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Heavy Metals

Problems and Solutions

With 111 Figures



Springer

Series Editors

Dr. Rod Allan

Canada Centre for Inland Waters

867 Lakeshore Road, P.O.B. 5050, Burlington, Ontario L7R 4A6, Canada

Prof. Dr. Ulrich Förstner

Arbeitsbereich Umweltschutztechnik

Technische Universität Hamburg-Harburg

Eißendorfer Straße 40, D-21071 Hamburg, Germany

Prof. Dr. Wim Salomons

GKSS Research Center

Max Planck Straße, D-21502 Geesthacht, Germany

On leave of absence from:

Institute for Agrobiology and Soil Fertility (AB-DLO)

P.O. Box 129, N-9750 AC Haren (Gn), The Netherlands

Volume Editors

Prof. Dr. Wim Salomons

Prof. Dr. Ulrich Förstner

addresses see above

Dr. Pavel Mader

University of Agriculture

Faculty of Agronomy

126 21 Prague 6-Suchbát, Czech Republic

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Preface

This book has its origin in a meeting between dr. G. Mader, P. Cibulka and N. De Oude during a SETAC meeting in Washington. Their discussions on the highly adverse environmental effects of poorly managed production of metals and associated emissions to air and soils in Central and Eastern Europe resulted in an international workshop on Heavy Metal Contamination in Liblice, Czech Republic. The theme of this workshop was to determine the pathways of metals, develop answers and to present case studies on heavy metal pollution. During part of the workshop also regulators, environmentalists and journalists took part in order to present their viewpoints.

A number of the presentations at the workshop were expanded to chapters for this book to give a state-of-the-art overview of environmental issues on heavy metals relating not only to East, Central and Western Europe but also to other parts of the world.

This book would not have been possible without active support by the European Environmental Research Organisation (EERO), the Regional Environmental Centre for Central and Eastern Europe (REC), the German Umweltbundesamt, The Federal Committee for the Environment (CSFR) and Procter and Gamble who sponsored the workshop and in this way prepared the basis for this book.

N. De Oude
(Executive Director SETAC-Europe)

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I Metal Behavior in the Environment

1 Agricultural Problems Related to Excessive Trace Metal Contents of Soils

Alina Kabata-Pendias

Institute of Soil Science and Cultivation of Plants 24-100 Pulawy, Poland

1 Introduction

Behaviour of trace metals in soils depends upon complex reactions among micro- and macro cations and anions, and different components of various soil phases: solid, aqueous and gaseous. The main features of the soil biogeochemical system governing the behaviour of trace elements are: (1) heterogeneous distribution of compounds and components; (2) seasonal and spatial alteration of major soil variables; (3) transformation of element species; (4) transfer between phases; and (5) bioaccumulation.

The ability of root to take up trace metals is based on the processes at soil-soil solution-root interfaces. The accessibility of an element to plants is determined primarily by its origin, which influences its chemical forms, and by its association with soil components.

Soils of several regions of the world (and especially of Europe) have been subjected, and will be in the future to mineral fertilization, pesticide application, industrial pollution and waste disposal. All these activities will affect both chemical and physical soil properties, and will lead to changes in the behaviour of trace elements in soils. The impact of soil acidification, alkalization, salinization and losses of organic matter on trace metal uptake by vegetation (especially crop plants) has already become serious environmental and health problems.

The assessment of soil pollution and adoption of acceptable standards for permissible trace metal levels in soils are the key to the protection of ecological function of soils and for the sustainable agriculture.

2 Trace Metals in Soils

The natural system of a soil is under a great impact of climatic conditions. Therefore, the predomination of either migration or accumulation of trace elements can be predicted for a given soil type and climatic zone. Climatic and soil factors influence the speciation and mobility gradient of the metals in soils, and therefore control their phytoavailability (Table 1).

Table 1. Relative mobility and phytoavailability of trace metals species in soils

Metal species and association	Availability-mobility
Simple or complex cations in solution phase	Easy
Exchangeable cations in organic and inorganic complexes	Medium
Chelated cations	Slight
Metal compounds precipitated on soil particles	After dissolution
Metals bound or fixed inside organic substances	After decomposition
Metals bound or fixed inside mineral particles	After weathering and/or decomposition

An estimation of background levels of trace metals in European soil is almost impossible because truly pristine ecosystems no longer exist. The data obtained for soils from areas not exposed directly to pollution indicate that trace metal levels in these soils have not been changed significantly. Average "background" metal contents of soils calculated for the world-wide basis, Western European countries, and Poland show a relative increase comparing to the Clarke's values (Table 2). This is especially pronounced for Cd, while Zn and Pb are less accumulated, and Cu content rather decreases in soils.

More precise method to compare the relative abundance of trace metals in soils is a normalization to an element universally found and relatively stable in most geochemical environments, e.g., aluminum. Enrichment factors calculated on the base of the Al content show that several metals, and in particular Cd, Pb and As are concentrated in topsoil when compared to their occurrence in the Earth's crust (Kabata-Pendias 1992).

