sun was derived from gravitational collapse. In 1897 he revised this estimate downward to the range of 20 to 40 million years. Geologists were particularly skeptical of Kelvin's revised estimate, feeling the Earth must be older than this, but had no quantitative means of supporting their arguments. Radioactivity had been discovered about the same time (1896) by Frenchman Henri Becquerel. Only eleven years elapsed before Bertram Boltwood, an American chemist, published the first 'radiometric age'. He determined the lead concentrations in three samples of pitchblende, a uranium ore, and concluded they ranged in age from 410 to 535 million years.

Beyond providing precise ages of geologic events, radioactive decay is important because it provides natural tracers of geologic processes and because it provides information on the rates and pathways of geologic evolution. We might add dye to downwelling ocean water to trace deep ocean currents, or add a radioactive tracer to subducting lithosphere to trace mantle convection currents. In practice, however, even the contemplation of such experiments is a bit absurd. We would need far too much dye or radioactive tracer: the scales of distance and mass are simply too large for this kind of experiment. Even if we could overcome that obstacle, we would be long dead before any useful results came from our experiment: the rates of geologic processes are simply too slow. Nature, however, has provided natural tracers in the form of the radiogenic isotopes, which are products of natural radioactivity, and these tracers have been moving through the Earth since its beginning. With more quantitative observations we can use isotope ratios to estimate the rate of crustal evolution.

Two fundamental assumptions are involved in virtually all geologic uses of radiogenic isotope ratios. The first is that the rate of radioactive decay is independent of all external influences, such as temperature, pressure, etc. The second is that two isotopes of the same element are chemically identical and therefore that chemical processes cannot change, or fractionate, the ratio of two isotopes of the same elements.

10.2 The Structure of Nuclei

Nuclei are made up of various numbers of neutrons and protons. N represents the number of neutrons, the neutron number, and Z represents the number of protons, or proton number. Z is also the atomic number of the element, because the chemical properties of elements depend almost exclusively on the number of protons (since in the neutral atom the number of electrons equals the number of protons). The sum of Z and N is the mass number A.

Not all possible combinations of protons and neutrons result in stable nuclei. Typically for stable nuclei holds $N \approx Z$. Thus a significant portion of the nucleus consists of protons, which tend to repel each other. From the observation that nuclei exist at all, it is apparent that another force must exist which is stronger than coulomb repulsion at short distances. This force, called the strong force also binds quarks together to form hadrons, a class of particles that includes neutrons and protons. The intensity of the strong force decreases rap-

idly with distance, so that at distances more than about 10^{-14} m it is weaker than the electromagnetic force.

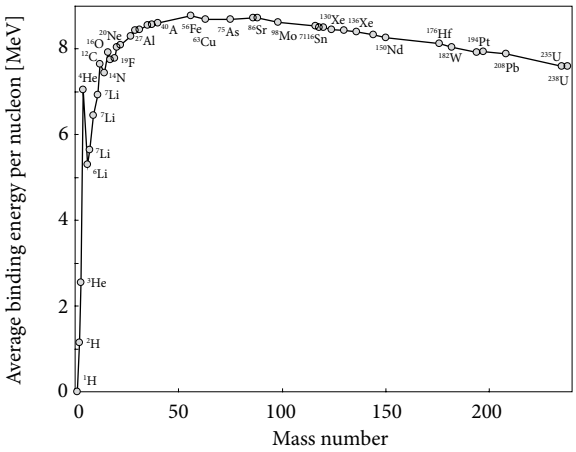


Figure 10.1 Binding energy per nucleon vs. mass number.

We expect that ^{4}He is stable relative to two free neutrons and two free protons, and then from Einstein's mass-energy equivalence

$$E = m\,c^2 \qquad 10.1$$

we can predict that the ^{4}He nucleus will have less mass that 2 free neutrons and 2 free protons. Thus we are able to predict the relative stability of various nuclei from their masses alone.

Calculation of the nominal weight of an atom from the sum of the mass of the constituent particles yields:

proton: 1.007593 daltons
(formally called amu,
atomic mass units) = 1.6726231 x 10^{-27} kg
neutron: 1.008982 daltons
electron: 0.000548756 daltons = 9.10093897×10^{-31} kg

Then we define the mass decrement of an atom as:

$$\delta = W - M \qquad 10.2$$

where W is the sum of the mass of the constituent particles and M is the actual mass of the atom.

For example, W for ^{4}He is $W = 2m_p + 2m_n + 2m_e$ = 4.034248 daltons. The mass of ^{4}He is 4.003873 daltons, so δ = 0.030375 daltons. Converting this to energy using Equation 10.1 yields 28.28 MeV. This energy is known as the binding energy. Dividing by A, the mass number, or number of nucleons, gives the binding energy per nucleon, E_b:

$$E_h = \left[\frac{W - M}{A}\right]c^2 \qquad 10.3$$

E_b is a measure of nuclear stability: those nuclei with the largest binding energy per nucleon are the most stable. Figure 10.1 shows E_b as a function of mass. Note that the nucleons of intermediate mass tend to be the most stable.

Some indication of the relative strength of the nuclear binding force can be obtained by comparing the mass decrement associated with it to that associated with binding an electron to a proton in a hydrogen atom. The mass decrement above is of the order of 1%, 1 part in 10^2. The mass decrement associated with binding an electron to a nucleus of the order of 1 part in 10^8, so bonds between nucleons are about 10^6 times stronger than bonds between electrons and nuclei.

Problem: Calculate the binding energies of ^{50}V, ^{50}Cr, and ^{50}Ti. Which of these 3 nuclei is the least stable? Which is the most stable?

Solution: The nucleus of ^{50}V consists of 23 protons and 27 neutrons, that of ^{50}Cr consists of 24 protons and 26 neutrons, that of ^{50}Ti consists of 22 protons and 28 neutrons. Atoms of these elements also have, respectively 23, 24, and 22 electrons. First we calculate W for each:
W (^{50}V) = 23 × 1.007593 + 27 × 1.008982 daltons + 23 × 0.000548756 = 50.429774 daltons
W (^{50}Cr) = 24 × 1.007593 + 26 × 1.008982 daltons + 24× 0.000548756 = 50.428934 daltons
W (^{50}Ti) = 22 × 1.007593 + 28 × 1.008982 daltons + 22 × 0.000548756 = 50.430615 daltons The actual masses (M) of these nuclides are: ^{50}V: 49.947162 daltons; ^{50}Cr: 49.946047 daltons; ^{50}Ti: 49.944792 daltons. Using equation 10.2 we calculate the mass decrement, and then divide by 50 to calculate the mass decrement per nucleon. We convert the result to kg using the conversion factor 1 dalton = 1.66 × 10^{-27} kg. We then multiply by the square of the speed of light (2.998 × 10^8 m/sec) to obtain the binding energy in kg-m/sec or joules. We use 1 J = 6.2415 × 10^{12} MeV to convert our answer to MeV. The results are shown in the table below.

Nuclide	Δ	δ	δ / A	E_b	E_b
daltons		kg	kg/nucleon	J/nucleon	MeV
^{50}V	0.482612	8.011449×10^{-28}	1.60229×10^{-29}	1.4401×10^{-12}	8.9885
^{50}Cr	0.482887	8.016014×10^{-28}	1.60320×10^{-29}	1.4410×10^{-12}	8.9937
^{50}Ti	0.484568	8.043919×10^{-28}	1.60878×10^{-29}	1.4460×10^{-12}	9.0245

Our results indicate that of the three, ^{50}V is the least stable and ^{50}Ti the most stable, though the difference is not that great.

Nuclei with even number of protons and neutrons are more stable than those with odd numbers of protons

or neutrons. Stable even-even configurations are most common; stable odd-odd configurations are particularly rare, as can be seen in Figure 10.2.

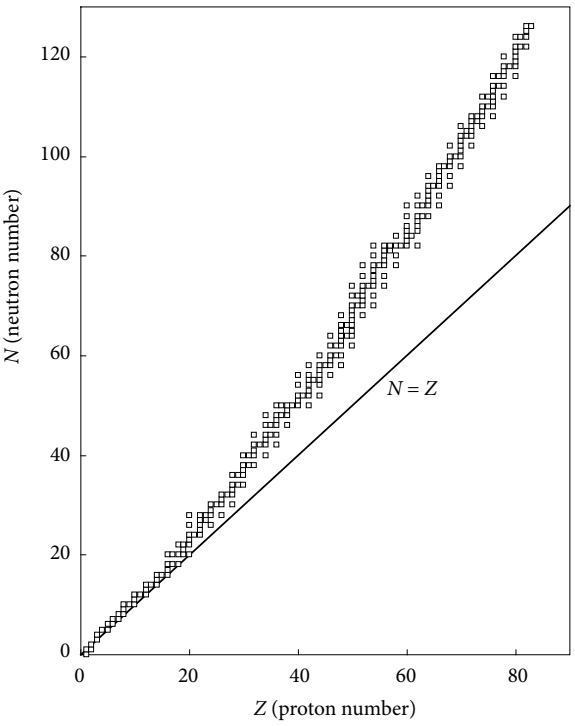


Figure 10.2. Neutron number vs. proton number for stable nuclides.

10.3 The Decay of Excited and Unstable Nuclei

Just as an atom can exist in any one of a number of excited states, so too can a nucleus have a set of discrete, quantized, excited nuclear states. The behavior of nuclei in transforming to more stable states is somewhat similar to atomic transformation from excited to more stable sites, but there are some important differences: (1) energy level spacing is much greater; (2) the time an unstable nucleus spends in an excited state can range from 10^{-14} sec to 10^{11} years, whereas atomic life times are usually about 10^{-8} sec; (3) excited atoms emit photons, but excited nuclei may emit other particles as well as photons. The photon emitted through the decay of unstable nuclei is called a gamma ray. In addition to the decay of an excited nucleus to a more stable state, it is also possible for an unstable nucleus to decay to an entirely different nucleus, through the emission or absorption of a particle of non-zero rest mass.

Nuclear decay takes place at a rate that follows the law of radioactive decay. The decay rate is dependent only on the nature and energy state of the nuclide. It is independent of the past history of the nucleus, and essentially independent of external influences such as temperature, pressure, etc. Also, it is impossible to predict when a given nucleus will decay. We can, however, predict the probability of its decay in a given time interval. The probability of decay of a nucleus in some infinitesimally small time interval, dt, is λ, where λ is called the decay constant. The probability of a decay among some number, N, of nuclides within dt is λ N. Therefore, the rate of decay of N nuclides is:

$$\frac{\mathrm{dN}}{\mathrm{d}t} = -\lambda \mathrm{N} \qquad 10.4$$

The minus sign simply indicates N decreases with time. Equation 10.4 is a first-order rate law.

10.3.1 Gamma decay

Gamma emission occurs when an excited nucleus decays to a more stable state. A gamma ray is simply a high-energy photon (i.e., electromagnetic radiation). Its frequency, ν, is related to the energy difference by:

$$h\nu = E_{\mathrm{u}} - E_{\mathrm{l}} \qquad 10.5$$

where E_{u} and E_{l} are the energies of the upper (excited) and lower (ground) states and h is Planck's constant. The nuclear reaction is written as:

$$^{\mathrm{N}}\mathrm{Z}^{*} \rightarrow {}^{\mathrm{N}}\mathrm{Z} + \gamma \qquad 10.6$$

where Z is the element symbol, N is the mass number, and γ denotes the gamma ray.

10.3.2 Alpha decay

An α-particle is simply a helium nucleus. Since the helium nucleus is particularly stable, it is not surprising that such a group of particles might exist within the parent nucleus before α-decay. Emission of an alpha particle decreases the mass of the nucleus by the mass of the alpha particle plus a mass equivalent to the energy lost during the decay, which includes the kinetic energy of the alpha particle, and the remaining nucleus, and any gamma ray emitted. The daughter may originally be in an excited state, from which it decays by γ decay. Figure 10.3 shows an energy-level diagram for such decay.

Alpha-decay occurs in nuclei with masses above the maximum in the binding energy curve of Figure 10.1, located at ^{56}Fe. Quite possibly, all such nuclei are un-

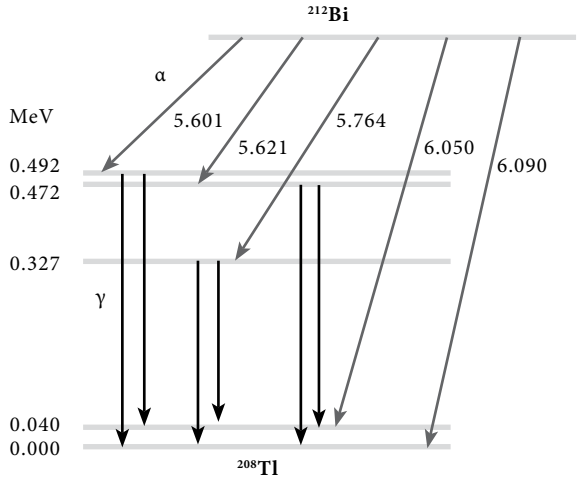


Figure 10.3 Nuclear energy-level diagram showing decay of bismuth 212 by alpha emission to the ground and excited states of thallium 208.

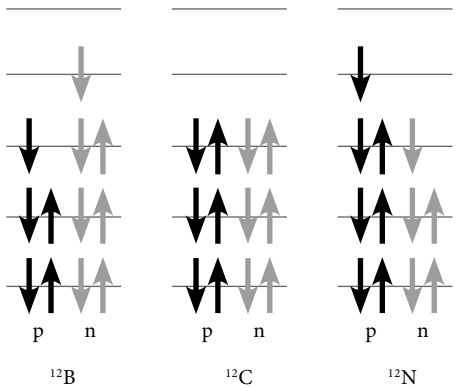


Figure 10.4 Proton and neutron occupation levels of boron 12, carbon 12 and nitrogen 12.

stable relative to alpha-decay, but the half-lives of most of them are immeasurably long.

10.3.3 Beta Decay

Beta decay is a process in which the charge of a nucleus changes, but not the number of nucleons. Beta-decay results in the emission of an electron or positron (a positively charged electron). Consider the 3 nuclei in Figure 10.4. These are known as isobars, since they have the same number of nucleons (12; isotopes have the same number of protons, isotones have the same number of neutrons). We can predict that the ^{12}C nucleus is the most stable of these three, because the spins of the neutrons and protons cancel each other. This is the case: ^{12}B decays to ^{12}C by the creation and emission of a β^- particle and the conversion of a neutron to a proton. ^{12}N decays by emission of a β^+ and conversion of a proton to a neutron. In β^- decay, a neutron is converted to a proton, giving up electron with –1 charge and leaving +1 charge in nucleus. In β^+ decay, a proton is converted to a neutron, giving up its +1 charge to a neutrino, which is converted to a positron.

10.3.4 Electron Capture

Another type of reaction is electron capture. This is sort of the reverse of beta decay and has the same effect, more or less, as β^+ decay. Interestingly, this is a process in which an electron is added to a nucleus to produce a nucleus with less mass than the parent! The missing mass is carried off as energy by an escaping neutrino, and in some cases by a γ. In some cases, a nucleus can decay by either electron capture, β^-, or β^+ emission. An example is the decay of ^{40}K, which decays to ^{40}Ar by β^+ or electron capture and to ^{40}Ca by β^-.

β decay and electron capture often leave the daughter nucleus in an excited state. In this case, it will decay to its ground state (usually very quickly) by the emission of a γ-ray. Thus γ rays often accompany β decay.

10.3.5 Spontaneous Fission

Fission is a process in which a nucleus splits into two or more fairly heavy daughter nuclei. In nature, this is a very rare process, occurring only in the heaviest nuclei, ^{238}U, ^{235}U, and ^{232}Th (it is, however, most likely in ^{238}U). When fission occurs, some free neutrons are produced and nuclear fragments (the daughters, which may range from A = 30, zinc, to A = 64, terbium) are too rich in neutrons to be stable. The immediate daughters will decay by β^- decay until enough neutrons have been converted to protons. It is this tendency to produce unstable nuclear by-products, rather than fission itself, which makes fission in bombs and nuclear reactors such radiation hazards.

Some unstable heavy nuclei and excited heavy nuclei are particularly subjected to fission. An important example is ^{236}U. When one ^{238}U undergoes fission, some of the released neutrons are captured by ^{235}U nuclei, producing ^{236}U in an excited state. This ^{236}U then fissions producing more neutrons, etc. This is the basis of nuclear reactors and bombs (actually, most now use some other nuclei, like Pu). In general, however, the concentration of U in nature is not high enough for this reaction to happen.

Individual fission reactions are less rare. When fission occurs, there is a fair amount of kinetic energy produced, the fragments literally flying apart. These frag-

ments damage the crystal structure through which they pass, producing 'tracks', whose visibility can be enhanced by etching. This is the basis of fission track dating.

10.4 Basics of Radiogenic Isotope Geochemistry

The basic equation of radioactive decay is:

$$\frac{dN}{dt} = -\lambda N \qquad 10.4$$

λ is the decay constant, which we defined as the probability that a given atom would decay in some time dt. It has units of time^{-1}. Let's rearrange equation 10.4 and integrate:

$$\int_{N_0}^{N} \frac{dN}{N} = \int_0^t dt \qquad 10.7$$

where N_0 is the number of atoms of the radioactive, or parent, isotope present at time t = 0. Integrating, we obtain:

$$\ln \frac{N}{N_0} = -\lambda t \qquad 10.8$$

This can be expressed as:

$$\frac{N}{N_0} = e^{-\lambda t} \qquad \text{or} \quad N = N_0\, e^{-\lambda t} \qquad 10.9$$

Suppose we want to know the amount of time for the number of parent atoms to decrease to half the original number, i.e., t when N/N_0 = 1/2. Setting N/N_0 to 1/2, we can rearrange 10.8 to get:

$$\ln 1/2 = -\lambda\, t_{1/2} \qquad \text{or} \quad \ln 2 = \lambda\, t_{1/2}$$

and finally:

$$t_{1/2} = \frac{\ln 2}{\lambda} \qquad 10.10$$

This is the definition of the half-life, $t_{1/2}$.