Table 2. Average "background" levels of some trace metals in soils of the World, Europe (EC), and Poland (PL)

Metal	Locality	Soil/Clarke's coefficient	Podzols	Cambisols	Fluvisols
Cu	World	0.7	13	23	24 ^a
	EC		10	15	47
	PL		5	10	15
Cd	World	10	0.3	0.5	0.4 ^a
	EC		0.5	0.6	0.4
	PL		0.4	0.5	0.5
Zn	World	2	45	60	65 ^a
	EC		28	48	63
	PL		37	58	84
Pb	World	3	20	30	23
	EC		23	29	37 ^b
	PL		18	20	23

^a Kastanozems

^b Various soils

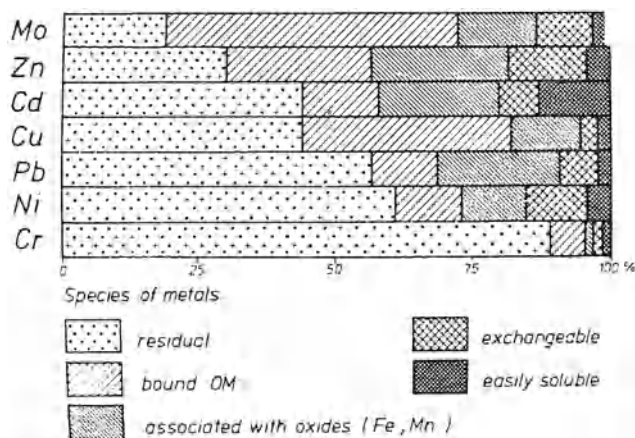


Fig. 1. Speciation of trace elements in soils (in percent of total content) (Kabata-Pendias 1992)

Present-day soils contain trace metals of various origin. Lithogenic metals are those which are directly inherited from the lithosphere (parent material). Anthropogenic metals in soils are all those deposited into soils as direct or indirect results of human activities. Pedogenic metals are of lithogenic and anthropogenic origins but their distribution in soil horizons and among soil particles is changed due to mineral transformation and other pedogenic processes. Chemical equilibria of a soil can be characterized by dissolution, diffusion, sorption and precipitation reactions. Depending upon the variability in physical and chemical characteristics of metals, their affinity to soil components governs their speciation (Fig. 1). Easily mobile trace metals (Zn and Cd) exist mainly as organically bound, exchangeable, and water soluble species. Cu and Mo predominate in organically bound and exchangeable species, and their behaviour is strongly influenced by changing soil conditions. Slightly mobile metals (Pb, Ni and Cr) are mainly bound in silicates (residual fraction).

Soluble, exchangeable and chelated species of trace elements are the most mobile in soils, and govern their migration and phytoavailability (Table 2). The behaviour of trace elements reflected in their speciation depends greatly upon added forms or compounds as well as upon soil conditions. It is clearly illustrated by the diversity of Zn and Cd species after sewage sludge application (Fig. 2).

Pedogenic processes, soil management and various other anthropogenic factors are likely to control the total contents and mobility of trace metals in a soil. Main soil variables involved in the metal status are: pH, Eh, organic matter (SOM), hydrous oxides, clays, carbonates and salt contents. The role of parent material and of water (regime and cycling) is also of great importance (Table 3).

The budgets for some trace metals in soils of Europe, based on the total atmospheric input and leaching with seepage or drainage waters, are positive in most cases (Table 4). Increased leaching over the deposition of Mn and Zn has been

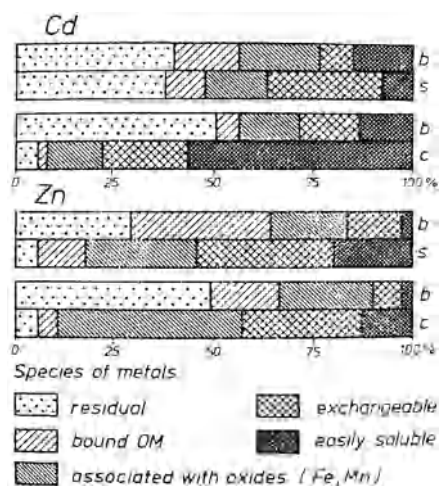


Fig. 2. Impact of sewage sludge on Cd and Zn speciation in soil. (Chlopecka 1992, and Dudka and Chlopecka 1990). Soil treatments: b - blank, s - sewage sludge (Cd - 0.5, Zn 400 mg kg⁻¹), c - metals as carbonates (Cd - 50, Zn - 1500 mg kg⁻¹)

reported only for acid forest soils. However, when including the input from other sources, e.g. fertilizers (mineral and organic) and harvest residues, man-induced cycling of trace metals is likely to increase their levels in soils of most regions.

Table 3. Parameters relevant in the status of trace metals in soils

PARENT MATERIAL:	CaCO ₃ content
	Texture
	Weathering degree
SOIL:	Texture
	Hydrous oxides (Fe, Al, Mn)
	Clay minerals
	Redox, pH, CEC, SOM
	Free CaCO ₃
	Ground water
	- level
	- fluctuation
	- composition
WATER:	Rainfall - intensity
	Irrigation - cations
	Seepage - salinity
	- acidity (SO ₂ , NO _x)
	- DOC

Table 4. Metal budgets of surface soils in Europe ($\text{g ha}^{-1} \text{yr}^{-1}$)

Ecosystem (method)	Country	Cd	Cu	Mn	Pb	Zn
Pine forest (seepage water)	W.Germany	3	10	-360	104	134
Spruce forest (lysimeter)	Sweden	-1	5	-600	75	-130
Farmland (drainage water)	Denmark	3	-	-	260	130
Farmland (seepage water)	Poland	2	14	90	160	360

3 Excess of Trace Metals in Soils

Agricultural soils, nowadays, are exposed to both input and losses of trace metals at a much higher rate, and on a larger scale than in previous periods. Soils of Europe have been exposed to pollution for a long time. Also the emission of metals has been larger in Europe than in other continents. In any industrial region of all continents or countries, soils are polluted, especially with trace metals (Table 5). A continuous increase of metallic pollutants in soils of Europe has already been a matter of real concern, and as De Bruijn and De Walle (1989) calculated, at the present metal budgets of soils in the Netherlands, there will be a 50% increase in their content in the coming years: Cu 25-30, Hg 45-50, Zn 50-60, Pb 120-160, Cd 120-300, Cr 190, and Ni 120-300.