The decay of the parent produces some daughter, or radiogenic, nuclides. The number of daughters produced is simply the difference between the initial number of parents and the number remaining after time t:

$$D = N_0 - N \qquad 10.11$$

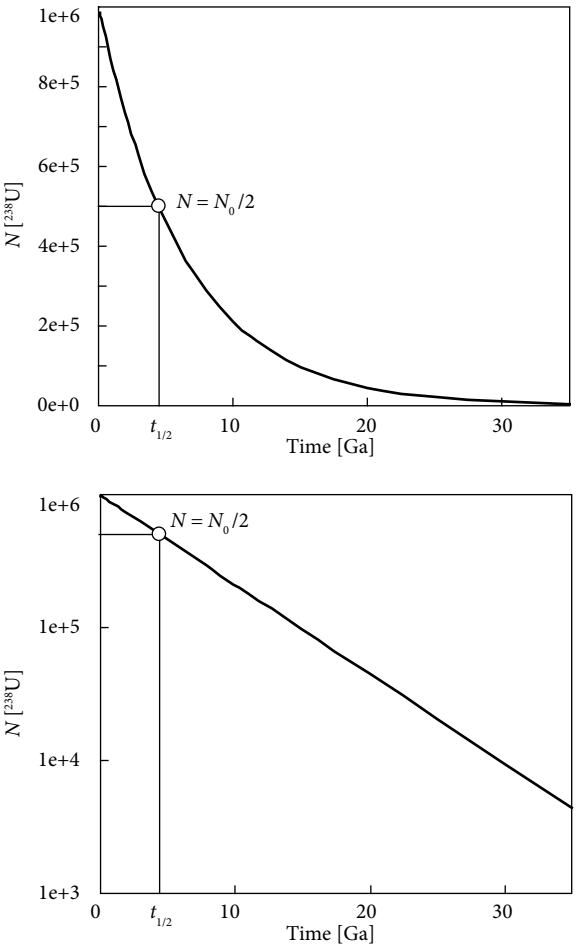


Figure 10.5 Radioactive decay is a first order reaction. Time dependence of ^{238}U atoms is on the left diagram. At half-time the number of ^{238}U is half of the original value (half-time for ^{238}U is 4.47 Ga). On logarithmic scale we get straight line (left diagram).

Rearranging 10.9 to isolate N_0 and substituting that into 10.11, we obtain:

$$D = N\, e^{\lambda t} - N = N\,(e^{\lambda t} - 1) \qquad 10.12$$

The number of daughters produced is a function of the number of parents present and time. Since in general there will be some atoms of the daughter nuclide around to begin with, i.e., when t = 0, a more general expression is:

$$D = D_0 + N\,(e^{\lambda t} - 1) \qquad 10.13$$

where D_0 is the number of daughters originally present. An exponential function can be expressed as a Taylor Series expansion:

$$e^{\lambda t} = 1 + \lambda t + \frac{(\lambda t)^2}{2!} + \frac{(\lambda t)^3}{3!} + \cdots \qquad 10.14$$

Provided $\lambda t << 1$, the higher order terms become very small and can be ignored; hence for times that are

short compared to the decay constant (i.e., for $t << 1/\lambda$), equation 10.13 can be written as:

$$D \quad D_0 + N \lambda t \qquad 10.15$$

Let's now write equation 10.13 using a concrete example, such as the decay of ^{87}Rb to ^{87}Sr:

$$^{87}Sr = {}^{87}Sr_0 + {}^{87}Rb\,(e^{\lambda t} - 1) \qquad 10.16$$

It is generally much easier, and usually more meaningful, to measure the ratio of two isotopes than the absolute abundance of one. We therefore measure the ratio of ^{87}Sr to a non-radiogenic isotope, which by convention is ^{86}Sr. Thus the useful form of 10.16 is:

$$\left(\frac{^{87}Sr}{^{86}Sr}\right) = \left(\frac{^{87}Sr}{^{86}Sr}\right)_0 + \left(\frac{^{87}Rb}{^{86}Sr}\right)\left(e^{\lambda t} - 1\right) \qquad 10.17$$

Similar expressions can be written for other decay systems.

Equation 10.17 is a concise statement of Sr isotope geochemistry: the $^{87}Sr/^{86}Sr$ ratio in a system depends on: (1) the $^{87}Sr/^{86}Sr$ at time $t = 0$, (2) the $^{87}Rb/^{86}Sr$ ratio of the system (in most cases, we can assume the $^{87}Rb/^{86}Sr$ ratio is directly proportional to the Rb/Sr ratio), and (3) the time elapsed since $t = 0$.

Table 10.1 lists the radioactive decay schemes of principal geologic interest. The usefulness and significance of each of the decay schemes are different and depend on the geochemical behavior of the parent and daughter, the half-life and the abundance of the parent.

Table 10.1 Long-Lived Radioactive Decay Systems of Geochemical Interest

Parent	Decay Mode	λ (y^{-1})	Half-life (y)	Daughter	Ratio
^{40}K	β^+, e.c., β^-	5.543×10^{-10}	1.28×10^{9}	^{40}Ar, ^{40}Ca	$^{40}Ar/^{36}Ar$
^{87}Rb	β^-	1.42×10^{-11}	4.8×10^{10}	^{87}Sr	$^{87}Sr/^{86}Sr$
^{138}La	β^-	2.67×10^{-12}	2.59×10^{11}	^{138}Ce	$^{138}Ce/^{142}Ce$, $^{138}Ce/^{136}Ce$
^{147}Sm	α	6.54×10^{-12}	1.06×10^{11}	^{143}Nd	$^{143}Nd/1^{44}Nd$
^{176}Lu	β^-	1.94×10^{-11}	3.6×10^{10}	^{176}Hf	$^{176}Hf/^{177}Hf$
^{187}Re	β^-	1.64×10^{-11}	4.23×10^{10}	^{187}Os	$^{187}Os/^{186}Os$, $^{187}Os/^{188}Os$
^{232}Th	α	4.948×10^{-11}	1.4×10^{10}	^{208}Pb, ^{4}He	$^{208}Pb/^{204}Pb$, $^{3}He/^{4}He$
^{235}U	α	9.849×10^{-10}	7.07×10^{8}	^{207}Pb, ^{4}He	$^{207}Pb/^{204}Pb$, $^{3}He/^{4}He$
^{238}U	α	1.551×10^{-10}	4.47×10^{9}	^{206}Pb, ^{4}He	$^{206}Pb/^{204}Pb$, $^{3}He/^{4}He$

Note: The branching ratio, i.e. ratios of decays to ^{40}Ar to total decays of ^{40}K is 0.117. The production of ^{4}He from ^{147}Sm decay is insignificant compared to that produced by decay of U and Th.

10.5 Geochronology

Geochronology is not our main interest here, but it is one of the most important applications of isotope geochemistry and the two are often closely intertwined. Let's rewrite equation 10.17 in more general terms:

$$R = R_0 + R_{P/D}\,(e^{\lambda t} - 1) \qquad 10.18$$

where R_0 is the initial ratio and $R_{P/D}$ is the parent/daughter ratio. Measurement of geologic time is based on this equation or various derivatives of it. Given a measurement of an isotope ratio, R, and a parent daughter ratio, $R_{P/D}$, two unknowns remain in equation 10.18: t and the initial ratio. We can calculate neither from a single pair of measurements. But if we can measure R and $R_{P/D}$ on a second system for which we believe t and R_0 are the same, we have two equations and two unknowns and subtracting the two equations yields:

$$\Delta R = \Delta R_{P/D}\,(e^{\lambda t} - 1) \qquad 10.19$$

which we can solve for t. Rearranging:

$$\frac{\Delta R}{\Delta R_{P/D}} = e^{\lambda t} - 1 \qquad 10.20$$

t may then be solved for as:

$$t = \frac{\ln\left(\frac{\Delta R}{\Delta R_{P/D}} + 1\right)}{\lambda} \qquad 10.21$$

We can obtain the ratio $\Delta R/\Delta R_{P/D}$ from any two data points, regardless of whether they are related or not. To overcome this problem in practice, many pairs of measurements of R and $R_{P/D}$ are made. Note that equation 10.18 has the form $y = a + b\,x$, where y is R, a is the intercept, R_0, b is the slope, $e^{\lambda t} - 1$, and x is $R_{P/D}$. An equation of this form is, of course, a straight line on a plot of R vs. $R_{P/D}$ such as Figure 10.6. The slope of the line passing through the data is thus related to the age of the system and line is called an isochron. When multiple measurements of the daughter isotope ratio and parent-daughter ratio are available, the slope, $\Delta R/\Delta R_{P/D}$, can be calculated by the statistical technique of linear regression. The age is then obtained by substituting the value of the slope into equation 10.21. Regression also yields an intercept, which is simply the initial ratio R_0 since, as may be seen from equation 10.18, $R = R_0$ when $R_{P/D} = 0$.

There are two important assumptions built into the use of equation 10.18. (1) The system of interest was at isotopic equilibrium at time $t = 0$. Isotopic equilibrium in this case means the system had a homogeneous, uniform value of R_0. (2) The system as a whole and each

analyzed part of it was closed between $t = 0$ and time t (usually the present time). Violation of these conditions is the principal source of error in geochronology.

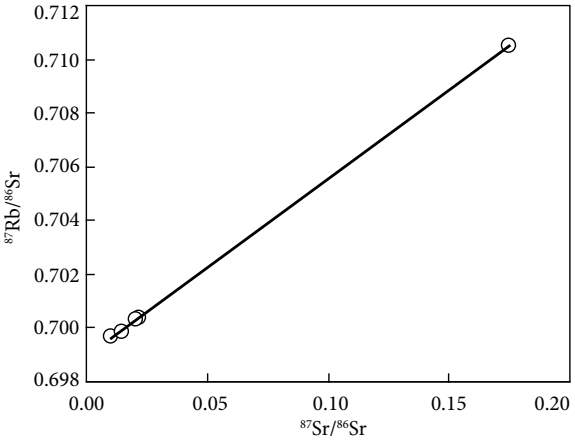


Figure 10.6 A Rb-Sr isochron. Five analyses from a clast in the Bholghati meteorite fall on an isochron, whose slope is related to the age of the system. Data from Nyquist et al. (1990).

10.6 Decay Systems and their Applications

10.6.1 Rb-Sr

This decay system was one of the first to be widely used in geochronology and remains one of the most useful geochemical tracers. An important advantage of the system is relatively large variations of the Rb/Sr ratio in rocks. Because of the difference in geochemical properties of the two elements, Rb/Sr can vary by several orders of magnitude. Since the accuracy of an age determination depends heavily on the spread of measured ratios, this makes the Rb-Sr system a useful geochronological tool. Rb is a highly soluble, highly incompatible element. Sr is also relatively soluble and is fairly incompatible in mafic and, particularly, ultramafic systems. However, it is relatively compatible in silica-rich igneous systems, partitioning preferentially into plagioclase. The result is that the mantle has a relatively uniform and low $^{87}Sr/^{86}Sr$ ratio, and the continental crust has a much more variable, and, on average, higher ratio.

Problem: The following $^{87}Rb/^{86}Sr$-$^{87}Sr/^{86}Sr$ data were measured by Nyquist et al. (1990) on a clast within the achondritic meteorite Bholghati. These data are plotted in Figure 10.6. What is the age and error on the age of this clast? What is the initial $^{87}Sr/^{86}Sr$ ratio of the clast and the error on this ratio?

$^{87}Rb/^{86}Sr$	$^{87}Sr/^{86}Sr$
0.01015	0.69966
0.17510	0.71052
0.02166	0.70035
0.02082	0.70029
0.01503	0.69988

Solution: We can calculate the age using equation 10.21 above. The value of $\Delta R/\Delta R_{P/D}$ is the 'slope' of the isochron, i.e., the slope of a line through the data on a plot of $^{87}Sr/^{86}Sr$ vs. $^{87}Rb/^{86}Sr$. We will use simple least squares linear regression to obtain the slope and intercept; the latter will be the initial $^{87}Sr/^{86}Sr$ ratio.

Spreadsheet is shown below. Usually toady the spreadsheets have built in statistical functions including linear regression (something like LINREG or similar). To make it easier to read, the cells containing calculated parameters have some explanatory notes. It is fairly straightforward to calculate the slope, *b*, the intercept, *a*, and the errors on the slope and intercept. Our result is that the age of the clast is 4.51 ± 0.02 Ga (Ga is the abbreviation for gigayears, 10^9 years). At that time, the $^{87}Sr/^{86}Sr$ ratio of the clast was 0.69893 ± 0.00003.

	$^{87}Rb/^{86}Sr$	$^{87}Sr/^{86}Sr$		
	0.01015	0,69966		
	0.17510	0,71052		
	0.02166	0,70035		
	0.02082	0,70029		
	0.01503	0,69988		
b =	0,06619769	0,698926	= a	
se_b =	0,00031116	2,49E-05	= se_a	
r^2 =	0,99993372	4,41E-05	= se_y	
F =	45259,4217	3	= degree of freedom	
ss_{reg} =	8,8103E-05	5,84E-09	= ss_{resid}	

λ =	1,42E-11	y^{-1}	se_a	standard error of a
$t = \ln(b+1)/\lambda$ =	4,514E+09	y	se_b	standard error of b
t =	4,514	Ga	se_y	standard error of y estimation
$t_{er} = \ln(se_b+1)/\lambda$ =	0,022	Ga	R^2	coeficient of determination
			F	F-statistic
			ss_{reg}	sum of regresion square
			ss_{resid}	sum of residual square

Exact meaning of each statistical parameter is beyond the scope of this text and you have to look in appropriate textbook

The Sr isotopic evolution of the Earth and its major silicate reservoirs (the continental crust and mantle) is illustrated in Figure 10.7, which is a plot of $^{87}Sr/^{86}Sr$

vs. time (in giga-annum, or billions of years). Such a plot is called an isotope evolution diagram. A characteristic of such diagrams is that a closed reservoir will evolve along a line whose slope is proportional to the parent-daughter ratio, in this case $^{87}Rb/^{86}Sr$. This is easy to show from equation 10.17. When $t << 1/\lambda$, then equation 10.17 becomes:

$$^{87}Sr / {}^{86}Sr = (^{87}Sr / {}^{86}Sr)_0 + (^{87}Rb / {}^{86}Sr)\,\lambda t \qquad 10.22$$

This equation has the form: $^{87}Sr / {}^{86}Sr = a + b\,t$ (i.e., the equation of a straight line on a plot of $^{87}Sr/^{86}Sr$ vs. t with slope $\lambda\ ^{87}Rb/^{86}Sr$ and intercept $^{87}Sr/^{86}Sr)_0$ (to the degree that the Taylor Series approximation is not exact, the line will actually be curved, but the approximation is fairly good in this case). In Figure 10.7 we have plotted geologic age rather than the time since $t = 0$; in other words, we have transformed t to $(4.55 - t)$, where 4.55 Ga is the assumed age of the Earth. Thus the intercept occurs at $t = 4.55$ rather than 0.

The initial $^{87}Sr/^{86}Sr$ ratio of the Earth can be estimated from the initial ratio in meteorites under the assumption that the entire solar system had a uniform $^{87}Sr/^{86}Sr$ at the time it was formed. Once it forms, the Earth is a closed system, so it evolves along a straight line with slope proportional to the bulk Earth $^{87}Rb/^{86}Sr$. This ratio has been estimated in various ways to be about 0.085 (as we noted is the $^{87}Rb/^{86}Sr$ is proportional to the Rb/Sr ratio; the bulk Earth Rb/Sr is about 0.029).

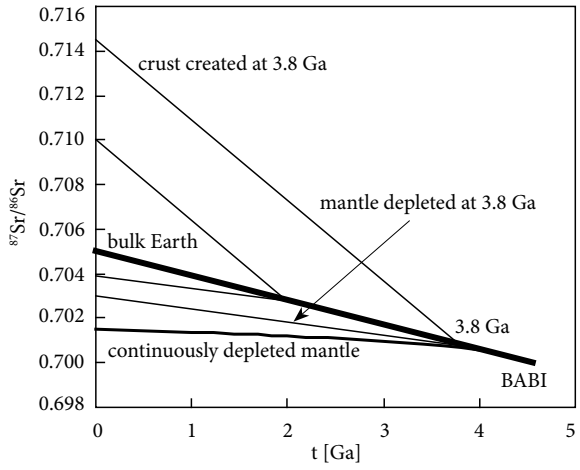


Figure 10.7 Sr isotopic evolution of the bulk Earth, evolution of high Rb/Sr crust created at 3.8 Ga, evolution of the resulting residual mantle and the evolution of a mantle being continuously depleted. 'BABI' stands for basaltic achondrite best initial, and is the assumed initial $^{87}Sr/^{86}Sr$ of the solar system

10.6.2 U-Th-Pb

The U-Th-Pb system is somewhat of a special case since there are 3 decay schemes producing isotopes of Pb. In particular two U isotopes decay to two Pb isotopes, and since the two parents and two daughters are chemically identical, we get two decay systems which together provide a particularly powerful tool.

Following convention, we will designate the $^{238}U/^{204}Pb$ ratio as μ, and the $^{232}Th/^{238}U$ ratio as κ. The ratio $^{238}U/^{235}U$ is constant in the Earth at 137.88. Now, we can write two versions of equation 10.18 as:

$$\frac{^{207}Pb}{^{204}Pb} = \left(\frac{^{207}Pb}{^{204}Pb}\right)_0 + \frac{\mu}{137.88}\left(e^{\lambda_{235}t} - 1\right) \qquad 10.23$$

and

$$\frac{^{206}Pb}{^{204}Pb} = \left(\frac{^{206}Pb}{^{204}Pb}\right)_0 + \mu\left(e^{\lambda_{238}t} - 1\right) \qquad 10.24$$

Equations 10.23 and 10.24 can be rearranged by subtracting the initial ratio from both sides. Using Δ to designate the difference between the initial and the present ratio, equation 10.24 becomes:

$$\Delta\frac{^{206}Pb}{^{204}Pb} = \mu\left(e^{\lambda_{238}t} - 1\right) \qquad 10.25$$

Dividing the equivalent equation for ^{235}U-^{207}Pb by equation 10.23 yields:

$$\frac{\Delta\frac{^{206}Pb}{^{204}Pb}}{\Delta\frac{^{207}Pb}{^{204}Pb}} = \frac{1}{137.88}\frac{\left(e^{\lambda_{238}t} - 1\right)}{\left(e^{\lambda_{235}t} - 1\right)} \qquad 10.26$$

The left-hand side of this equation is the slope of line on a plot of $^{207}Pb/^{204}Pb$ vs. $^{206}Pb/^{204}Pb$ such as Figure 10.8. The slope depends only on time and three constants (λ_{238}, λ_{235}, and $^{238}U/^{235}U$). Because its slope depends on time, a line on a plot of $^{207}Pb/^{204}Pb$ vs. $^{206}Pb/^{204}Pb$ is an isochron, analogous to the isochrons in a plot such as Figure 10.6.