Anthropogenic trace metals enter the soils by a variety of pathways: (1) aerial deposition, (2) pesticide and fertilizer application, (3) waste utilization, (4) dredged sediment disposal, and, (5) river and irrigation waters. The speciation and distribution of anthropogenic metals in soils are related to their chemical forms at the time of impaction. Thus, anthropogenic metals may form different species in soils, depending upon reaction surface and external binding sites with different bonding energy. The concentration of trace metals in soil solution is a good index of the mobile pool of metal in soils. Any chemical stress in soils is reflected in variations in the trace metal content of soil solutions. Most significant changes were observed in the solution from soil highly acidified, e.g. by sulfur deposition. Also in soils polluted by metal smelter emissions, the deposited metals increased markedly in the soil solution (Fig. 3).

Soils deteriorated by industrial emission are broadly investigated, and are known to be common within various industrial regions. Pollution of agricultural source can also effect a relatively high accumulation of several trace metals in soils (Table 5). Some features of soil contamination from two main source, aerial (mainly industrial) and agricultural pollution are presented in Table 6. In many cases, however, the load of heavy metals into soils is from both sources, and is

Table 5. Excessive levels (maximum values) of trace metals in surface soils as reported for some European and other countries (mg.kg⁻¹)

Element	Country	Source	
		Agricultural ^b	Industrial ^c
As	Japan	400	2470
	Canada	290 ^d	2000
Cd	G.Britain	167	336
	Poland	107	270
Cr	W.Germany	400	
	Poland		10 000
Cu	Japan	300	2020
	Netherlands	265	1090 ^e
Hg	Canada	11.5 ^d	2.0
	W.Germany	24	
Ni	G.Britain	850	600
	Canada		26 000
Pb	W.Germany	800	3075
	G.Britain	390	4560
V	India		840 ^f
Zn	Netherlands	760	3625
	USA	765	12400

^a Compilation based on data collected by Kabata-Pendias and Pendias (1992)

^b Mainly sludged farmland ^c Mining and metal-processing industry

^d After application of pesticides ^e Belgium ^f Vicinity of graphite industry

rather difficult to distinguish. Noticeable is the fact that most often soils become contaminated by several inorganic pollutants that are accompanied quite frequently by acid rain (mainly SO₂, NO_x, and HF), and also by organic pollutants (e.g. polycyclic hydrocarbons). Long-term effects of such pollution on deterioration processes in soils are not yet fully predictable, since the behavior of metallic pollutants controlling the phytoavailability and residence time in soils depends upon variable soil conditions.

Agricultural and environmental significance of soil pollution is rather unpredictable, especially as metal behaviour controlling phytoavailability and residence time in soils depends upon changeable soil conditions. The residence time of trace metals in soils in humid temperate climate, regardless of their variable mobility, is very long (Table 7).

The assessment and classification of soil contamination with trace metals and appropriate land use is of a vital importance. In spite of several monitoring and classification systems, the whole extent to which the soil environment is affected by heavy metals is yet unknown. Especially practices of soil amendment with metal-rich sludge and other metal-rich deposits (e.g., lime from metal mine-ponds, coal combustion residues) deserves great attention today and in the future.

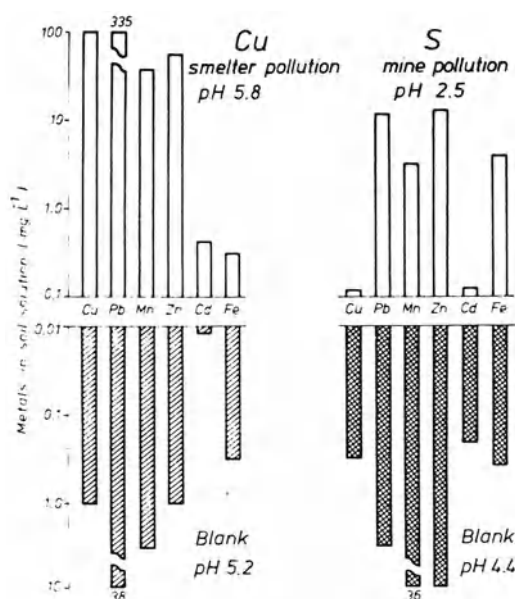


Fig. 3. Effects of pollution from copper smelter and sulfur mine on concentration of trace metals in soil solutions

A preliminary system for soil classification and land use is adopted in Poland (Table 8 and Fig. 4). For each degree of pollution, three soil groups are distinguished (e.g., light and acid, medium and acid, heavy or organic-rich and neutral). Acceptable land use is shortly described for a given class of pollution:

- I. Soils slightly polluted can be used for all field crops, with the exception of growing vegetables for infants and children.
- II. Soils moderately polluted are preferable for cereals, potatoes, sugar beets, and fodder plants. Growing of some vegetables like e.g., lettuce and spinach, should be forbidden.

Table 6. Some features of soil contamination with trace metals from aerial and agricultural sources

Aerial pollution	Agricultural pollution
Wide spread	Localized
Very recent	Beginning with fertilizer and waste application
Continuous deposition	Annual rate doses
Slow cumulative rise in concentrations	Variable loads
Accumulation in thin top layer	Distribution in organic and/or ploughed horizons
Increased pollution of top plants than roots	Increased concentration in roots than top plants

Table 7. Mobility condition and residence time of trace metals in soils

Element	Conditions	Plant/soil coefficient	Residence in soils (yr) ^a
Cd	pH (-), Eh (-)	10	70 - 1000
Zn	pH (-), OM (+)	1	70 - 3000
Hg	alkylation	1 (org.) 0.01 (min.)	500 - 1000
As	Eh (-), alkylation	0.1	1000 - 3000
Be	Eh (-)	0.1	500 - 1000
Pb	pH (-), Eh (-), OM (-)	0.01	700 - 6000

^a After Bowen (1979)

In brackets are identified effects.

III. Soils moderately polluted present a risk of contamination of any crops. Agricultural practices to decrease a metal uptake, and frequent control of plant food quality are recommended. Preferable are industrial plants and seed grasses.

IV. Soils heavily polluted should not be used for food plant production, especially when soils are acid and light. Recommended are industrial plants, and in particular, crops used for alcohol, technical oil, and energy production.

Table 8. Assessment of surface soil pollution with metals in Poland (mg kg⁻¹)

Metal	Soil group ^a	Classes of pollution ^b					
		0	I	II	III	IV	V
Cd	a	0.3	1	2	3	5	> 5
	b	0.5	1.5	3	5	10	> 10
	c	1	3	5	10	20	> 20
Cu	a	15	30	50	80	300	> 300
	b	25	50	80	100	500	> 500
	c	40	70	100	150	750	> 750
Ni	a	10	30	50	100	400	> 400
	b	25	50	75	150	600	> 600
	c	50	75	100	300	1000	> 1000
Pb	a	30	70	100	500	2500	> 2500
	b	50	100	250	1000	5000	> 5000
	c	70	200	500	2000	7000	> 7000
Zn	a	50	100	300	700	3000	> 3000
	b	70	200	500	1500	5000	> 5000
	c	100	300	1000	3000	8000	> 8000

Source: Kabata-Pendias et al. 1993

^a Soil group: (a) light & medium, pH < 5.5; (b) medium & heavy, pH < 5.5; (c) heavy & rich in SOM, pH 5.5 - 6.5^b Classes of pollution: (0) unpolluted, (I) slightly, (II) moderately, (III) considerably, (IV) heavily, (V) extremely

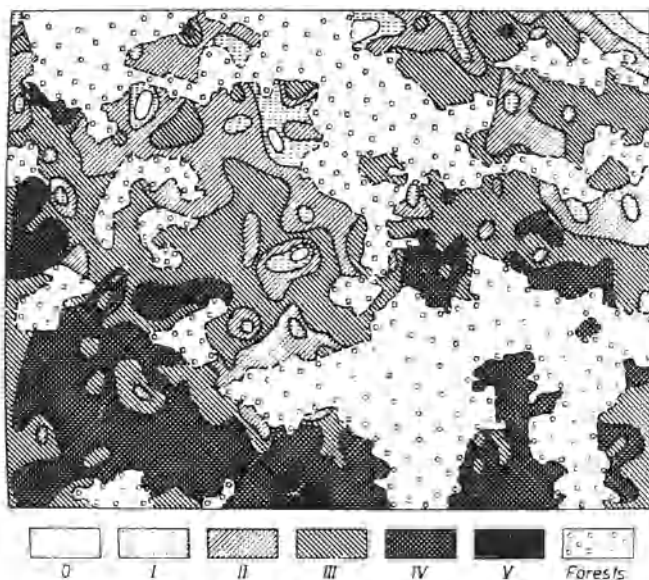


Fig. 4. Soil pollution classes in an industrial area (ca 4 000 ha) of Lower Silesia in Poland. Numbers denote classes of soil pollution: O - unpolluted, II - slightly polluted, III - moderately polluted, IV - heavily polluted, V - very heavily polluted (Kabata-Pendias et al. 1992).

- V. Soils extremely polluted should be excluded from agricultural use and, if possible, cleaned of the excess metals. On suitable sites some industrial plants (see item IV) can be cultivated.

4 Availability of Trace Metals to Plants

The soluble plus exchangeable fractions characterize the mobile, and therefore the phytoavailable species of trace metals in soils. There is always observed a highly significance correlation between metal contents of plants and concentration of their mobile species in soils. However, the uptake by roots is a complex metabolic and/or nonmetabolic process and is controlled by several plant and soil factors. There is a great diversity in plant ability either to accumulate or to exclude several trace elements from root media. The stress of both deficiency and excess of these elements alters plant reactions, and is known to produce even mutagenic changes in plants (Table 9). Among several soil factors the origin of trace elements has also significant impact on their availability. Mechanisms of selective sorption and transport of trace cations can be broken down under an excessive concentration of mobile species of trace metals (Ernst 1992, Kabata-Pendias and Pendias 1992). As

Table 9. Soil-plant interface processes

Plant reaction	Soil micronutrient status	
	Deficiency	Excess
Tolerance Root	low increased exudates	moderate or high selective uptake or immobiliza- tion in tissues
Compound produced	cations and acids (e.g. mugineic)	proteins: methioneins, phyto- chelatins, cysteins
Transmutation	mostly induced	natural and induced

an effect of passive uptake and passive flux of trace cations within a plant the increase of metal content is observed even in cereal grains (Fig. 5).