The equation 10.26 cannot be solved directly for t. However, we can guess a value of t, plug it into the equation, calculate the slope, compare the calculated slope with the observed one, revise our guess of t, calculate again, etc.

Because the half-life of ^{235}U is much shorter than that of ^{238}U, ^{235}U decays more rapidly. As a result, on a plot $^{207}Pb/^{204}Pb$ vs. $^{206}Pb/^{204}Pb$, Pb isotopic evolution follows curved paths. The exact path that is followed depends upon μ. Three such evolution curves are shown in Figure 10.8. All systems that begin with a common initial isotopic composition at time t_0 along a straight line at some later time t.

As for Th we can combine the growth equations for $^{208}Pb/^{204}Pb$ and $^{206}Pb/^{204}Pb$ in a way similar to equation 10.26. We end with

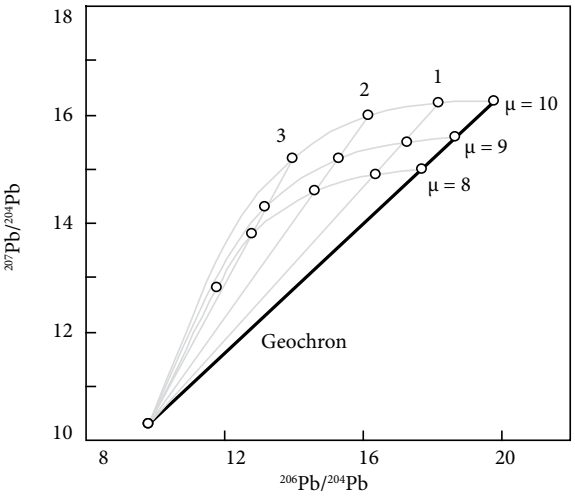


Figure 10.8 Evolution of Pb isotope ratios. The curve lines represent the evolutionary paths for systems having μ values of 8, 9, and10. The hash marks on the evolution curves mark Pb isotope compositions 1.0, 2.0, and 3.0 Ga ago.

$$\frac{\Delta\frac{^{208}Pb}{^{204}Pb}}{\Delta\frac{^{206}Pb}{^{204}Pb}} = \frac{\kappa\left(e^{\lambda_{232}t}-1\right)}{\left(e^{\lambda_{238}t}-1\right)} \qquad 10.27$$

where κ is the $^{232}Th/^{238}U$ ratio.

Provided κ is constant in a series of cogenetic rocks (by cogenetic we mean that at $t = 0$ they all had identical Pb isotope ratios), the slope of an array on a plot of $^{208}Pb/^{204}Pb$ and $^{206}Pb/^{204}Pb$ will depend only on t and κ, and not on the parent-daughter ratios. We can calculate κ from the slope of the data on a plot of $^{208}Pb/^{204}Pb$ *vs* $^{206}Pb/^{204}Pb$. U and Th are both highly incompatible elements. They have similar, but not identical, partition coefficients in most minerals. It seems unlikely that they will behave identically, and hence unlikely that κ will very often be constant. It can be shown that if κ varies and is positively correlated with variations in μ then equation 10.27, when solved for κ, will actually overestimate it.

10.6.3 U and Th Decay Series

U and Th do not decay directly to Pb, rather the transition from U and Th to Pb passes through many intermediate radioactive daughters (Figure 10.9). Many of these daughters have very short half-lives, ranging from milliseconds to minutes, and are of little use to geochemists. However, a number of these intermediate daughters have half-lives ranging from days to hundreds of thousands of years and do provide useful information about geological processes. Table 10.2 lists half-lives and decay constants of some of the most useful of these nuclides.

Table 10.2 Half-lives and decay constants of long-Isotopes lived U and Th daughters

Nuclide	Half-life, yrs	Decay constant, y^{-1}	Parent
^{234}U	246,000	2.794×10^{-6}	^{238}U
^{231}Pa	32,480	2.134×10^{-5}	^{235}U
^{230}Th	75,200	9.217×10^{-6}	^{238}U
^{226}Ra	1,622	4.272×10^{-4}	^{238}U
^{228}Ra	6.7	1.06×10^{-1}	^{232}Th
^{210}Pb	22.26	3.11×10^{-2}	^{238}U

The half lives of all of these daughter isotopes are short enough so that any atoms present when the Earth formed have long since decayed (to Pb). They exist in the Earth (and in all other bodies of the solar system) only because they are continually produced by the decay of U and Th. The abundance of such an isotope depends on the balance between its own radioactive decay and its production by the decay of its parent:

$$\frac{dN_D}{dt} = \lambda_P N_P - \lambda_D N_D \qquad 10.28$$

where subscripts P and D refer to parent and daughter respectively. This equation says simply that the rate of change of the abundance of the daughter isotope is equal to the rate of production less the rate of decay. This can be integrated to give:

$$N_D = \frac{\lambda_P}{\lambda_D - \lambda_P} = N_P^0\left(e^{-\lambda_P t} - e^{-\lambda_D t}\right) + {}_P - N_D^0 e^{-\lambda_D t} \qquad 10.29$$

Scientists dealing with the intermediate daughters of U and Th (and it is the daughters of ^{238}U that are of the most interest), generally work with activities, measured in the number of decays per unit time, rather than atomic abundances. One reason for this is that the abundances of these isotopes are generally determined by detecting their decay. Indeed, the shorter-lived ones are so rare they cannot be detected any other way. The other reason will become apparent shortly. Activities are related to atomic (molar) abundances by the basic equation of radioactive decay:

$$\frac{dN_i}{dt} = -\lambda_i N_i \qquad 10.30$$

where dN_i/dt is the *activity* of *i*. Activity is most commonly expressed in units of disintegrations per minute (dpm) and is denoted by writing parentheses around the isotope (or the isotope ratio). Thus (^{234}U) is the activity of ^{234}U.

The radioactive equilibrium state of the daughter and the parent is the condition where their activities are equal, i.e.:

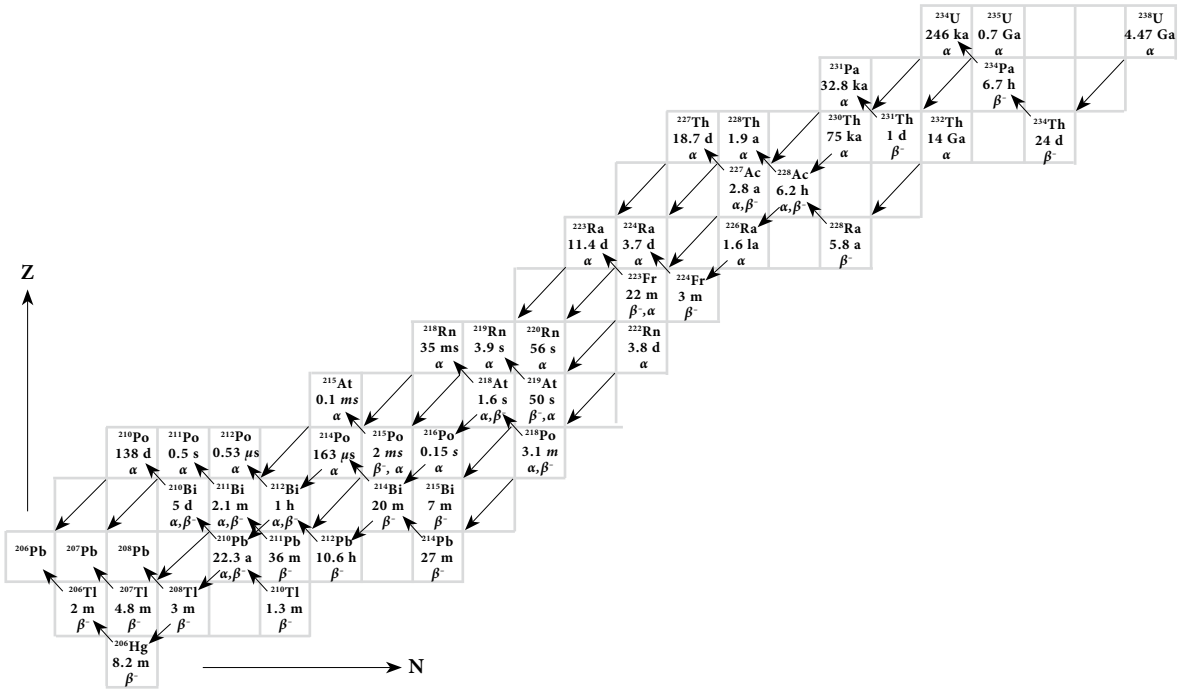


Figure 10.9 Part of the chart of the nuclides showing the series of decays that occur as ^{238}U, ^{235}U, and ^{232}Th are transformed to ^{206}Pb, ^{207}Pb, and ^{208}Pb respectively.

$$\frac{dN_D}{dt} = \frac{dN_P}{dt} \qquad 10.31$$

It shares the same fundamental characteristic as the chemical equilibrium state: it is the state that will eventually be achieved if the system is not perturbed (remains closed). We can demonstrate this is so in two ways. The first is a simple mathematical demonstration. The equilibrium state is the steady state where the abundance of the daughter does not change, i.e., where the left hand side of 10.28 is zero:

$$0 = \lambda_P N_P - \lambda_D N_D \qquad 10.32$$

We substitute the dN/dt terms for the λN terms in 10.31, rearrange, and we obtain 10.32.

Thus when a system is disturbed it will ultimately return to equilibrium. The rate at which it returns to equilibrium is determined by the decay constants of the parent and daughter. If we know how far out of equilibrium the system was when it was disturbed, we can determine the amount of time that has passed since it was disturbed by measuring the present rate of decay of the parent and daughter. Equilibrium is approached asymptotically, and these dating schemes are generally limited to time scales less than 5–10 times the half-life of the daughter. At longer times, the difference between actual activities and equilibrium ones becomes too small to measure reliably.

In most instances, the activities are measured by alpha-counting and fairly large quantities of material are necessary. But improvements in mass spectrometry have made it possible to measure the

^{230}Th/^{232}Th ratio (which is of the order of 10^{-6} in igneous rocks) in relatively small quantities of material with better precision than α counting.

10.6.4 Isotopes of He

Alpha particles are, of course, simply ^{4}He nuclei, and therefore ^{4}He is produced by alpha decay of U and Th. Thus the ratio of ^{4}He/^{3}He varies in the Earth. He is not conserved on the Earth: much of the He present when the Earth formed has been subsequently lost. Being a rare gas, He does not combine chemically with anything, and it also diffuses rapidly. Helium brought to the Earth's surface by magmatic processes eventually finds its way into the atmosphere. Once there, it can escape from the top of atmosphere because of its low mass. Since ^{4}He is continually produced and, for all practical purposes, ^{3}He is not, the ^{4}He/^{3}He ratio in the Earth is a very large number. For some reason, the He isotope ratio is generally expressed as ^{3}He/^{4}He, in contradiction to the normal convention of placing the radiogenic isotope in the numerator.

The ^{3}He/^{4}He ratio of the atmosphere is 1.384×10^{-6}. Since this ratio is uniform and atmospheric He available to all laboratories, it is a convenient standard and moreover provides the basis for a convenient normalization. He ratios are often reported and discussed rela-

tive to the atmospheric value. The units are called simply R/R_A, where R_A indicates the atmospheric ratio.

Figure 10.10 illustrates the He isotopic composition of various terrestrial reservoirs. Oceanic islands and other hotspots often have even higher ratios, up to about $R/R_A \approx 24$, though some islands, Tristan da Cunha for example, have lower ratios: $R/R_A \approx 5$ (e.g., Kurz et al., 1982). This suggests that most oceanic island basalts are derived from a less degassed, and in that sense more primordial, reservoir than MORB. This is consistent with the mantle plume hypothesis.

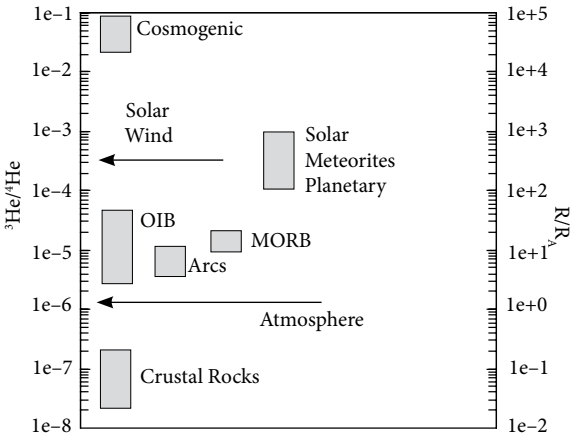


Figure 10.10 He isotope ratios in various terrestrial and solar system materials. "Solar" and "Planetary" refer to the solar and planetary components in meteorites. "Crustal rocks" shows the values expected for in situ production from α decay and neutron-induced nuclear reactions.

Island arc volcanics (IAV) seem also to be fairly uniform with $R/R_A \approx 6$ (Lupton, 1983). Ratios lower than MORB suggest the presence of a slab-derived component, but also indicate most of the He in IAV comes from the mantle wedge (a conclusion similar to the one reached from other radiogenic isotopes).

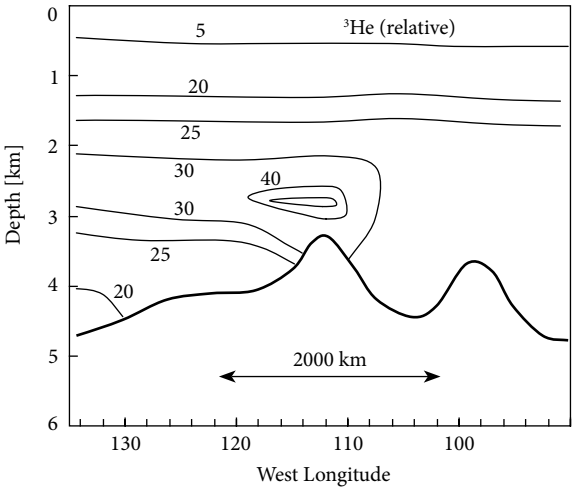


Figure 10.11 Contours of relative ^{3}He concentrations in seawater over the East Pacific Rise (Lupton and Craig, 1981).

Since He is injected at mid-ocean ridges, particularly in the Pacific, at depths of 2500–3000 meters, He isotopes can be used to trace water mass movements. Figure 10.11 shows the He plume of hydrothermal activity on the East Pacific Rise. Interestingly, the plume indicates water is flowing in the direction opposite to that which the physical oceanographers had thought. Another application is prospecting for ridge-crest hydrothermal activity. Several hydrothermal areas (including the first one) have been discovered from the He isotope anomalies in the water column. ^{4}He is also used as a tracer in U prospecting.

10.6.5 K-Ar-Ca

There are several aspects of the K-Ar system that make it particularly advantageous for some geochronological applications. First ^{40}K has one of the shortest half-lives of the decay systems in Table 10.1, making it more useful for dating young rocks than the other systems. In favorable cases, K-Ar ages on rocks as young as 50,000 yrs can be obtained with useful precision. Second, Ar is a rare gas and in most volcanic rocks and in many other rocks it is virtually totally lost when the system is reset. Thus an age can be obtained from a single K-Ar determination. Being a rare gas, Ar diffuses somewhat more readily than other elements. Further, K is concentrated in sheet silicates such as micas, which have comparatively open crystal structures. As a result, the closure temperature for the K-Ar system is low, making it a useful system for study of relatively low temperature phenomena (such as petroleum genesis). This of course, can be a disadvantage, as it means the K-Ar system is reset rather easily.

Most of ^{40}K (90%) decays to ^{40}Ca. This decay scheme has not yielded much geochemical or geochronological information so far. The reason is the low ratio of ^{40}K to ^{40}Ca in most geological materials, which in turn means the radiogenic contribution to ^{40}Ca is small and ^{40}Ca/^{42}Ca variations are very small. Also since the isotopes are rather light, they are comparatively easily fractionated.

10.6.6 Cosmogenic Isotopes

The Earth is constantly bombarded by 'cosmic rays' (we shouldn't feel picked on, the entire cosmos is). These are atomic nuclei (mostly H) stripped of their electrons and traveling at relativistic velocities. Some originate in the Sun, but most originate in high-energy regions of the cosmos such as supernovae. For the most part their origin is not well understood. What is understood is

that they have sufficient energy to shatter a nucleus when they collide with one. The nucleus breaks into several parts in a process called *spallation*. Spallation is the process in which a nucleus breaks into smaller nucleii as a result of a collision with a very high energy particle such as a cosmic ray.

Cosmic rays don't have much penetrating power. Thus the intensity of cosmic radiation increases with increasing altitude in the atmosphere. Most are stopped in the atmosphere, their interactions creating a cascade of lesser energy particles, or are slowed considerably. Even if they don't score a direct hit, they lose energy through electromagnetic interaction with matter (ionizing the atoms they pass by. Thus cosmic rays have their greatest effect in the atmosphere.

Nitrogen and oxygen, being the principal constituents of the atmosphere are the most common targets, yet there is no change in the isotopic abundances of these elements. Cosmic radiation is most interesting because of the production of nuclides whose half-lives are so short they would not otherwise exist. The nuclides of greatest interest are listed in Table 10.3 along with their half lives and their decay constants. These nuclides are created either directly through spallation (e.g., ^{10}Be), or by nuclear reactions with particles produced by spallation, e.g., ^{14}C: ^{14}N (n,p)$\rightarrow$^{14}C.

Table 10.3 Some Cosmogenic Nuclides of Geologic Interest.