There is usually observed a highly significant correlation between metal contents of plants and the concentration of their mobile species (often of anthropogenic origin). This relationship differs for a metal and part of plants. As data from Klope's experiment indicate, the rate of plant metal increase due to soil contamination is in the order: $Hg > Cd > Pb$, and always is much higher for leaves than for fruits and tubers (Table 10). However, the concentration of trace metals in above-ground parts of plants is affected also directly by the atmospheric deposition, and as Dalenberg and van Driel (1990) calculated it may account for 73-95% of lead in leaves. Pronounced differences in metal contents of winter wheat grown in European countries clearly illustrate a great impact of aerial pollution (Fig. 6). The

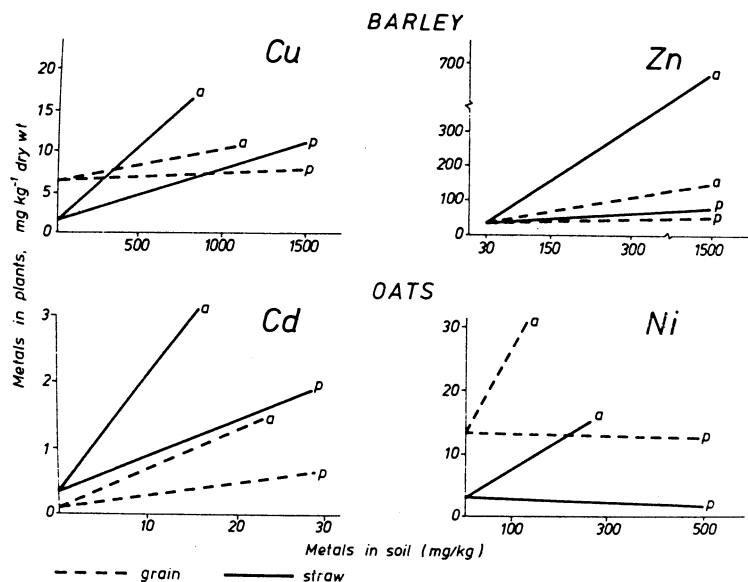


Fig. 5. Metal uptake by barley and oats as influenced by their origin (Chlopecka 1992, and Grupe and Kuntze 1988). p - pedogenic, a - anthropogenic

Table 10. Mercury, cadmium and lead in tomatoes and potatoes as influenced by their contents of soils (mg kg^{-1}): Klope (1985)

Metal contentent of soil		Tomato		Potato	
		leaves	fruits	leaves	tubers
Hg	0.16	0.2	< 0.005	0.03	< 0.005
	54	12.6	0.06	10.6	0.005
	150	56.8	0.4	52.9	1.5
Cd	7.3	11.5	1.6	16.2	0.8
	54	52.4	2.3	45.4	1.6
	209	172.3	5.6	20.8	1.8
Pb	36	3.6	0.1	6.6	< 0.05
	1055	68.5	0.2	29.4	0.3
	3800	200.8	0.8	172.8	1.1

transport from polluted leaves to roots has been also reported for some trace metals (Kabata-Pendias and Pendias 1992).

The stress of the excess of several trace metals alters plant reactions, and is known to produce various changes in plant metabolism reflected in the adaptability

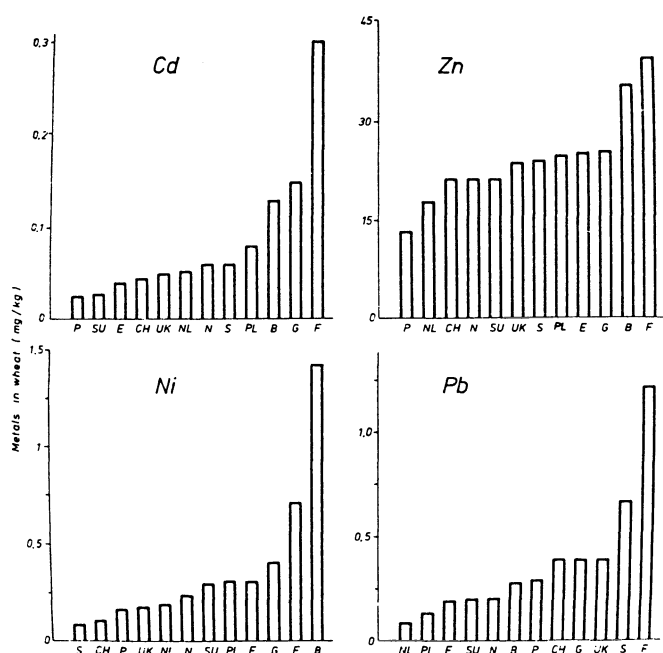


Fig. 6. Mean contents of Cd, Cu, Ni, and Pb in winter wheat (*Triticum vulgare* L.) from different countries of Europe (Kabata-Pendias et al. 1992). P - Portugal, S - Sweden, E - Spain, CH - Switzerland, UK - United Kingdom, NL - The Netherlands, N - Norway, SU - Finland, PL - Poland, B - Belgium, G - Germany, F - France

Table 11. Trace element removal with crop plants from soils

Metal	Content of soil kg ha ⁻¹	Output with plants			
		Reference g ha ⁻¹	% ^a	Accumulator g ha ⁻¹	% ^a
Mn	810	1000	0.1	5000	0.6
Cr	150	50	0.03	500	0.3
Zn	135	400	0.3	1500	1.0
Pb	75	100	0.1	500	0.6
Cu	45	100	0.2	500	1.0
Ni	39	50	0.1	100	0.3
Mo	6	30	0.5	250	4.0
Cd	1.5	1	0.06	100	10.0

Source: Kabata-Pendias and Pendias (1992)

^a Percent of the total content of soils

of plants to polluted growth media (Ernst 1993). The tolerance of plants, due to their ability to grow in contaminated soils, and due to the accumulation of high amounts (sometimes extremely high) of metals, may create a great risk by forming a polluted link in the food chain.

A possibility to remove an excess of some trace elements by vascular plants ("biological decontamination" of soils) can be easily evaluated from the figures given in Table 11. A relative proportion of trace elements accumulated by very high yield, and of very high trace element concentrations hardly exceeds 1% of their total contents of soils. This estimation is related to the background concentrations in soils. When a soil becomes polluted, the proportion of trace elements that may be removed by accumulating vegetation is even more negligible. The foliar uptake of trace metals in polluted regions is known to participate significantly to their concentration in the vegetation. Thus, a high metal content of plants is not necessarily equal to significant biological removal of metals from a soil.

5 Permissible Trace Metal Levels and Loads in Soils

Soil is a specific compartment of the biosphere because it is not only a geochemical sink for contaminants, but also acts as natural buffer controlling the transport of chemical elements and substances to the atmosphere, hydrosphere, and biota. An equally significant role of soil is its production of food and fodder. The maintenance of ecological and agricultural functions of a soil depends greatly upon the trace metal balance. The persistence of metals in soils is much longer than in other compartments of the biosphere. Especially contamination by some metals, e.g., Pb and Cr appears to be virtually permanent.

The effect of excessive levels of trace metals on soil properties depends upon complex reactions between the trace cations and other components of soil phases -

Table 12. Proposals for maximum acceptable concentrations (MAC) of trace metals considered as phytotoxic in agricultural soils (mg kg^{-1})

Metal	Austria	Canada	Poland	Japan	G.Britain ^a	Germany ^b
As	50	25	30	15	20	40 (50)
Be	10		10			10 (20)
Cd	5	8	3		1 (3)	2 (5)
Co	50	25	50	50		
Cr	100	75	100		50	200 (500)
Cu	100	100	100	125	50 (100)	50 (200)
Hg	5	0.3	5		2	10 (50)
Mo	10	2	10			
Ni	100	100	100	100	30 (50)	100 (200)
Pb	100	200	100	400	50 (100)	500 (1000)
Zn	300	400	300	250	150 (300)	300 (600)

Source: Kabata-Pendias and Pendias (1992), unless otherwise stated

^a Values are proposals of EEC for MAC in soils treated with sewage sludges. Values in parentheses are mandatory concentrations (Finnecy and Pearce 1986)

^b Tolerable and toxic (in parentheses) contents (Kloke and Einkmann 1991)

solid, liquid, and gaseous. Permissible levels of trace metals in soils can be calculated based on several factors. Thus, acceptable contents of trace metals in surface soils may differ upon local condition, land use, and authors. Nevertheless, the maximum acceptable concentrations of metals in soils, as estimated by different authors are quite comparable (Table 12).

Different soil types and kinds, plants species, and growing conditions contribute to the divergent influence of soil contamination on trace metals status in plants, as well as on soil ecological variables. There are still not enough data, however, to attempt to set up definite values for criteria needed to protect plants against trace metal pollution. Several ecological standards are used to assess the significance of trace metal levels and their permissible loading into soils.

In addition to general ecological effects, criteria should take into account damaging effects on crops, injury to animals - particularly hazards associated with the ingestion of soil during grazing, and accumulation effects that may occur in the food chain. The possible contamination of human food is an especially urgent problem. Values for any critical concentration or loading of trace metals that can be established at the present should be regarded as a tentative and approximate assessment that may be changed with improvements in the data and understanding of the significance of the presence of particular metals and their ratio to other chemical elements in a particular soil, land use, and ecosystems.

There is a real need for critical examination of the crucial question concerning the standards that should be used to establish the criteria for "safe" limits for trace metal content of soils. Guidelines for allowable loading of these metals are of a basic importance, especially when sewage sludge is used in the agriculture. Values for MAL proposed in recent directives for practical regulation are relatively similar (Table 13).