Nuclide	Half-life (y)	λ (y^{-1})
^{10}Be	1.5×10^{6}	0.462×10^{-6}
^{14}C	5730	0.1209×10^{-3}
^{26}Al	0.716×10^{6}	0.968×10^{-6}
^{36}Cl	0.308×10^{6}	2.25×10^{-6}
^{39}Ar	269	0.257×10^{-2}

10.6.6.1 ^{14}C and ^{13}C

The most well-known of the cosmogenic nuclide dating methods is based on ^{14}C. It is useful in dating archaeological, climatological, volcanological, seismological, paleontological, hydrological, etc., 'events'. Present technology utilizes accelerator mass spectrometry rather than traditional β-counting and useful information on samples as old as 40,000 years can be produced. The principle of this method is quite simple. One assumes a constant production of ^{14}C in the atmosphere. The atmosphere is well-mixed and has a uniform ^{14}C activity equal to 100 pmc (percent of modern carbon). The activity of ^{14}C isolated from atmosphere will decrease in time by decay with a half-life of 5730 years. Apparent age of a carbon sample is calculated as

$$t = -8267 \ln\left(\frac{\alpha_t\ ^{14}C}{\alpha_0\ ^{14}C}\right) \qquad 10.33$$

where α_t is ^{14}C activity measured in a sample and α_0 is initial ^{14}C activity (e.g., 100 pmc). In actuality, the production rate appears not to have been constant. Furthermore, the ^{14}C activity in present atmosphere is somewhat lower than it has been in the recent past due to the dilution with CO_2 released by extensive burning of fossil fuels. By comparing of ^{14}C ages with absolute ages derived from tree rings, variations in the atmospheric ^{14}C activity over the past several thousand years have been deduced. This means accurate ages ^{14}C ages can be obtained despite production rate variations. Efforts are underway to extend this calibration further by comparing ^{14}C ages with U-series disequilibrium ages.

There are some complications in the behavior of ^{14}C during recharge, so the "absolute" age of a groundwater cannot be determined reliably. These complications stem from the fact that ^{14}C is not a part of water molecule, but is only incorporated into dissolved inorganic carbon (DIC) transported by ground water flow. Then ^{14}C activity may be modified by geochemical reactions. However, if the ^{14}C activity is measured at several points along a flow line within an aquifer, the differences in age between the points and hence the flow velocity can be determined. The complications are as follows: (1) dissolution of carbonate minerals or oxidation of organic matter within the aquifer may add carbon to the water, which has no detectable amount of ^{14}C giving an erroneously old age; (2) mixing of waters. A low ^{14}C activity may mean that we have relatively old water, or a mixture of relatively young water and old water. ^{14}C measurements can be interpreted as ages only where mixing is insignificant.

There are many sophisticated methods of ^{14}C age corrections and their complete review is beyond scope of this text. Detailed treatment of this issue is, for example, in Clark and Fritz (1997), and in Kalin (2000). Correction is performed by multiplication of initial ^{14}C activity by correction factor *q*.

So called Statistical approach (STAT), when typical correction factors *q* are:
0.65 – 0.75 for karst
0.75 – 0.90 for sediments with carbonates in matrix
0,90 – 1.0 for crystalline rocks

Tamers model based on alkalinity (ALK model): This method assumes a system closed to CO_2 and generally results in $q = 0.5$.

$$q_{ALK} = \frac{m_{H_2CO_3} + 0.5\ m_{HCO_3}}{m_{H_2CO_3} + m_{HCO_3}} \qquad 10.34$$

where *m* indicates concentrations of different dissolved carbon species.

Method based on the application ^{13}C: The ^{13}C is stable isotope of carbon, which does not decay, but can undergo fractionation in geochemical reactions. For example, dissolution of carbonates changes ^{13}C concentration in water (makes ^{13}C concentration higher). Concentration of ^{13}C is expressed in so called delta notation as $\delta^{13}C$. Correction factor is calculated as

$$q_{\delta^{13}C} = \frac{\delta^{13}C_{DIC} - \delta^{13}C_{carb}}{\delta^{13}C_{recharge} - \delta^{13}C_{carb}} \qquad 10.35$$

where $\delta^{13}C_{DIC}$, $\delta^{13}C_{carb}$, and $\delta^{13}C_{recharge}$ indicate values of $\delta^{13}C$ for DIC, carbonates and recharging water, respectively. Situation is complicated by the fact that value of $\delta^{13}C_{recharge}$ for recharging water in the past is not known and has to be estimated. The value depends especially on pH value and there is a possibility of significant errors (see examples in Clark and Fritz, 1997).

There are other correction methods like method of Fontes and Garnier, based on both $\delta^{13}C$ and water chemistry and mass-balance geochemical modeling (Plummer et al., 1994) based on concentration changes along flow path (Clark and Fritz, 1997).

Other interesting applications include determining the 'age' of deep water in the oceans. By comparing ^{14}C activities of benthic and planktonic foraminifera in a single sedimentary horizon, it is possible to determine bottom water ages in the past, and hence constrain 'paleocirculation' rates.

10.6.6.2 ^{36}Cl in hydrology

^{36}Cl has been applied to hydrological problems for some time. The general principle is that ^{36}Cl is produced at a constant rate in the atmosphere, carried to the surface of the Earth in rain and incorporated into hydrological systems. Cl is an excellent candidate element for such studies because it should remain in solution in most instances, and hence the only loss should be through radioactive decay. In a simple system the rainwater is incorporated into an aquifer at some unknown time in the past. In this case, if we can specify the number of ^{36}Cl atoms per liter in rain and if we can assume this value is time-invariant, then we can determine the age of water in the aquifer by measuring the number of ^{36}Cl atoms per liter since:

$$^{36}Cl = {}^{36}Cl_0\, e^{-\lambda t} \qquad 10.36$$

Determining the age of water in underground aquifers is an important problem because of the increasing demands placed in many parts of the world on limited water resources. A prudent policy for water resource management is to withdraw from a reservoir at a rate no greater than the recharge rate. Determination of recharge rate is thus prerequisite to wise management.

Dealing with just the number, or concentration, of ^{36}Cl atoms can have disadvantages, and can be misleading. Evaporation, for example, would increase the number of ^{36}Cl atoms. Thus the $^{36}Cl/Cl$ ratio (Cl has two stable isotopes: ^{35}Cl and ^{37}Cl) is often used. This also can have problems since chlorine can be leached from rocks. This chlorine will be nearly free of ^{36}Cl (some ^{36}Cl will be produced naturally by neutron capture), and hence this process will decrease the $^{36}Cl/Cl$ ratio. Further complications arise from the nuclear bomb-produced ^{36}Cl. Particularly large amounts were produced by nuclear bomb testing at sea, where bomb-produced neutrons were captured by ^{35}Cl in seawater.

In a somewhat different application, Paul et al. (1986) used ^{36}Cl to determine the accumulation time of dissolved salt in the Dead Sea. The Dead Sea is a particularly simply hydrologic system because it has no outlet. In such a simple system, we can describe the variation of the number of ^{36}Cl atoms with time as the rate of input less the rate of decay:

$$\frac{dN}{dt} = I - \lambda t \qquad 10.37$$

where I is the input rate (precipitation of chloride is assumed negligible). Integration of this equation yields:

$$N = \frac{I}{\lambda}\left(1 - e^{-\lambda t}\right) \qquad 10.38$$

Paul et al. measured $^{36}Cl/Cl$ in Mt. Hermon snow, in various rivers in the Dead Sea system, and in saline springs in the Dead Sea basin. These results are summarized in Table 10.4. Using equation 10.36, they estimated an accumulation time of 20,000 years for the salt in the Dead Sea. The Dead Sea basin has been estimated to be 15,000 years old based on ^{14}C. The difference suggests some of the Cl now in the Dead Sea was inherited from its less saline Pleistocene predecessor, Lake Lisan. The data in Table 10.4 also illustrates how a combination of Cl and ^{36}Cl data can distinguish between addition of Cl from rock leaching and evaporation, both of which are processes that will increase the concentration of Cl. Evaporation should not significantly change the $^{36}Cl/Cl$ ratio, while addition of Cl derived from rock leaching should decrease this ratio. There is a general southward (downstream) increase in Cl concentration in the Jordan River – Dead Sea system. It is apparent from the data in Table 10.4 that this is due to both addition of rock-derived Cl and evaporation.

Table 10.4 ^{36}Cl measurements in the Dead Sea system.

Site	$^{36}Cl/Cl$ (10^{-15})mg/l	Cl 10^6 atoms/l	^{36}Cl
Mt. Hermon Snow	1580±120	1.50	40±5
Banias River	400±60	11.9	80±15
Snir River	430±125	11.0	80±20
Dan River	725±140	10.5	129±25
Lake Kinneret	49±15	252	210±65
Jordan River	121±19	646	1,320±210
Dead Sea	17±2	2.30×10^5	6.6×10^4
Ashlag Spring (saline spring)	4±2	2.6×10^5	

10.6.6.3 ^{222}Rn

The decay of uranium and thorium to lead is one of the most widely used dating techniques in geology, but it is not directly applicable to hydrology. Several intermediate products in the decay scheme have been used in water studies. ^{222}Rn is produced by decay of ^{226}Ra (radium), which is itself a decay product of ^{238}U. ^{222}Rn is a gas, and when it is formed in sediment it diffuses into the overlying water. It has a half-life of 3.8 days, so that its concentration decreases with distance from the sediment. The profile of ^{222}Rn above the sediment depends on the rate at which it is transported upward in the water. If the rate is slow, the profile will be compressed close to the sediment; if it is fast, radon will be carried to greater distances from the sediment before it disappears by decay. Knowledge of transport rates near the sediment-water interface is important, because these rates determine the rate at which other species such as nutrients are transported from the sediment into the overlying water.

^{222}Rn has also attracted a great deal of attention as a potential health hazard. It is generated in rocks and soil by decay of ^{238}U and diffuses upward into the atmosphere. In the open air, rapid dilution by mixing, coupled with the short half-life of ^{222}Rn, makes it insignificant as a health hazard. When it seeps into buildings from below, however, it may build up to dangerous concentrations.

10.6.6.4 ^{3}H (Tritium)

Tritium (^{3}H or T) has a half-life of 12.43 years. It is produced naturally in atmosphere by interaction of cosmic rays with nitrogen and oxygen in the atmosphere, but by far the most important source for modern studies is thermonuc1ear weapons testing which took place in the atmosphere between 1952 and 1969. The natural level in rainwater was about 5–10 TU [one TU (tritium unit) = one T atom per 10^{18} ^{1}H atoms]. During the 1960s, the tritium levels in rainwater rose above 10^3 TU (maximum in 1963), and modern values are usua1ly between 20 and 100 TU, varying considerably with time and location.

Tritium in groundwater is not significantly affected by chemical processes because is a part of water molecule. Its most important use is in distinguishing between water that entered an aquifer prior to 1952 and water that was in contact with the atmosphere after 1952. Older water contains no tritium detectable by normal procedures; post-1952 water contains relatively high levels of tritium.

It can also be used for determination of ground water recharge. If some characteristic maximum such as a peak from 1963 can be identified, then it is assumed that all water above the peak recharged after 1963 and recharge R is calculated as

$$R = \frac{nH}{t} \tag{10.39}$$

where H is depth of the peak, t is time since 1963, and n is porosity expresed as fraction. More complicated methods are based on determination of tritium input function (TIF), which is concentration of tritium in precipitation corrected for decay. The TIF is compared with tritium values in ground water and a relative distribution of ages can be determined.

However, in some situations the methods above are not applicable. In that case, simultaneous determination of tritium and ^{3}He represents an advantage because ^{3}He is formed by decay of tritium (Clark and Fritz, 1997). Then ground water age is determined as

$$t = \frac{12.43}{\ln 2} \ln\left(1 + \frac{^{3}He_t}{^{3}H_t}\right) \tag{10.40}$$

where 12.43 is half-life for tritium decay and $^{3}He_t$ and $^{3}H_t$ are concentrations of ^{3}He and tritium at time of sampling, respectively. This method is very useful because there is no requirement of information about initial tritium activity, but is complicated by relatively difficult sampling for helium. The properties of tritium make it useful in studies of mixing in the upper layers of the ocean and mixing in lakes.

10.6.6.5 ^{10}Be in Subduction Zone Studies

One of the usual uses of cosmogenic nuclides is the use of ^{10}Be to trace sediment subduction (Tera et al., 1986). Since ^{10}Be does not exist in the Earth's interior, its pres-

ence there could result only from subduction of sediment (which concentrates cosmogenic ^{10}Be). ^{10}Be has been identified in some island arc volcanics, but not in other volcanic rocks (at least not above the background level of 10^6 atoms per gram, i.e. 1 atom in 10^{18}). This is strong evidence that subducted sediment plays a role in island arc magma genesis, something suspected on the basis of other geochemical evidence.

10.6.7 Transport of Radionuclides

There are some general rules applicable to transport of radionuclides in ground water. First of all, speciation of radionuclides is very important because often determines their behavior. For example, U(VI) is present as positively charged uranyl ion UO_2^{2+} at low pH range and is increasingly adsorbed with increasing pH. However, at neutral and alkaline pH range neutral and negatively charged carbonate complexes of U(VI) predominate and adsorption is almost negligible (Langmuir, 1997). This means that adsorption modeling based on linear adsorption isotherm K_d (see Chapter 3) is applicable only for relatively constant geochemical conditions. There also is a possibility of precipitation of minerals of radionuclides such as amorphous UO_2(am) in the case of U(IV) or co-precipitation such as incorporation of Ra into solid solution with gypsum (Ca, Ra)$SO_4.2H_2O$. However, concentrations of radionuclides are generally low and, thus, adsorption is much more important attenuation mechanism. Adsorption also increases residence time of radionuclides before reaching potential receptors (water supply wells, lakes etc.). This means that adsorption parameters like K_d and decay half-life are principal parameters governing transport of radionuclides and deciding about their potential threat.

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Chapter 11: Organic Contamination

11.1 Types of Organic Contaminants

There are two principal groups of organic contaminants from hydrogeological viewpoint. First group includes organic contaminants lighter than water, called in LNAPLs (*l*ight *n*on-*a*queous *p*hase *l*iquids). They are represented by aromatic hydrocarbons, which float on water table. Principal subgroup are BTEX (*B*enzene, *T*oluene, *E*thylbenzene, *X*ylene) (Fig. 11.1). These organic compounds contain benzene ring, and are partially soluble in water, with maximum solubility reaching in the case of benzene 1780 mg/L.

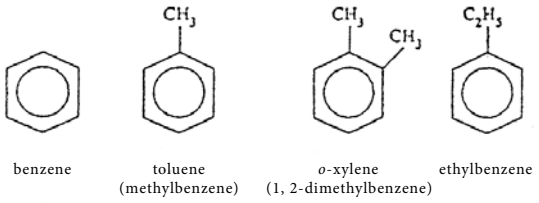


Figure 11.1 Examples of BTEX.

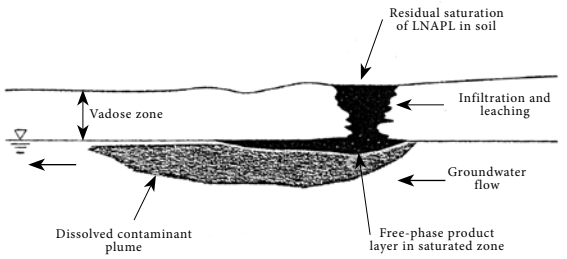


Figure 11.2 Migration of LNAPLs (after Bedient et al., 1994).

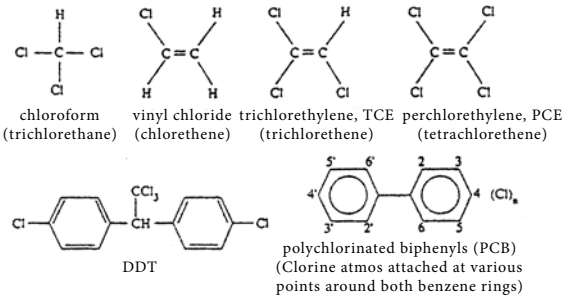


Figure 11.3 Examples of DNAPLs.

LNAPLS occur as free phase floating on water table, which is a source of dissolved plume (Fig. 11.2). Free phase may be present as *residual contamination* (free phase blobs and ganglia are disconnected and surrounded by water) or as *continuous free phase* (free phase is connected in a part of free phase zone at least). After penetration of unsaturated plume they leave behind residual free phase, which can be a source of vapor contaminant plume. Migrating dissolved contamination leaves behind contamination adsorbed on soil organic matter.

Second principal group are DNAPls (*d*ense NAPLs). Typical compounds are chlorinated solvents like trichloroethylen, TCE, and tetrachloroethylen, PCE (Fig. 11.3). These organic compounds have higher density than the density of water and they sink towards the base of an aquifer. There they form *pools* (e.g., continuous free phase accumulations) on the top of low permeability units (Fig. 11.4) and spread in the direction of the dip of aquifer basis, in some cases against the direction of ground water flow. After penetration of both unsaturated and saturated zone they leave behind

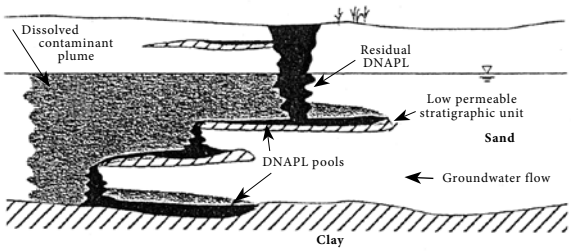


Figure 11.4 Migration of DNAPLs.

residual concentration. The residual concentration is a source of vapor plume in unsaturated zone and dissolved plume in saturated zone. A part of dissolved concentration can be adsorbed on organic matter in solid phase. Solubility of these contaminants is low, but not negligible (1100 mg/L for TCE). The maximum contaminant level (MCL) for TCE is only 5 μg/L and even small release of free phase TCE can contaminate large quantities of water.

11.2 Hydraulics of Free Phase Migration

When free phase of NAPLs penetrates porous media, its migration takes a tortuous path. NAPL is non-wetting phase which stays in the middle of large pores, and, on the other hand, water is wetting phase with respect to solid phase grains. This rule applies for majority of geological materials except for pure organic matter surfaces like peat. Degree of wettability of a fluid is estimated on the basis of contact angle (Fig. 11.5). If the contact angle is < 90°, the tested liquid is wetting, if it is > 90°, then the liquid is non-wetting.

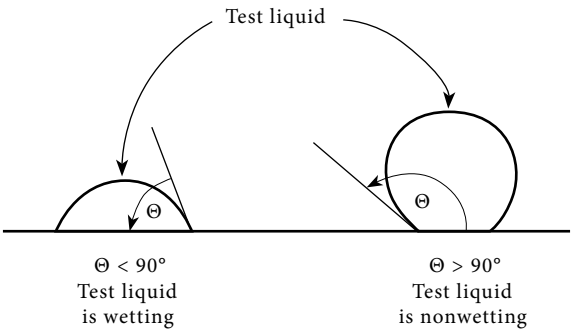


Figure 11.5 Determination of contact angle (modified from Domenico and Schwartz, 1998).

During their migration, NAPLs preferentially enters large pores. When porous media is initially saturated with water, NAPL has to exert displacement pressure P_d to push water out from a water saturated pore. Capillary pressure is defined as the difference between pressure of non-wetting fluid (NAPL) and wetting fluid (water) and is expressed as

$$P_c = P_{NW} - P_W = h_{NW}\rho_{NW}g - h_W\rho_W g \qquad 11.1$$

where P_{NW} pressure of non-wetting fluid, P_W is pressure of wetting fluid, h and ρ indicate height of columns and densities of both fluids, and g is acceleration of gravity. There are similar curves $P_c = f(S_w)$ for system NAPL-water like for unsaturated porous media. Instead of the air, the non-wetting fluid is NAPL in this case. Capillary pressure has to be equal or higher than displacement pressure for NAPL penetration to pores:

$$P_c = P_d = 2\,\delta \cos\gamma / r = h_{NW}\rho_{NW}g - h_W\rho_W g \qquad 11.2$$

After rearrangement (and substitution $h_{NW} = h_W$ because the height of both columns is the same):

$$h_{NW} = 2\,\delta \cos\gamma \,/\, [r\,g\,(\rho_{NW} - \rho_W)] \qquad 11.3$$

where δ is surface tension between water and organic contaminant [N/m], γ is contact angle and r is pore radius. The equation expresses the height of NAPL column, which has to accumulate on the top of less permeable layer to cause penetration of NAPL into the layer. The column is higher for smaller size of pores and for smaller density contrast between NAPL and water. The term ($h_W\rho_W g$) can change during pumping of underlying aquifer and in this case we can pull the contaminant into less permeable layer. There is a similar relation as equation (11.3) for penetration to a fracture. In denominator there can be 2 or other coefficient depending on fracture geometry and r indicates fracture aperture. During migration in a fracture contaminant can penetrate into surrounding blocks by diffusion and can completely disappear in blocks after long period (Parker et al., 1994).

Problem: Calculate the height of DNAPL necessary for penetration to silt (r = 0.000005 m), when δ = 0.040 N/m, ρ_{DNAPL} = is 1600 kg/m^3, and γ = 30°.

Solution: Use equation 11.3:
$h = 2\times0.040\times\cos 30° / 0.000005\times9.8\times(1600–1000) =$
$= 2.356$ m

There is relation between size of pores, hydraulic conductivity, and displacement pressure. The lower is hydraulic conductivity, the higher is displacement pressure. The height of column necessary for penetration

to a layer with hydraulic conductivity k is (McWhorter, Kueper, 1996)

$$h_{DNAPL} = 9.6\ (\rho_W/\Delta\rho)\ (\sigma/\sigma_{aw})\ (k/n)^{-0.403} \qquad 11.4$$

where $\Delta\rho$ is density difference between contaminant and water, σ is surface tension between organic contaminant and water, σ_{aw} is surface tension between water and air, and k is hydraulic conductivity.

A consequence of inverse relation between displacement pressure and pore size is that free phase of NAPL enters the largest pores by-passing small ones, and its migration often changes direction. In controlled experiments of TCE spreading in sand (Poulsen and Kueper, 1992) was found that spreading was influenced of permeability changes in the scale of mm, and residual saturation was between 2 and 18 %. It was also found that concentrated release in small drops caused penetration of TCE to greater depth than in the case of TCE spill on ground surface. This is partially related to smaller area of infiltration and thus, to more concentrated flow in the first case.

There is similar behavior of NAPLs in fractured media. In a fracture water also covers walls and a NAPL is located in the central zone. When fracture aperture is reduced, spreading of a NAPL can stop. If there is other fracture with larger aperture available, then direction of flow can be completely deflected.

11.3 Partitioning of Organics Between Phases

As stated above, in porous media free phase can be present in continuous form (pool) at the base of an aquifer or on the top of low permeability layers (in the case of DNAPL) or as a layer floating on water table (in the case of LNAPL), and as residual concentration in the form of disconnected blobs and ganglia. Organic contaminant can also be present in the form of dissolved contamination, contamination of adsorbed on solid phase, and as vapor plume in unsaturated zone. There is partitioning between free phase, water phase, solid phase, and vapor phase (in unsaturated zone) during migration of an organic contaminant. Parameters of transfer between phases are in Table 11.1.

Vapor pressure is parameter which describes volatility of organic contaminant. This parameters determines if soil vacuum extraction (SVE) can be used for remediation of a contaminant. Effective vapor pressure, P_i^{eff} in a mixture of contaminants is lower than for a single contaminant and is calculated using Raoult's Law:

Table 11.1 Partitioning parameters.

Parameter	Transfer	Indication	Units
Vapor pressure	free phase-air	P_i	atm
Solubility	free phase-water	S_i	mg/L
Henry Law's constant	water-air	H_{cc}	dimensionless
Coeff. octanol-water	water-solid phase	K_{ow}	dimensionless

$$P_i^{eff} = X P_i \qquad 11.5$$

where P_i is vapor pressure for pure organic contaminant and X_i is its molar fraction in mixture. This means that vapor pressure of a contaminant in mixture may be much lower than vapor pressure of a pure contaminant.

Solubility in water S_i [mg/L] describes dissolution of a contaminant in water and, thus, potential efficiency of pump-and-treat method of remediation. This is maximum possible dissolved concentration because analogy of Raoult's Law also applies for dissolution of a mixture of contaminants:

$$S_i^{eff} = X_i S_i \qquad 11.6$$

where S_i^{eff} is solubility in a mixture and X_i is its molar fraction.

Problem: Calculate molar fractions in mixture of 500 g of benzene and 500 g of toluene. Respective molecular weights are 78.1 and 92.14.

Solution:

- molar mass of benzene is 500/78.1 = 6.4, molar mass of toluene is 500/92.14 = 5.43,
- molar fraction of benzene $X_{benzene}$ = 6.4/(6.4+5.43) = 0.54, molar fraction of toluene $X_{toluene}$ = 5.43/(6.4+5.43) = 0.46.

One of consequences of Raoult's Law is that we generally find dissolved benzene concentrations about 20 mg/L in spite of its much higher solubility of 1780 mg/L. Commercial gas is a mixture of more than 100 compounds and benzene molar fraction is only about 2 %. However, in countries like Brazil at some sites concentration of benzene reach more than 50 mg/L because there is the effect of co-solvency with alcohol. Alcohol is sold at gas stations in Brazil as fuel and there often are both gas and alcohol plume present at the same site.

Another reason for much lower concentrations than theoretical solubilities is dilution by dipersion in aquifer and during sampling in a well. When free phase occurs on the top of less permeable layer as a pool, then there is saturated micro-layer close to the

pool, but saturation sharply decreases with increasing height above the pool. Vertical distribution of dissolved contaminant above the pool is expressed as (Johnson and Pankow, 1996):

$$C(z) = C_{ef}.\text{erfc}\{z/[2\,(D_v\,L/v)^{0.5}]\} \qquad 11.7$$

where z is height above a pool, C_{ef} is effective concentration calculated by Raoult's Law, D_v is vertical dispersion coefficient (calculated as $D_v = \alpha_v \times v + D_e$, where α_v is vertical dispersivity coefficient, v is flow velocity, and D_e is molecular diffusion coefficient), L is length of a pool in the direction of flow and erfc is complementary error function (Chapter 7.7). On the basis of the formula, we can conclude that the concentration above accumulation of free phase is higher for longer pool, higher vertical dispersivity, and lower flow velocity. On the other hand, if free phase is in the form of residual concentration, then a well in close proximity of residual concentration may show concentrations close to theoretical maximum because residual concentration has much better contact with flowing ground water than free phase in a pool. Next dilution occurs in a sampling well. For example, if thickness of dissolved plume is about 2 m and thickness of screen zone of a well is about 4 m, concentration in sampled water will be about a half of concentration in aquifer. A rule of only 1 % of theoretical maximum concentration was accepted as a possible indicator of presence of free phase (Feenstra and Cherry, 1996), but it has been questioned recently.

Partitioning between dissolved contaminant and air is described by Henry Law's coefficient, H_{cc}, which is defined as

$$H_{cc} = C_{air}/C_{water} \qquad 11.8$$

where C_{air} is concentration in air [mol/m^3], and C_{water} is concentration in water [mol/m^3]. The value of H_{cc} is dimensionless in the case above, but there can be different versions of Henry Law's constant depending on units used for concentrations and caution is necessary when we accept data from literature.

Problem: Convert Henry Law's constant for PCE equal to 0.295 in dimensionless form H_{cc} to form H_{pc} in units [atm/mol×m^3].

Solution:

$H_{pc} = p_{PCEair}/C_{PCEwater}$

$p \times v = n \times R \times T$ and $n/V = p/R \times T = C_{PCEair}$

for T = 298.15°C (25°C), $R = 8.206 \times 10^{-5}$ m^3.atm/mol K

$n/V = 40.873\,p$ or $p = 2.447 \times 10^{-2}\,n/V$ for V in m^3,

then $H_{pc} = 2.447 \times 10^{-2} \times H_{cc}$ and $H_{pc} = 17.73 \times 10^{-3}$ atm/mol×m^3.

Partitioning between organic carbon in solid phase is related to the distribution coefficient octanol-water K_{ow}, defined as

$$K_{ow} = C_{octanol}/C_{water} \qquad 11.9$$

where $C_{octanol}$ and C_{water} are concentrations of organic contaminant in octanol and in water, respectively. The value of K_{ow} is generally listed in logarithmic form and increases with increasing degree of hydrophobicity of organic contaminant (e.g., with increasing tendency to partition into organic matter from water). For example, log K_{ow} for PCB is about 6.0 which means that PCB is about million times more concentrated in solid phase organic carbon than in water. Adsorption on organic matter also depends on fraction of organic matter in aquifer solids, f_{oc}. First we have to calculate distribution coefficient organic carbon-water K_{oc}, which is positively correlated to K_{ow}. Generally we use K_{ow} from tables (for example, Bedient et al., 1994, Fetter, 1999, etc.) and then we calculate K_{oc} using empirical equations. Examples are equation of Schwarzenbach and Westall,

$$\log K_{oc} = 0.49 + 0.72 \log K_{ow} \qquad 11.10$$

or equation of Karickhoff et al.,

$$\log K_{oc} = 0.088 + 0.909 \log K_{ow} \qquad 11.11$$

Sometimes the value of K_{oc} is directly indicated in literature. Distribution coefficient for adsorption of organic contaminant is calculated as

$$K_d = K_{oc} f_{oc} \qquad 11.12$$

and is used in equation for retardation coefficient R (Domenico and Schwartz, 1998):

$$R = v_{water}/v_{organic} = 1 + (\rho_b/n)\,K_d \qquad 11.13$$

where v_{water} and $v_{organic}$ are velocities of water flow and organic contaminant transport, respectively, ρ_b is bulk density of aquifer solids and n is porosity. The term (ρ_b/n) indicates the amount of solid phase in contact with 1 L of water. For R = 4.0, for example, transport of an organic contaminant is 4 times slower than advective velocity of water flow. Value of R = 1.0 means no adsorption and retardation.

Retardation coefficient R is easily implemented into both analytical and numerical models. There are, however, several problems:

– Organic matter fraction f_{oc}, which is determined in laboratory for solid samples taken out of contaminant plume should be at least 0.01 (or 1 %). For lower

values adsorption on inorganic surfaces becomes important. Considering that many plumes are in sand and gravel aquifers with low concentration of organic matter, there is a potential for significant errors.
- This method applies for hydrophobic organic compounds with solubility less than 10^{-3} mol/L.

Problem: Organic carbon fraction in aquifer solids f_{oc} is 0.01. Calculate K_d and R for 1,2-dichloroethan with log K_{ow} = 1.48. Bulk density of solids is 1.9 g/cm^3 and porosity is 0.25.

Solution: Use Schwarzenbach and Westall equation to calculate K_{oc},
log K_{oc} = 0.49 + 0.72×(1.48) = 1.556
and $K_{oc} = 10^{1.556}$ = 35.94
K_d = 35.94×0.01 = 0.359 mL/g
finally R = 1 + (1.9/0.25)×0.359 = 3.731, which means that transport of 1,2-dichloroethan is 3.731 times slower than water flow.

Both Henry Law's coefficient and distribution coefficient K_d do not depend on Raoult's Law because they describe partitioning of dissolved contaminant into other phases. On the other hand, vapor pressure and solubility depend on Raoult's Law because they describe partitioning of free phase contaminant.

11.4 Biodegradation

Biodegradation is a process that belongs to *natural attenuation* processes. Natural attenuation can be non-destructive, e.g., concentration of a contaminant is reduced by processes like dispersion and mass of a contaminant does not change ($C\downarrow$, M = const.) or destructive, when there is a decrease of both concentration and mass of a contaminant ($C\downarrow$, $M\downarrow$).

Biodegradation is destructive process with resulting reduction of mass of organic contaminant, which is often described as *kinetic process of 1st order* (e.g., rate of biodegradation depends on concentration) and is expressed as

$$C_t = C_0\, e^{-\lambda t} \qquad 11.14$$

where C_t is concentration at time t, C_0 is initial concentration, and λ is *decay constant* [t^{-1}]. Often we can found in literature *half-life* $t_{1/2}$ [t] related to decay constant as $t_{1/2} = \ln 2/\lambda$. It is necessary to distinguish between half-life and decay constant because their meaning is inverse, e.g., high decay constant means fast biodegradation, and high half-life means slow biodegradation. The concept of first order biodegradation kinetics does not include any limiting factors for biodegradation (see later) and values of decay constant depends on site specific conditions (pH, redox conditions etc.) and may not be applicable for other sites. This means that decay constant for organic contaminants is not a constant in strict sense like decay constant for radionuclides. Alvarez (1996) indicates decay constant for benzen in the range from almost 0 to 0.0085 day^{-1}, with an average of 0.0046 day^{-1}.

Biodegradation of petroleum products like BTEX occurs in oxidizing environment with participation of bacteria. In the process O_2 and other oxidized species are used as electron acceptors and organic contaminants are substrate for bacterial population. For example, the reaction of benzen with O_2 is expressed as

$$C_6H_6 + 7.5\, O_2 = 6\, CO_2 + 3\, H_2O \qquad 11.15$$

Theoretical sequence of electron acceptors consumption is the same as in uncontaminated aquifers: $O_2 \rightarrow NO_3^- \rightarrow Mn^{4+} \rightarrow Fe^{3+} \rightarrow SO_4^{2-} \rightarrow$ methanogenesis (Borden et al., 1995). However, the rate of electron acceptors consumption in biodegradation of BTEX plume is much faster, and there often is an overlap between different electron acceptors zones. Resulting ground water has low redox potential (often Eh < –200 mV) and high concentration of dissolved metals (Baedecker et al., 1993). This is a consequence of dissolution of hydroxides such as $Fe(OH)_3$ and MnOOH in solid phase with adsorbed metals like Zn and Pb. In this process, concentration of dissolved inorganic carbon (DIC) and partial pressure of CO_2 (P_{CO2}) also increase. High P_{CO2} values and concentrations of metals represent a serious challenge during remediation because precipitation of calcite due to de-gassing of CO_2 and $Fe(OH)_3$ due to oxidation of Fe^{2+} can completely block air stripping colon for treatment of water. Thus, there is often necessary to do pre-treatment of ground water prior to air stripping. Typical geochemical zonation observed in BTEX plume at Bemidji site in Minnesota, USA, is in Fig. 11.6.

There is an important role of transverse vertical dispersion, which can supply water with electron acceptors into plume. However, most of biodegradation takes place in source zone with free product, when ground water with electron acceptors flows through it. According to Wiedermeier et al., (1995), 1 mg/L of O_2 can biodegrade 0.32 mg/L of BTEX, 1 mg/L of NO_3^- can biodegrade 0.21 mg/L of BTEX, just like biodegradation of 1 mg/L of SO_4^{2-}. Biodegradation of 1 mg/L of BTEX results in production of 21.8 mg/L of Fe^{2+} from

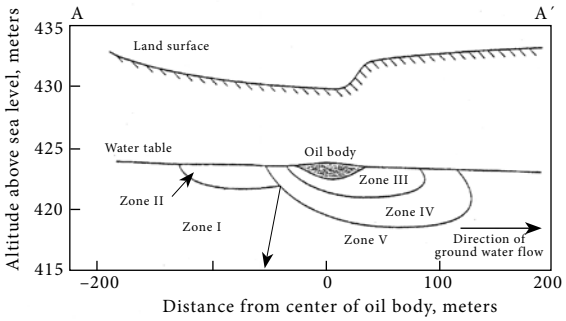


Figure 11.6 Geochemical zone at BTEX contaminated site at Bemidji, Minnesota, USA (adapted from Baedecker et al., 1993). Zone I is background water with high oxygen concentration, Zone II has low oxygen and increased Ca, Mg, and P_{CO2}, Zone III in contact with free phase has methane and high manganese and iron concentration, Zone IV has traces of oxygen and lower concentrations of metals, and Zone V is similar as Zone I.

$Fe(OH)_3$ in solid phase, and production of 0.78 mg/L of methane. Total *biodegradation capacity BC* based on instantaneous consumption of electron acceptors is

$$BC = \Sigma[(AE)_i/F_i] \qquad 11.16$$

where $(AE)_i$ is concentration of electron acceptor (O_2, NO_3^- etc.), and F_i is utilization factor equal to amount of an electron acceptor necessary for biodegradation of 1.0 mg of BTEX (for example, for O_2 it is 1/0.32 = 3.1 mg). There are generally enough electron acceptors in ground water and common length of BTEX plumes is around 100 m. When biodegradation rate is the same as the rate of contaminant input and transport, then there is formation of *steady-state plume* (plume which does not move).