Table 13. Maximum allowable concentration (MAC) and maximum allowable loading (MAL) of trace metals to arable soils

Metal	MAC ^a (mg kg ⁻¹)	MAL (kg ha ⁻¹ yr ⁻¹)		
		G.Britain ^b	European Communi- ties ^c	Poland ^a
Zn	2000	15	30	10
Cr	1000	-	-	15
Pb	1000	15	15	10
Cu	1000	7.5	5	5
Ni	150	3	3	3
Cd	20	0.15	0.15	0.2
Hg	10	0.1	0.1	0.2

^a Kabata-Pendias and Piotrowska (1987)^b Code Practice GB (1989)^c Council Directive EC (1989)

Criteria for regulating the application of trace metals with sewage sludge and compost in agriculture should take into account, in addition to general ecological effects, the quality of crops and ground water. Thus, the tolerable input of metals is set often equal to average uptake by crop plants. However, no equilibrium relation between input, concentration in the soil and output has been achieved. Since there is still lacking an acceptable model for the trace cation uptake mechanisms by plants, and trace cation migration within soil profiles, the application of various waste material should be prohibited if reference values ("target values") are exceeded (Table 13). However, reviewed monitoring of heavy metal accumulation in agricultural soils treated with sewage sludge has shown that it will be unreasonable to assume, without checks, whether these metals in soils will become immobilized with time or not.

6 Final Remarks

Contemporary industrial technology and farming have already contributed to excessive trace metal contents of soils in various regions. Various methods proposed for cleaning soils contaminated with metals are reviewed by Rulkens et al. (1993). In most cases of the pollution of agricultural soils, however, a reasonable approach is to control the transfer of trace metals from soils to the food chain. This can be achieved by the management of pH, Eh, SOM, and water regime, as well as by the cultivation of special species of plants deprived of certain metals present in the growth media. Also mixing polluted topsoil with unpolluted soil material, as well as covering the polluted soils, or replacement of the polluted top layer have been used for arable soils.

Each standard value for trace metal levels in soils, as well as any purification and land use system should consider the risk of water pollution. There are already observed excessive levels of trace metals in all kinds of waters (e.g., ground, wells, lakes, rivers) due to their migration from soils.

The global problem relevant to trace metal status of soils is to limit their total load and to control, by soil management, their mobility. With regard to environmental balances of trace metals, and especially to protection against pollution of water cycles and the food chain, guiding principles and regulations for acceptable levels of trace metals have to be adopted at the national and international levels.

The mobility and phytoavailability of trace metals, especially crop plants, under soil acidification, alkalization, salinization and losses of organic matter should be studied for the formulation of general guidelines for maintenance of sound soil, and for sustainable land use. These are the main prerequisites for the protection of ecological multifunctions of soils for the next generations to come.

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2 Speciation of Heavy Metals in Soils and Groundwater and Implications for Their Natural and Provoked Mobility

Alain C. M. Bourg

Department Geochemistry and Physical Chemistry, BRGM BP 6009,
F-45060 Orléans Cedex 02, France

(present address: Faculty of Sciences, Univ of Limoges, 123 ave Albert-Thomas
87060 Limoges Cedex, France)

1 Introduction

Anthropic activities can greatly modify natural geochemical cycles of toxic heavy metals. Their accumulation in the pedosphere and lithosphere is of great concern since, contrary to organic xenobiotic compounds, they are not subject to any degradation. It is now widely recognized that it is not the total amount or concentration of a given heavy metal which is most important for understanding its environmental behaviour but rather that the key to the flux of a metallic element is its speciation.

For a given element, the term speciation refers to its distribution amongst its chemical forms or species. The various forms under which a heavy metal can occur in natural aquatic and terrestrial systems can be divided in many ways according to the question of interest. For example, solid species tend to be less mobile than colloidal or dissolved forms. Labile complexes are in equilibrium with their local environment while inert complexes are not. The identification of such classes of species can have great implications for understanding the behaviour of heavy metals in natural and polluted systems, providing the level of information necessary for their safe management.

The speciation of heavy metals in aquatic and terrestrial systems and its incidence on their mobility have been described many times (e.g., Förstner 1987; Morgan 1987; Campbell and Tessier 1987; Bourg 1988). These reviews focused on the most commonly investigated aquatic/sediment systems rather than the subsurface environment. The objective of the present paper is not to present the latest theories on the speciation of heavy metals but rather to attempt a very general and short review of speciation processes and discuss them in terms of practical implications for soils and groundwater systems as related to current contamination problems.

Behind the concept of speciation lies a connotation of geochemical reactivity. For our practical objective of heavy metal pollution, this concept should also be related as much as possible to transport and fixation (trapping). We will try, therefore, to relate speciation to mobility in the subsurface environment.

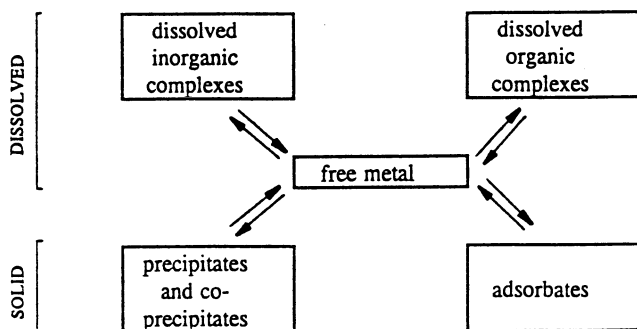


Fig. 1. Geochemical speciation of heavy metals (All of these processes are prone to concurrent reactions with other cations, including H^+)

2 Processes and General Trends

The mobility of heavy metal pollutants depends on a more or less complex network of interactions between aqueous and heterogeneous chemical reactions as well as particle coagulation and flocculation phenomena. Hydrolysis and dissolved complexation tend to increase the solubility of heavy metals while precipitation and adsorption will delay metal availability and transport (Fig. 1). The distribution of a metal between its various possible species is the result of a series of heterogeneous and dissolved chemical reactions.