Situation is more complicated in the case of chlorinated solvents. Their rate of biodegradation is often limited and biodegradation takes place in reducing environment with high concentration of H_2 generated by redox processes. Principal process is reductive dechlorination, when Cl^- in a chlorinated compound is replaced by hydrogen. In this process a contaminant is electron acceptor. Typical reductive de-chlorination sequence is PCE (tetrachloroethen) →TCE(trichloroethen) → 1,2-DCE(dichloroethen) →VC(vinylchlorid)→ ethen. If more than 80 % of DCE is in the form of cis-1,2-DCE, then there probably is reductive dechlorination (Wiedemeier et al., 1996).

Nyers and Duffin, (1997), distinguished 3 types of environments for biodegradation of chlorinated solvents (Fig. 11.7). Type 1 correspond to simultaneous occurrence of chorinated solvents with BTEX, and biodegradation of BTEX creates reducing environment necessary for reductive dechlorination. Type 2 is related by high natural concentration of organic matter, which also creates reducing environment like Type 1. Type 3 is environment with low both natural and antropogenic organic matter and with detectable O_2. In this environment there is no reductive dechlorination and principal attenuation mechanism is dispersion. Exception is biodegradation of VC and partially also 1,2-DCE, which can be biodegraded in oxidizing environment. Nyer and Duffin (1997) also present point system for evaluation of possibility of reductive dechlorination.

In the case of BTEX biodegradation, there can be application of more complicated *Monod kinetics,* which includes parameters of bacterial population in ground water. Basic equation is

$$\mu = \mu_{max}\,[C/(K_c + C)] \qquad 11.17$$

where μ is rate of bacteria growth $[t^{-1}]$, μ_{max} is maximum rate of bacterial growth $[t^{-1}]$, C is concentration of rate-limiting substrate [mg/L], and K_c is concentration of substrate for half-rate of maximum growth. When $K_c << C$, we obtain $\mu = \mu_{max}$ and rate of growth is at its maximum. Amount of decayed contaminant by consumption of oxygen is

$$\Delta C = M_t\,\mu_{max}\,[C/(K_c + C)]\,[O/(K_O + O)]\,\Delta t \qquad 11.18$$

where M_t is total microbial population, O is oxygen concentration, K_O is oxygen half saturation constant, and Δt is time period of biodegradation. However, equations above are not frequently used because there generally is lack of information about bacterial population.

Problem (from Bedient et al., 1999): There is concentration of dissolved benzene of 12 mg/L in an aquifer. Concentration of oxygen available for biodegradation is 8 mg/L, and decay constant for benzene is 0.1386 day^{-1}. Compare first-order decay, Monod kinetics, and instantaneous reaction biodegradation for period of 10 days.

Solution:

- Instantaneous reaction: 0.32 mg of benzene are biodegraded by 1 mg/L of O_2, so 3 mg/L of O_2 biodegrade 1 mg/L of benzene, final benzene concentration is 12 – (8/3) = 9.33 mg/L,
- First-order decay: final benzene concentration (equation 14) = $12 \times e^{-1.386 \times 10}$ = 3.0 mg/L
- Monod kinetic: assuming O_2 half saturation constant of 0.1 mg/L, benzene half saturation constant 22.16 mg/L, maximum utilization rate 9.3 day^{-1}, and microorganisms population of 0.05 mg/L, we substitute into equation 18: benzene reduction=9.3×[12/(12+22.16)]×[8/(8+0.1)]×10×0.05=1.59 mg/L, final benzene concentration = 12 – 1.59 = 10.41 mg/L.

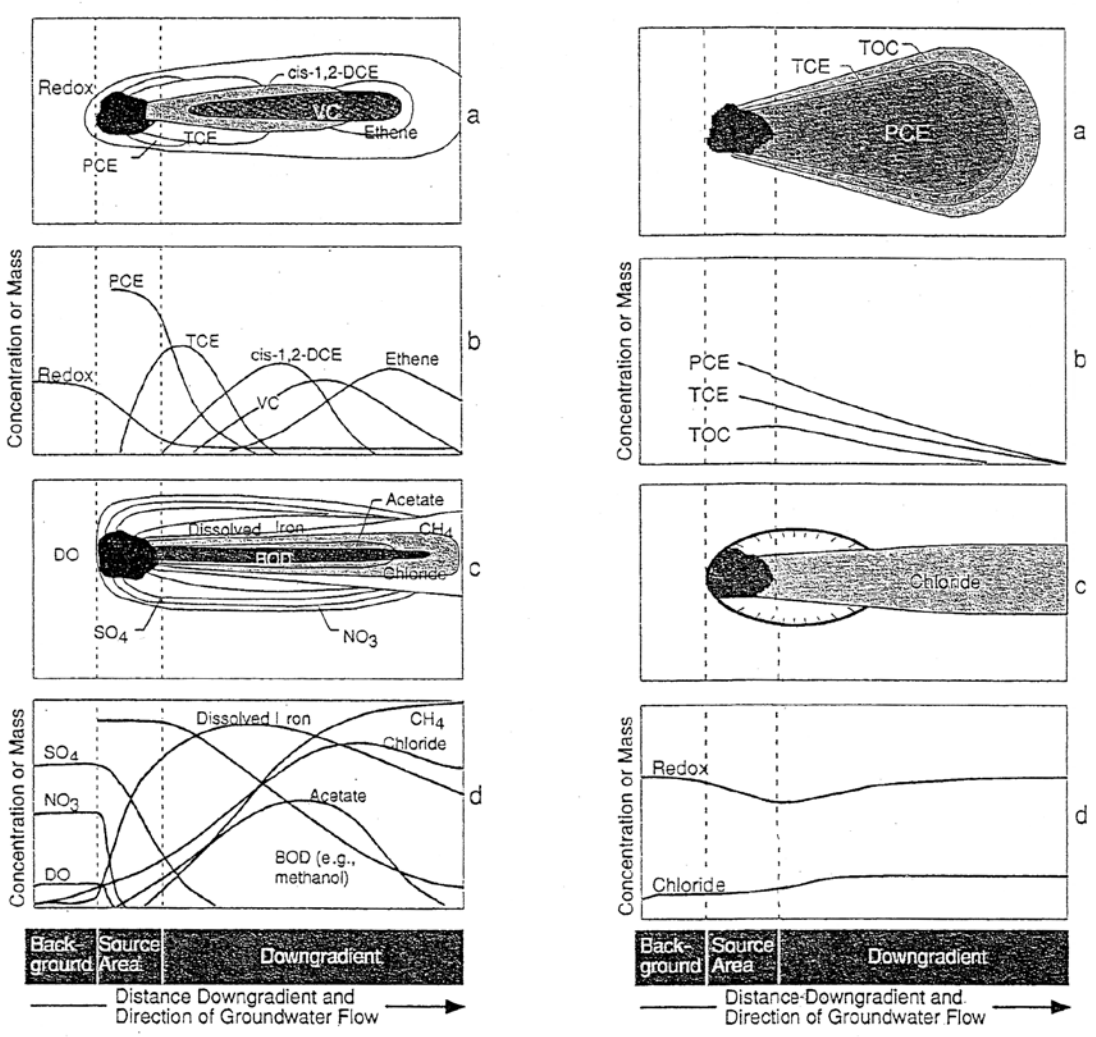


Figure 11.7 Types of environment in biodegradation of chlorinated solvents (adapted from Wiedemeier et al., 1996). Type 1 (left) and Type 3 (right).

This means that first-order decay approach may overpredict biodegradation rate because limiting factors like electron acceptors concentrations are not taken into account.

11.5 Mass Balance Calculations

Free phase localization has pivotal importance for remediation because free phase generally serves as long term source of dissolved contamination. However, in many cases we cannot make visual observation of free phase. In this case, we can evaluate the possibility of free phase presence on the basis of mass balance calculations (Feenstra et al., 1991). Mass balance for a sample from saturated zone is

$$M_{\text{total}} = C_{\text{water}} V_{\text{water}} + K_{\text{d}} \rho_{\text{solids}} V_{\text{solids}} C_{\text{water}} \qquad 11.19$$

and after rearrangement

$$C_{\text{water}} = M_{\text{total}} / (K_{\text{d}} \rho_{\text{solids}} V_{\text{solids}} + V_{\text{water}}) \qquad 11.20$$

where M_{total} is total amount of contaminant in a sample, V_{solids} and V_{water} are volumes of solid and water phase, respectively, ρ_{solids} is density of grains of solid phase, K_{d} is distribution coefficient for contaminant, and C_{water} is concentration of contaminant in water. The same equation for unsaturated zone is

$$M_{\text{total}} = C_{\text{water}} V_{\text{water}} + K_{\text{d}} \rho_{\text{solids}} V_{\text{solids}} C_{\text{water}} + H_{\text{cc}} V_{\text{air}} C_{\text{air}} \qquad 11.21$$

where H_{cc} is Henry Law's constant, V_{air} is volume of air, and C_{air} is concentration in air.

When calculated water concentration is higher than effective solubility (calculated on the basis of Raoult's Law), then we assume that there is free phase in the sample. However, when the calculated concentration is lower, we cannot exclude the possibility of free product for the following reasons: (a) there may not be equilibrium between phases in sample, and (b) it is possible that real effective solubility is lower because all compounds in mixture possibly have not been determined.

Problem: Determine if there can be free phase of TCE in a sample with total TCE 200 μg/g. Porosity is 33 %, f_{oc} = 0.02 %, ρ_s = 2.67 g/cm^3, log K_{ow} = 2.29 and solubility of pure TCE = 1100 mg/L.

Solution:

- 1 cm^3 has 0.33 cm^3 of water and 0.67 cm^3 of solids or 0.67×2.67 = 1.789 g of solids,
- TCE in 1 cm^3 = 1.789×200 μg = 357.78 μg
- K_d = 0.0002×10 exp[0.72(2.29)+0.49] = 0.0275 mL/g
- C_{water} = 357.78/(0.0275.2.67.0.67 + 0.33) = 943 μg/L = 943 mg/L, this is less than 1100 mg/L, so we cannot confirm presence of free product.

11.6 Investigation of Contaminated Sites

This is very extensive topic discussed in several publications (for example, Bedient et al., 1999, Fetter et al., 1999, etc.) and only principal points are mentioned in this text.

During investigation of contaminated sites we have to determined distribution of contaminant between phases because this information decides about the choice of remediation method. For example, highly adsorbed PCB cannot be remediated by pumping. Benzene, on the other hand, can be at least partially pumped out with ground water, and in unsaturated zone can also be remediated by soil vacuum extraction (SVE) because of its volatility.

Localization of free phase has pivotal importance because both residual concentrations and pools are long term sources of dissolved contamination. Methods for localization of free phase include:

- Direct observation: this is generally plausible in the case of LNAPLs floating on water table. On the other hand, pools of DNAPLs at the base of aquifer are difficult to find. Residual concentration of LNAPLs and especially BTEX have specific smell and color. This is not the case of DNAPLs, which often cannot be detected by senses in small concentrations.
- Application of UV light because there is fluorescence of many organic contaminants.
- Application of atmogeochemical prospection in unsaturated zone: in the proximity of free phase saturated vapor concentrations can be reached. In this case, we need to know free phase composition and calculate expected saturated concentrations by Raoult's Law. However, positive indication is a proof, negative indication is inconclusive because there are several factors which can decrease vapor concentrations. Soil gas sampling also serves to determine limits of vapor plume.
- Comparing dissolved concentrations with theoretical saturated concentrations in saturated zone: There may be saturated concentrations in close proximity of residual free phase. However, we have to include the effect of mixture by application of Raoult's Law again. Also in this case positive indication is proof, negative indication is inconclusive.
- Application of mass balance approach presented in problem above. Once more, negative results are not a proof of free phase absence.

In general, when total soil concentration, C_{org}, of organic contamination is determined, it is converted to relative saturation value:

$$S_{org}\,(\%) = \rho_b\, C_{org}/(\rho_{org}\, n\, 10^6) \qquad 11.22$$

where S_{org} is saturation of pore space by organic contaminant in %, ρ_b is bulk density of solid phase in g/cm^3, C_{org} is concentration of organic contaminant in soil sample in mg/kg, ρ_{org} is bulk density of organic contaminant in g/cm^3, and n is porosity. Mass of free phase in source zone is calculated as

$$M_{org}\,(\mathrm{g}) = L\, W\, H\, n\, \rho_{org}\, S_{org} \qquad 11.23$$

where L, W, and H are length, width, and height of source zone, respectively.

We also need to determine limits of dissolved contamination plume. In the first phase we locate sampling wells or piezometers along direction of flow. Maximum theoretical distance of plume movement can be determined from Darcy's Law (plus some additional distance for dispersion allowed) when time of release is known. In the next phase we locate sampling points in the direction perpendicular to ground water flow to determine transversal size of plume. Finally, it is convenient to install at least one piezometric nest to determine vertical dimension of plume.

Wells for measurement of thickness of free product of LNAPLs have to be screened above maximum elevation of water table to allow the entry of free product. When there is drilling for location of DNAPLs in depressions at the base of aquifer, there has to be continuous monitoring of dissolved concentration. When the top of a pool is found, drilling has to be stopped because further drilling could contaminate underlying formations.

During sampling we should use positive pressure devices and avoid any splashing of sampled water which could cause degassing of samples. Samples should be deposited in cold environment. It is recommended to add a bactericide to avoid biodegradation

of samples during deposition, especially when there is a time lag between sampling and analysis. There often is strong concentration gradient within a plume (concentration differences by several orders of magnitude), and logarithms of concentrations are recommended for plotting instead of absolute numbers.

Samples of soils for determination of soil organic matter fraction f_{oc} should be taken out of the contaminated area to avoid influence of anthropogenic carbon. Number of samples depends on financial constraints, but several samples are recommended. Equation 11.13 is used to calculate theoretical retardation factors for different contaminants.

11.7 Evaluation of Natural Attenuation

When we need to verify the possibility of natural attenuation, the following approach is used:

(1) Trends of dissolved concentrations in the plume have to be determined by several samplings. Non-parametric statistic tests (for example, Mann-Whitney test) are used to check decreasing concentrations.

(2) Background concentrations of electron acceptors (O_2, NO_3^- etc.) are determined in ground water out of plume. Then we compare background concentrations with concentrations in the plume to decide if bioremediation takes place. Products of biodegradation like Fe(II) and methane are sampled only within the plume. Equation 11.16. can be used to convert changes in concentrations of electron acceptors to the amount of biodegraded BTEX compounds. In the case of chlorinated solvents, geochemical indicators are used only as qualitative indicators of intrinsic bioremediation.

(3) Laboratory test in microcosmos with contaminated water and sediments may be run and bacterial population parameters are determined.

Last point is only optional, but first two points are necessary according to U.S. EPA methodology.

Concentration plots with time for single wells based on Equation 11.14 can be used to calculate time-based natural attenuation constants. Space-based natural attenuation constant can be determined by plotting $\ln (C/C_0)$ as a function of distance from source. From Equation 11.14. we obtain after substitution for $t = x/v$ (x is distance from source, v is advection velocity)

$$\ln (C/C_0) = - (k/v)\, x \qquad 11.24$$

which is a straight line with slope $- (k/v)$. Thus, natural attenuation constant can be calculated by multiplication of slope by advection velocity. More advanced version of this interpretation is the equation of Buscheck and Alcantar (1995).

Finally, when total mass in a plume is known from dense network of sampling points on profiles (including adsorbed contamination), Equation 11.14 can be used on mass bases and decay constant is calculated instead of natural attenuation constant:

$$\lambda = -\ln(M_2/M_1) / \Delta t \qquad 11.25$$

where λ is decay (biodegradation) constant, M_2 and M_1 are concentration in time t_2 and t_1, and Δt is time of flow between profile 1 and profile 2.

It is convenient to use analytical screening models like BIOSCREEN for BTEX and BIOCHLOR for chlorinated solvents or numerical models like RT3D to estimate natural attenuation parameters. It is always useful to have a conservative tracer like MTBE (methyl tert-butyl ether, added to gas as anti-detonator) for BTEX to separate bioremediation from other attenuation processes like dispersion. When parameters of natural attenuation are known, models can be used for prediction of concentrations in receptors (water supply wells etc.), which are necessary for risk analysis (see Chapter 13).

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Chapter 12: Geochemical Aspects of Remediation of Contaminated Aquifers

12.1 Introduction

Remediation of contaminated underground environment is complicated process. When a contaminated ground water is pumped out, there is an initial fast reduction of concentration in water, but asymptotic behavior of concentration can be observed in later phases (Fig. 12.1). The behavior is also called *tailing*. In many cases, the more or less constant concentration in late phase of pumping is higher than maximum contaminant level (MCL). Both physical and chemical processes can be responsible for this behavior.

Principal physical process is limited diffusive contaminant transport from low permeability zones (Mackay and Cherry, 1989). During pumping, the most of pumped ground water comes from high permeability preferential flow zones. Contamination from low permeability zones slowly diffuses to preferential flow zones and maintains relatively high concentration in pumped ground water. The reverse diffusion during pumping is slow process because concentration gradient dC/dx is lower than it was during contaminant migration. Thus, this behavior is related to the heterogeneity of permeability in an aquifer. This effect is even more pronounced in double porosity media. In that case, there is diffusion supply of contamination from low permeability blocs into preferential flow zones in fractures.

Another reason is related to the shape of pumping well *capture zone*. When natural flow exists, the capture zone is asymmetric and elongated upgradient. In that case, contaminant path in the middle zone of capture zone is shorter than at the periphery of capture zone. Later arrival of contamination from periphery of capture zone may also result in tailing effect (Palmer and Fish, 1994).

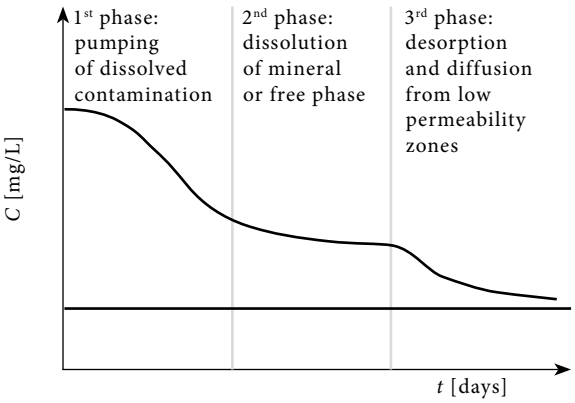


Figure 12.1 Tailing effect during remediation.

12.2 Geochemical Aspects

12.2.1 Desorption of Contaminants

When contamination is in dissolved form only, remediation is relatively straightforward. Time necessary for remediation would be simply

$$t = (V\,n)/Q \qquad 12.1$$

where V is volume of contaminated aquifer, n is porosity, and Q is pumping rate. However, in many cases most of contaminant is in solid phase. When contaminant is adsorbed and adsorption/desorption follows the linear isotherm K_d, resulting time for remediation is obtained

by multiplication of the time calculated by equation 8.1 by retardation factor R (Chapter 7.5). Thus,

$$t_{adsorbed} = (R\ V\ n)/Q \qquad 12.2$$

The equation makes sense because R indicates how many times slower moves a contaminant compared to the ground water flow velocity. Both equations above neglect the effect of dispersion, which results in some tailing compared to the case of piston flow. The exchange factor EF (Deutsch, 1997), defined as a ratio between water concentration before and after flushing of one pore volume, is

$$EF = C_1/C_2 = 1 - (1/R) \qquad 12.3$$

where C_1 and C_2 are dissolved concentrations before and after flushing, respectively. It is evident that when R (and, thus, K_d) increases, the value of exchange factor decreases as a consequence of slower desorption rate. Number of flushings necessary to reduce concentration from initial concentration $C_{initial}$ to limiting concentration C_{limit} is

$$NF_{desorp} = \log (C_{initial}/C_{limit}) / \log EF \qquad 12.4$$

Situation becomes more complex in the case of non-linear isotherm (Appelo and Postma, 1993). Retardation factor R is defined as

$$R = 1 + (\rho_b/n)(dS/dC) \qquad 12.5$$

and for linear isotherm

$$R = 1 + (\rho_b/n)\ K_d \qquad 12.6$$

where dS/dC is equal to K_d e.g., to slope in graph $S = f(C)$, ρ_b is bulk density of solid phase, and n is porosity. For non-linear isotherm such as the Freundlich isotherm, $S = K_F C^n$, and R becomes

$$R = 1 + (\rho_b/n)(dS/dC) = 1 + (\rho_b/n)\ n\ K_F\ C^{n-1} \qquad 12.7$$

Thus, the value of R is no longer constant, but depends on dissolved concentration C. When C is high, retardation is low, (it is even more pronounced for the Langmuir isotherm with upper limit for adsorption), but the value of R increases at low dissolved concentrations. This non-linear desorption can produce a tailing of the curve C vs. t. It is worth mentioning that the process of diffusion from low permeability zones (e.g. physical process), represented as immobile water zones towards high permeability zones (mobile water zones) can produce the same effect.

12.2.2 Dissolution of precipitated minerals

Situation is even more complicated in the case of precipitation of inorganic contaminants as minerals. For example, lead can precipitate as cerussite, $PbCO_3$, Cr(VI) can precipitate as hashemite, $BaCrO_4$, or, after reduction, as amorphous chromium hydroxide, $Cr(OH)_3$(am). The precipitated mineral serves as a source of dissolved contamination during pumping (2nd zone, Fig. 12.2), and maintains dissolved equilibrium concentration with the mineral. The theoretical number of flushings necessary for dissolution of mineral of contaminant is

$$NF_{dissol} = [(\rho_b/n)C_{solid}]/C_{eq} \qquad 12.8$$

where C_{solid} is concentration of contaminant present as a mineral in solid phase and C_{eq} is equilibrium concentration of dissolved contaminant in ground water. This concentration includes free ions and complexes (for example, for lead it is $Pb_{total} = Pb^{2+} + PbCl^+ + PbSO_4^0$ etc.) and is calculated by a program such as PHREEQC (Parkhurst, 1995).

Total number of flushings is calculated as

$$NF_{total} = 1 + NF_{dissol} + NF_{desorp} \qquad 12.9$$

where 1 represents first volume of contaminant dissolved in ground water. The change of concentration during pumping is shown in Fig. 12.2. First volume of dissolved contamination is pumped out quickly, but dissolution of mineral keeps concentration high. After complete dissolution of mineral, desorption and diffusion from low permeability zones supplies contamination and asymptotic behavior is observed..

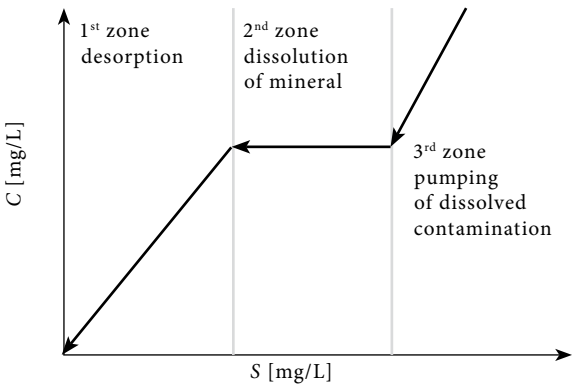


Figure 12.2 Processes during remediation. S and C indicate solid phase and aqueous phase concentrations, respectively. Desorption is considered to be linear and reversible.

12.2.3 Dissolution of Free Phase

Dissolution of free phase of organic contaminants is an analogy of dissolution of minerals of inorganic contaminant. This process is complicated by a common presence of organic contaminants in mixtures. For example, commercial gasoline comprises more than 100 compounds. Solubility of compounds in mixture depends on the Raoult´s Law (Chapter 11) and is lower compared to the solubility of a single compound. Let us consider, for example, mixture of TCE with solubility of 1100 mg/L and 1,2-DCP (dichloropropan) with solubility of 2700 mg/L. Solubilities of both compounds in mixture are in Table 12.1.

Thus, during pumping the dissolution of 1,2-DCP will be faster and mixture of free phase will be enriched in less soluble TCE. This means that transfer of mass and rate of free phase dissolution will be decreasing with time. Remaining mass after each flushing step is equal to

$$M_2 = M_1 - [(S_i^{ef}/MW)\ V_{water}] \qquad 12.10$$

where M_2 and M_1 are remaining and previous masses of free phase, respectively, S_i^{ef} is effective solubility of a compound in mixture, MW is molecular weight of the compound and V_{water} is volume of water in contact with free phases. When the mixture has about 28.95 % of 1,2-DCP and 71.05 % of TCE, the solubilities of both compounds will be the same, equal to 781.6 mg/L. The changes in free phase composition will also result in changes of the composition of dissolved contamination plume. This behavior is sometimes erroneously interpreted as a consequence of biodegradation. Dissolution is further complicated by the lack of equilibrium between fast-flowing water and relatively slow transfer of dissolving free phase.

Slow dissolution of free phase is an analogy of dissolution of inorganic contaminant mineral and seriously complicates remediation. Thus, localization of free product in source zone and its removal or isolation plays a pivotal role in remediation projects.

12.3 Basic Types of Remediation

In this section, we present some typical remediation methods. This outline is by no means complete and much more details can be found in specialized publications such as Suthersan, (1996) and Nyers, (1996).

Pump-and-treat (PT): This is classical method, which works quite well when most of contamination is in dissolved form. However, for reasons indicated above the efficiency of the method becomes limited when adsorbed contamination, free phase of organic contamination, and precipitated mineral of contaminant are present. Even when complete remediation of contaminated aquifer by this method is impossible, the method can be used for *containment* of dissolved plume, e.g., the pumping prevents further spreading of contaminant plume towards potential receptors (water supply wells, surface water bodies etc.). The efficiency of PT depends on heterogeneity of an aquifer and pumping wells have to be properly located to prevent escape of contaminated ground water. The location and spacing of pumping wells is often determined by hydrogeological modeling. The pumped water contaminated by organics is treated above ground in filters with granular activated carbon (GAC) or in air-stripping colons (Nyers, 1996).

Chemical enhancement of PT: This method is used to enhance the transfer of adsorbed or precipitated contaminant from solid phase to pumped ground water (Palmer and Fish, 1992). Typical transfer-enhancing processes are: a) competitive adsorption/desorption (example: phosphate displacing arsenic from adsorption sites), b) complexation of metals (example: citric acid complexing Cr(III)), c) cosolvent effects (example: ethanol increasing solubility of free phase of BTEX), d) application of surfactants (they decrease interfacial tension and increase mobility of NAPLs), e) reduction/oxidation (example: organic matter reducing Cr(VI) to Cr(III), which precipitates as $Cr(OH)_3$), f) precipitation/dissolution (example: injection of alkaline solution causes precipitation of lead as $PbCO_3$). A chemical enhancement system has several subsystems: 1) injection system, 2) reaction zone, 3) extraction system, and 4) treatment system for recovered water with contaminant and reactive agent. Principal problem often is the delivery of reaction agent to contaminated zones. Transport of reaction agent follows preferential flow path and may completely miss contamination. Another problem is disposal of sludge from treatment of pumped water.

Impermeable walls: These walls are made from materials such as bentonite slurry and they have low permeability ($<10^{-10}$ m s^{-1}). They are generally located in source zone of contamination (around free phase zone,

Table 12.1 Solubilities of TCE and 1,2-DCP in mixture.

Molar fraction 1,2-DCP	0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
1,2-DCP	0	270	540	810	1080	1350	1620	1890	2160	2430	2700
TCE	1100	990	880	770	660	550	440	330	220	110	0

around landfills etc.). Their purpose is to stop advective flux across source zone and, thus, to prevent formation of dissolved plume. However, even low permeability materials are permeable for diffusion, which can deliver considerable quantities of contaminants into aquifers.

Impermeabilization of ground surface: This is a relatively simple method which aims to reduce infiltration and, thus, formation of contaminated plume in saturated zone. The impermeable layer can be clay liner, geotextile or combination of both. Typical value of hydraulic conductivity of the layer is $<10^{-10}$ m s^{-1} and a protective layer (for example, gravel) on the top of low permeability layer is required to prevent destruction of the layer by drying and by roots of plants. Common applications are related to landfills and mine tailings sites, where low permeability layer maintains high water saturation and also reduces diffusion flux of oxygen (Chapter 9). A variant of the method is placement of impermeable layer at the base of future source of contamination. An example is construction of low permeability layers and drainage system at the base of projected landfill.

Soil vacuum extraction, (SVE): This is an efficient approach for remediation of unsaturated zone with residual free phase of organic contaminants. Suction is applied in air wells located in unsaturated zone. Flow of air is introduced and a contaminant partitions into air and is carried away towards suction wells. This approach has an advantage compared to the pumping of ground water because the flow rate for air is much higher than for water. This method is applicable only for volatile contaminants with high values of vapor pressure P_i and in permeable soils with high value of intrinsic permeability k. In some cases, the method is combined with air-sparging. The air-sparging is based on injection of air into saturated zone. Air bubbles then rise towards water table and there is partitioning between dissolved contamination and air bubbles depending on the value of Henry Law constant H_{cc} for a given contaminant. When bubbles reach water table, contaminants enter unsaturated zone and they are removed by soil vacuum extraction.

Soil flushing: This method is in the stage of development. It is based on the application of solution of surface-active compounds (surfactants) for flushing of residual free phase in unsaturated zone. Solubility of organic contamination increases and they drain towards the saturated zone, where they are captured by classical pumping methods. Compared to soil vacuum extraction (SVE), the method is only applicable at relatively low depth, but is applicable also for cleaning of capillary fringe, where SVE fails.

Permeable reactive barriers (PRB): These are in-situ reactive zones, where reaction agents are added to create favorable environment for remediation of contaminants. Typical applications include both organic and inorganic contaminants. In the case of acid plume with high metals and sulfate concentrations, the barrier is filled by organic matter and sulfate reduction and precipitation of sulfides take place:

$$2CH_2O + SO_4^{2-} = H_2S + 2HCO_3^- \qquad 12.11$$

$$Me^{2+} + H_2S = MeS + 2H^+ \qquad 12.12$$

where Me^{2+} represents metal. A common reactive material for chlorinated solvents is zero valence iron Fe^0, causing reductive dechlorination:

$$2Fe^0 + 3H_2O + X\text{-}Cl = 2Fe^{2+} + 3OH^- + H_2(g) + \\ + X\text{-}H + Cl^- \qquad 12.13$$

where X represents functional group of chlorinated solvents. The reactive barrier has to be more permeable than the surrounding aquifer because a plume would by-pass the barrier in the opposite case. This fact represents a limitation for the method because in some cases the residence time in the barrier may not be sufficient to complete remediation.

Natural attenuation (NA): This is a process of natural reduction of contaminant concentration, without human involvement. It can be both non-destructive (concentration decreases, but mass of contaminant remains the same, an example is dispersion) or destructive (mass is also reduced, an example is biodegradation). Natural attenuation of petroleum products takes place in relatively oxidizing environment and, in contrast, natural attenuation of chlorinated solvents takes place in relatively reducing environment (see Chapter 11). Basic criterions for evaluation of natural attenuation according to U.S. EPA are:

(1) Trends of dissolved concentrations in the plume have to be determined by several samplings. Non-parametric statistic tests (for example, Mann-Whitney test) are used to check if concentrations are decreasing. Trend of decreasing concentrations is the principal proof of natural attenuation.
(2) Background concentrations of geochemical indicators (electron acceptors O_2, NO_3^- and sulfate) are determined in ground water out of plume. Then we compare background concentrations with concentrations in the plume to decide if intrinsic bioremediation takes place. Products of biodegradation like Fe(II) and methane are sampled only within the plume. Concentration of geochemical indica-

tors can be converted to biodegradation capacity for BTEX. In the case of chlorinated solvents and inorganic contaminants, geochemical indicators are generally used only for qualitative indication of suitability of an environment for natural attenuation.

(3) In the case of organic contamination, laboratory tests in microcosmos with contaminated water and sediments may be run and bacterial population parameters and rates of biodegradation are determined.

Detailed methodology for evaluation of natural attenuation of organic contaminants is in Wiedemeier et al. (1999). Natural attenuation of inorganic contamination and redox conditions in contaminant plumes are discussed by Christensen et al. (2000). The natural attenuation approach is not nothing-to-do approach. Careful monitoring is required to confirm that NA really occurs and calculation of risk for potential receptors is performed to verify potential risks (so called RBCA, Risk Based Corrective Action).

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Chapter 13: Risk Analysis

13.1 Basic Concepts

Risk analysis often is a last step of contamination studies. There are several stages of risk analysis (LaGrega et al., 1994, Masters, 1998):

(1) *Hazard identification:* this is a process of determining if a particular chemical, which is linked to particular health effects like cancer, birth defects etc. Human data are rather limited, thus data on animals or other test organisms are generally used.

(2) *Dose-response assessment:* in this process the relationship between the dose of a chemical and incidence of health effects is determined. Most tests are performed using high doses on animals and extrapolation to low doses is commonly performed.

(3) *Exposure assessment:* this process involves assessment of exposure concentration, duration and size of population exposed to a particular chemical. Several factors like age and health of exposed population, pregnancy, smoking history, etc., have to be taken into account to evaluate possible synergic effects. In this stage, geochemical and transport models are used to calculate future possible exposure out of the site of contaminant release. For example, when a chemical is released from landfill site and migrates downgradient towards municipal wells in a nearby village, a transport model can be used to predict concentration of the chemical in drinking water from municipal wells in future.

(4) *Risk characterization:* in this stage previous stages are integrated and risk magnitude is calculated. This is compared with a regulatory limit and a decision about possible remediation of a contaminant source may be taken.

There are several possible ways of exposure, including *ingestion* by drinking of contaminated water, *inhalation* by breathing of contaminated air, and by *dermal contact* with contaminated soil. In human body, a chemical can be stored (for example, in fat like DDT), eliminated from body by excretion (in urine etc.) or can be transformed to other compounds (sometimes even more toxic, an example is transformation of trichlorethylene, TCE, to vinylchloride, VC).

Several human organs are especially vulnerable. The liver filters blood and, thus, can be directly damaged by a chemical transported in blood stream. Chemicals damaging liver are called *hepatotoxic*. Examples are arsenic, trichlorethylene (TCE), and anabolic steroids. Kidneys also filter blood and can be damaged by *nephrotoxic* compounds like cadmium, lead and chlorinated solvents. Chemicals acting on blood are called *hematotoxic* and include carbon monoxide and nitrogen compounds. They interfere with blood ability to transmit oxygen. Benzen affects formation of platelets in blood and, thus, also is hematotoxic compound. *Pulmonotoxicity* is related to compounds like asbestos, and quartz dust, which can cause cancer of lungs.

13.2 Concept of Toxicity

Two principal groups are considered: chemicals with *acute toxicity* and chemicals with *carcinogenic effects*. Some chemicals like arsenic belong to both groups.

Acute toxicity refers to effects that may happen within a short period of time after a single exposure to a chemical. Not every exposed individual will react in the same way and a *dose-response curve* shows a percentage of tested population that is affected as a

function of dose received. Dose is normalized per kg of body weight and is expressed, for example, in mg/kg. It is assumed that is a *threshold dose*, below which there is no toxic effect. Thus, the dose-response curve for acute toxicity (non-carcinogenic) chemicals does not pass through origin (Fig. 13.1), but starts at some non-zero concentration of a chemical.

In contrast, for substances with carcinogenic effect it is assumed that any exposure to a carcinogen may create some probability of cancer. In that case the dose-response curve passes through origin (Fig. 13.1).

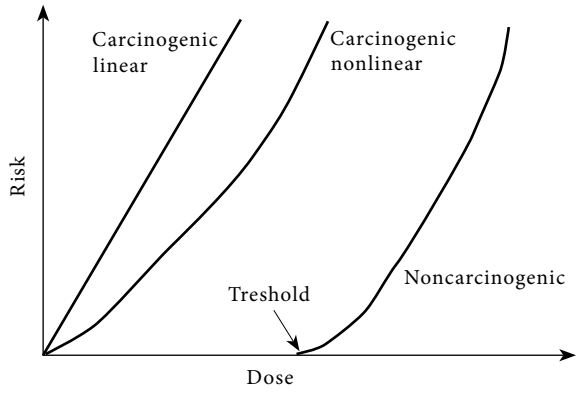


Figure 13.1 Dose-response curves for carcinogens and for non-carcinogens.

In some cases, there are epidemiological data based on the study of human population exposed to a toxic chemical. These studies cannot be generally performed under completely controlled conditions and their results are often interpreted using statistical methods.

However, the dose-response curves are generally based on *animal bioassays* and a *scaling factor* must be used for extrapolation from animals to humans. In general, testing is performed on animals like selected species of rats and tested doses are much higher than expected doses for human population exposures. Several extrapolation methods are used. Commonly used model is the *one-hit model* (Masters, 1998) which gives the relationship between dose (d) and lifetime probability $P(d)$ of cancer as

$$P(d) = 1 - e^{-(q_0 - q_1 d)} \qquad 13.1$$

where q_0 and q_1 are fitting parameters for dose-response curve. When we substitute $d = 0$, we will obtain background risk of cancer. For small values of x, we can develop e^x using the Taylor expansion as $e^x \cong 1 + x$ and assuming that background risk is small, we can write:

$$P(0) = 1 - e^{-q_0} \cong 1 - \left[1 + \left(-q_0\right)\right] = q_0 \qquad 13.2$$

Thus, background risk for cancer incidence is equal to q_0. Life-time probability of cancer can be evaluated, using the Taylor expansion again, as

$$P(d) = 1 - (1 - (q_0 + q_1 d)) = q_0 + q_1 d = P(0) + q_1 d \qquad 13.3$$

For low doses, the additional risk of cancer $A(d)$ is

$$A(d) = P(d) - P(0) = q_1 d \qquad 13.4$$

Thus, the model predicts that the additional risk of cancer for low doses is linearly related to dose. There are other models such as *multistage model*. See, for example, Masters (1998).

13.3 Carcinogenic Contaminants

There are several categories of carcinogens according to U.S. EPA.:

Group A: human carcinogens, based on sufficient epidemiological evidence to support a causal relation between exposure to a chemical and cancer.

Group B: probable human carcinogen, divided into *group B1* and *group B2*. For a chemical in group B1, there is limited epidemiological evidence. For group B2, there are insufficient human data, but sufficient evidence of carcinogenecity in animals.

Group C: possible human carcinogens, based on limited animal data, but without human data.

Group D: not classified, both human and animal evidence is insufficient or there are no data at all.

Group E: evidence of non-carcinogenecity, there is evidence about lack of carcinogenic effects in both humans and animals.

The dose-response curve for carcinogenic contaminants is used to calculate the incremental risk of cancer (e.g., above the background incidence). At relatively low doses, the slope of dose-response curve is called *slope factor SF* (also potency factor PF) and dimensionless *incremental risk IR* is calculated as

$$IR = SF\ CDI \qquad 13.5$$

where *CDI* is *chronical daily intake* [mg/kg day] and *SF* is slope factor (slope of dose-response curve) with units $[(\text{mg/kg.day})^{-1}]$. The value of *CDI* is calculated for different exposures (ingestion, inhalation, dermal contact) during 70 years of life time. For example, for ingestion via drinking of contaminated water the *CDI* is

$$CDI\ [\text{mg/kg day}] = \text{Average daily dose [mg/day]/Body weight [kg]} \qquad 13.6$$

The values of slope factor *SF* can be obtained from database of U.S. EPA called IRIS (integrated risk infor-

mation system), available on the web under U.S. EPA Home Page. Values of incremental risk > 10^{-6} are generally considered as unacceptable, but there is a transition between 10^{-4} and 10^{-6}, when other circumstances are considered.

Problem: Calculate incremental risk for chloroform (class B2 contaminant) with slope factor $SF = 6.1\times10^{-3}$ $[mg/kg.day]^{-1}$ when 70-kg person drinks 2L of water with 0.2 mg/L of chloroform.

Solution:
$CDI = (2.0\times0.2)/70 = 0.00572$ mg/kg.day, then
$IR = 0.00572\times6.1\times10^{-3} = 34.8\times10^{-6}$
e.g., the probability to get cancer is about 35 in 1 million.

13.4 Non-carcinogenic Contaminants

As indicated earlier in the text, there is a threshold concentration for non-carcinogenic contaminants, below which no adverse effects are observed. Furthermore, lack of some elements which are toxic at high administered doses also has a negative impact on human health. Examples are selenium and zinc. Thus, there is some optimum concentration below which and above which there is an adverse effect on human health. In contrast, contaminants like lead, cadmium, and arsenic are not necessary for human organism even at extremely low doses.

The lowest administered dose resulting in a response is called *the lowest observed effect level (LOEL)*. The highest dose without response is called *the no observed effect level (NOEL)*. When adverse effect levels are included, then there are *the no observed adverse effect level (NOAEL)* and *the lowest observed adverse effect level (LOAEL)*.

The concept of *reference dose, RfD* (also called acceptable daily intake) is based on the NOAEL divided by safety factor (uncertainty factor). The safety factor includes uncertainties for extrapolation from animals to humans, for presence of more vulnerable individuals in human population etc. Thus, the reference dose is several orders of magnitude lower than the observed value of NOAEL. Reference dose RfD with units [mg/kg.day] indicates a level of human exposure without an appreciable risk.

Hazard index HI (also called hazard quotient) is calculated as

$$HI = \text{Average daily dose during exposure [mg/kg day]}/RfD\text{[mg/kg day]} \quad 13.7$$

Results of *HI* are dimensionless. When $HI > 1.0$, the risk becomes unacceptable. Average daily dose *ADD* is calculated only for a period of exposure and not over life time as it is for carcinogenic contaminants. For several contaminants, the hazard index is the sum of individual hazard indexes. Values of reference doses for different chemicals can be found in database IRIS, just like slope factors for carcinogenic contaminants.

Problem: Calculate hazard index for drinking of 2 L of water with 2.0 mg/L of toluene for a person with body weight of 70 kg. The *RfD* for toluene is 0.200 mg/kg.day.

Solution:
First calculate average daily dose *ADD*
$ADD = (2.0\text{ mg/L} \times 2\text{ L/day})/70\text{ kg} =$
$= 0.058$ mg/kg×day
Hazard index
$HI = 0.058\text{ mg/kg}\times\text{day}/0.200\text{ mg/kg}\times\text{day} = 0.14$
$0.14 < 1.0$, suggesting that drinking of the water is safe.

13.5 Risk Analysis Methodology

Several steps are performed during risk analysis (LaGrega et al., 1994). Let us consider a case of a municipal landfill. First of all, contaminants of interest have to be selected and exposure has to be estimated. Data for the source zone, in this case landfill area, are collected. Concentrations of chemicals in water, soil, and air are determined. In this preliminary screening, *toxicity scores TS* for both carcinogens and non-carcinogens are determined using slope factors and reference doses. The toxicity scores for individual contaminants are summed up and contaminants comprising 99 % of toxicity score are selected.

Then exposure is determined at exposure (receptor) points. This exposure point may be directly at source zone or may be located at some distance from source zone. Say the contaminant selected on the basis of toxicity score is lead and exposure point is a water supply well about 400 m downgradient from the landfill. In that case, we have to calculate prediction of future concentration of lead in drinking water from the water supply well. This can be performed using an analytical or numerical model of transport, which are an extension of flow model. Relevant processes for lead transport (advection, dispersion, adsorption, precipitation of lead minerals like cerussite, $PbCO_3$) should be included in the model. If only advection is included

in model, then the prediction of lead concentration represents the worst case scenario (maximum level of exposure).

After calculation of exposure, the risk is calculated separately for both carcinogens and non-carcinogens. If the risk is acceptable, natural attenuation processes only may be sufficient to stop spreading of the plume. In contrast, if risk calculated for exposure point is unacceptable, then some remediation technology (pumping and treatment of ground water, reactive barriers etc., see Chapter 12.3) should be used. The approach based on risk analysis is called *Risk Based Corrective Action (RBCA)* and is implemented by the U.S. EPA.

References

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Masters G.M., 1998: I*ntroduction to Environmental Engineering and Science*, 2nd Edition, Prentice Hall, Upper Saddle River, New Jersey 07458, 651.

Meeting Report Form

Send to
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Project Number and Title:IGCP/SIDA 594
IMPACT OF MINING ON THE ENVIRONMENT IN AFRICA

MEETING: Training Course: The assessment of impacts of mining on the environment: The geochemist´s approach
Date: July 13-15, 2013
Place:Johannesburg, Republic of South Africa
Itinerary: July 13: Lectures
July 14: Field trip to the Witwatersrand area
July 15: Lectures and exercises



Attendants and lecturers of the training course “The assessment of impacts of mining on the environment: The geochemist´s approach” held in Johannesburg, Republic of South Africa, July 13-15, 2013.

SCOPE AND RESULTS OF MEETING:

Itinerary of the Training Course

JULY 13
08:30-09:00 Opening and Introduction of the course lecturers (*Isabel Weiersbye, University of the Witwatersrand*)
09:00-09:45 Principles of environmental geochemistry (*Ondrej Sracek, Palacky University*, *Olomouc, Czech Republic*)
09:45-10:30: Geochemistry of mine drainage I and II (*Ondrej Sracek, Palacky University, Olomouc, Czech Republic*)
10:45-11:30:Mobility and bioaccessibility of metals in soils: an experimental approach (*Martin Mihaljevič, Charles University, Prague*)
11:30-12:15: Methods of environmental monitoring in mining areas (*Bohdan Kříbek, Czech Geological Survey, Prague*)
12:15-13:00: Assessment of hazardous properties of mining wastes: An European Union experience (*Bohdan Kříbek, Czech Geological Survey, Prague*)
13:45-14:30: Geochemical modeling and environmental monitoring (*Francois Lubala, University of Lubumbashi, DR Congo*)
14:40-15:15: Characterisation of mine leachates emanating from gold mining activities on the Witwatersrand (*Hlanganani Tutu, University of the Witwatersrand*)
15:30-16:15: Lead and copper isotopes in environmental applications (*Martin Mihaljevič, Charles university, Prague*)
16:15-17:00: Nodelling resuspension of dust particles in mining districts in Namibia and Zambia (*Bohdan Kříbek, Czech Geological Survey, Prague*)
17:00-17:10 Closing of day 1; Field trip arrangements
JULY 14
08:00-10:00: Travel from WITS to AngloGold Ashanti Limited
10:00-10:30: Phytotechnologies: Decontamination of polluted water and soils: Societal and Socio-economic aspects (*Isabel Weiersbye, University of the Witwatersrand*)
10:30-15:00: Tour to different types of mine wastes and phytoremediation sites
15:00-17:00: Travel from mine sites to Witwatersrand.
July 15
08:30-9:15: Principles of geochemical modeling (talk) (*Ondrej Sracek, Palacký University, Czech Republic*)
9:15-10:00: Applications of geochemical modeling (part I) (*Ondrej Sracek, Palacký University, Czech Republic*)
10:30-12:45: Applications of geochemical modeling (part II) (*Ondrej Sracek, Palacký University, Czech Republic*)
13:30-14:15: Applications of geochemical modeling (part III) (*Ondrej Sracek, Palacký University, Czech Republic*)
14:15-15:00: An overview of surface and sub-surface flow models (*Jason Hallowes, Danish Hydrological Institute, South Africa Branch*)
15:00-15:30: Phase dependent phytoavailability of thallium: a synthetic soil experiment (*Aleš Vaněk, University of Life Sciences, Prague)*
15:30-16:00: Metals and arsenic in cassava: Indicators of contamination in the Zambian Copperbelt mining district (*Bohdan Kříbek, Czech Geological Survey, Prague*)
16:30-17:15:Presentation of the IGCP/SIDA project 594 and GENERAL DISCUSSION
(Bohdan Kříbek, Czech Geological Survey and Isabel Weiersbay, University of the Witwatersrand)

17:15-17:30: Closing of training course.

Attendance:

Mr. T. Uvanga and P. Reinecke (Dundee Precious Metals, Namibia), K. Phala and J. Ncongwame, S. A. Kanu (TUT, South Africa) B. Yalala*, M.Joubert*, Z. Noluvu*, M. Maya*, S. Grindley*, T. Ramped*, R. Carnie*, B. Canden-Smith*, L. Uruski*, J. Lusilao*, M. Zamxaka*, Ch. Curtis* B. McLeroth*, E. Bakatula* D. Saad* T. Mophancane* H. Wilson* M. Muller* I. Weierssbye, H. Tutu, (University of the Witwatersrand) G. van Dyck and H. Nel (Anglogold Ashanti) N. MacGorge (BHP Billitong) T. Cruz (AGA, Southt Africa) L.Loete (RSA-AGA, South Africa) S. Alidu (Geological Survey of Ghana), S. Clark (BGS, South Africa) A. Bake*, S. le Roux*, R. Rentel*, (Stellenbosh University, South Africa) A. Tembho* (University of Zambia) F. Lubala, P. Mambwe*, B. Madnasi*, N., N. Mugisho* (University of Lumumbashi, Democratic Republic of Congo) P. Nanbambe* (University of Namibia) N. L. T. Chinguno* (University of Zimbabwe) M. Wanenge (Digby Well Survey) J. McDonald, J. Muhlanti (Palabora Mining SA) P. Goga (Consultant) A. Kanku (WFP DR Congo)
** students*
Students: 27, Women:15

Scope of the Meeting

The course participants were taught and trained in the use of geochemical-environmental monitoring and modelling to solve the problems arising from contamination of surface and ground waters in mining districts.

Environmental-geochemical monitoring and modelling enables:

- to establish the speciation of contaminants in aqueous environment, the kinetics and thermodynamics of their dissolution, transport and precipitation,
- to solve problems linked to mixing of contaminated and uncontaminated waters,
- to predict the spread of contamination of surface and ground waters,
- to asses the degree of contamination of soils and plants in contaminated areas,
- to evaluate bioavailability and bioaccessibility of potentially harmful elements in soils and plants.

Geochemical-environmental mapping and modeling also enables to select and propose the most efficient methods and procedures of remediation of contaminated waters and to assess the effectiveness of applied remedial measures.

Achievements of the Meeting

The course was intended to teach and train the participants in using geochemical methods to solve problems linked to contamination of surface and ground waters, soils and plants in mining districts.

The course participants received PDF versions of all presentations of the Training Course, PDF version of the Risk Assessment Manual of Abandoned Mine Sites elaborated by the Geological Survey of Namibia and an operating manual enabling the trainees to learn progressively and independently the methods of geochemical modeling.

Signature of Project Leader and Date
September 9, 2013

Attachments:

Attendance List of the Training Course,
Programme and Presentations of the Training Course (CD version).

IGCP/SIDA Project 594, IMPACT OF MINING ON THE ENVIRONMENT IN AFRICA

TRAINING COURSE: Applications of geochemical modelling and reactive transport with emphasis on the impact of mining industry was held in Windhoek, Namibia on July 4th, 2012

Instructor: Ondra Sracek, Palacky University Olomouc, Czech Republic



Some attendants of the Training course Applications of geochemical modelling and reactive transport with emphasis on the impact of mining industry held in Windhoek, Namibia, July 4, 2012.

Itinerary:

09:00-09:45 Fundamentals of transport, geochemistry and sampling
10:00-10:45 Introduction to geochemical and reactive transport modeling
11:00-11:45 Introduction to acid mine drainage

11:45-13:00 Lunch
13:00-13:45 Installation of the PHREEQC software (freeware), installation of input files
14:00-16:00 Interactive exercises:

1. Modification of data base and speciation in PHREEQC: Example of arsenic
2. Inverse geochemical modeling of permeable reactive barrier (PRB) at Milovice, Czech Republic
3. Direct geochemical modeling of mine drainage at Smolnica site, Poland
4. itration of acid mine drainage (AMD) water with calcite
5. Direct geochemical modeling of acid mine drainage neutralization by calcite
6. Modeling of acid mine drainage in a column, breakthrough curve (concentration vs. PV)
7. Adsorption of zinc in a batch
8. Transport of cadmium in column with adsorption, a breakthrough curve (concentration vs. PV)
9. Transport of cadmium in column with adsorption, concentration vs. distance curve
10. Kinetic dissolution of quartz
11. Acid injection into carbonate reservoir: equilibrium dissolution of calcite, kinetic dissolution of quartz
12. Modeling of diffusion in a column

16:00-17:00 Discussion: Capabilities of the PHREEQC program in dealing with issues arising from contamination of waters in South Africa, Namibia and in other African countries, possibilities of further education in geochemical modeling.

Attendance:

Amukwa Lovisa (Student, University of Namibia),
Kaundikiza G (F and G Mineral resources)
Shigwedha S. R. (Student, University of Namibia)
Tjikuzu Manuella (Student, University of Namibia)
Muroua Don (CSA Consulting Company)
Ipinge Helmi (Student, University of Namibia)
Hijamutiti Michelelle (Student, University of Namibia)
Mileusnic, Marta (University of Zagreb, Croatia)
Huisamen Althus (Student, University of Pretoria)
Shaningwa Johanna (Student, University of Namibia)
Uukulev Selma (Student, University of Namibia)
Jeremiah Simon (Geologist, Ministry of Mines, Namibia)
Simubah Gloria (Geologist, Geological Survey of Namibia)
Hamakwa Justina (Student, University of Namibia)
Nesonga Lisias (Student, University of Namibia)
Emwula Monika (Student, University of Namibia)
Benjamin Mapani (University of Namibia),
Shivoko N.H (Geologist, Geological Survey of Namibia)
Bohdan Kribek (Teacher, Czech Geological Survey)
Vít Penízek (Teacher, Czech University of Life Sciences, Prague).

Scope of the Meeting (program or outline of geological study)

The course participants were taught and trained in the use of geochemical modeling to solve the problems arising from contamination of surface and ground waters in mining districts.

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Geochemical modeling enables:

- to establish the speciation of contaminants in aqueous environment, the kinetics and thermodynamics of their dissolution, transport and precipitation,
- to solve problems linked to mixing of contaminated and uncontaminated waters,
- to predict the spread of contamination of surface and ground waters,
- to assess the rate of neutralization of acid mine waste waters by carbonates.

Geochemical modeling also enables to select and propose the most efficient methods and procedures of remediation of contaminated waters and to assess the effectiveness of applied remedial measures.

Achievements of the Meeting

The course was intended to teach and train the participants in using geochemical modeling to solve problems linked to contamination of surface and ground waters in mining districts.

The course participants received a software for geochemical modeling (PHREEQC, freeware, USGS) and an operating manual enabling the trainees to learn progressively and independently the methods of geochemical modeling.