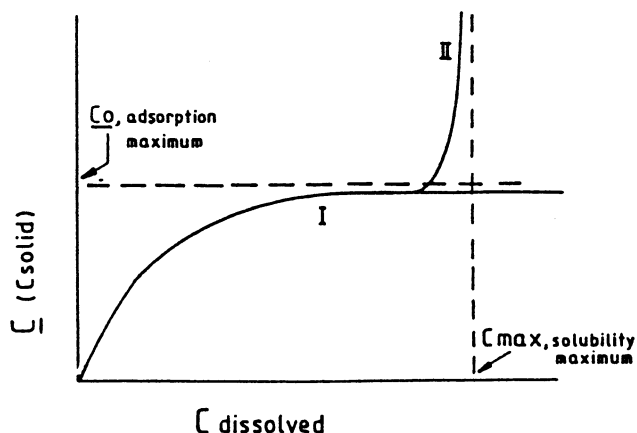


Fig. 2. Sorption isotherm and maximum solubility: physical form speciation (with C_s and C_d , solid and dissolved concentrations, respectively; I : adsorption, represented as an isotherm of the Langmuir type; II : precipitation) (from Bourg 1993)

2.1 Reactions Decreasing Solubility (Fig. 1)

Precipitation. Under a given water chemistry (which is governed by interactions with solids of the porous medium through which the water is circulating), the precipitation of solids such as metal carbonates, oxides, phosphates, silicates, sulfides or mixed solids, limits metal solubility (Fig. 2) and thus imposes a maximum limit for the concentration susceptible to transit through soils or aquifers. For example, it has been postulated by Nriagu (1974) that Pb concentrations in aquatic systems are limited by the precipitation of mixed lead-phosphate minerals (pyromorphite and plumbogummite).

Adsorption. Soils and aquifer solids provide surfaces available for heterogeneous reactions with solutes in soil interstitial water and groundwater. Specific surface areas of soils are in the same range as some minerals reputed to be good adsorbers while for aquifer solids they tend to be from one to several orders of magnitude smaller (Table 1).

Various types of adsorption isotherms can be observed for trace metals. The Langmuir type is given in Fig. 2. Our intention here is not to review the theory and applicability of these isotherms, as this has already been done in detail elsewhere (e.g., Voice and Weber 1983; Sposito 1983), but rather to point out that the isotherm is rarely linear and that its position is very dependent on the water chemistry. Adsorption isotherms determined for one metal and one solid, and this for a given set of water chemistry parameters, cannot be extrapolated to other chemical conditions. This is easily explainable by the influence of water chemical conditions on dissolved speciation (competition by other cations, including protons, for adsorption reactions, dissolved complexation, hydrolysis). The isotherm approach, while very convenient for modelling transport through porous media of adsorbable solutes (especially if the isotherm is linear or almost linear), is not very practical for predictive purposes when the water chemistry and natural solids are not homogeneous. The surface complexation model (e.g., Stumm 1982; Dzombak and Morel 1987; Bourg 1989; Davis and Kent 1990) can account for all the heavy metal

Table 1. Typical surface properties^a

Soils and soil minerals	Surface area (m ² .g ⁻¹)
Clays and loams	20-270
Silty loams	20-200
Sandy loams and loamy sands	10-70
Rendzinas	15-170
Kaolinite	7-30
Illite	65-100
Montmorillonite	700-800
Mn oxides	30-300
Goethite	40-80
Calcareous aquifer sand ^b	0.5-5

^a From Kabata-Pendias and Pendias 1984.

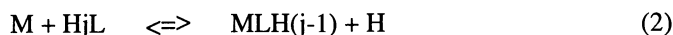
^b From Curtiss et al 1986; Bourg and Richard-Raymond 1994.

adsorption competing processes due to the chemical composition of water including the effect of pH on trace metal adsorption and on surface charge (see the generic equation (1) where M is the metal cation with the corresponding surface complexation constant $K_{\text{Surf-M}}$). This model is very practical for geochemical speciation codes because adsorption is taken into account as a classical solution reaction, but with surface sites instead of dissolved ligands.



2.2 Reactions Enhancing Solubility: Dissolved Inorganic and Organic Complexation (Fig. 1)

A number of chemical reactions in solution can enhance the solubility of trace metals (inorganic complexation, including hydrolysis, and organic complexation, both with natural and synthetic molecules) according to the generic equation (with L a protonable ligand):



where the analogy with adsorption reactions (equation (1)) becomes evident.

Chloride is most likely, under natural and polluted aquatic conditions, the most efficient inorganic complex former for solubilizing heavy metals (see, for example, the experiments of Doner (1978) and the speciation calculations of Bourg (1983)). High concentrations are nevertheless required (typically greater than 0.01 M Cl^- , but this depends on the metal). For example, in a laboratory experiment, mercury (as the nitrate salt) was percolated through a sandy soil column first in the absence and later in the presence of chloride ions (Behra, 1987). In the first part of the experiment, when injected in a 1 M NaNO_3 solution, mercury (calculated to be present mostly as the neutral $\text{Hg}(\text{OH})_2$ species) was significantly retained by the sandy solids. When the supporting electrolyte was switched to a chloride medium (1 M NaCl), the sorbed mercury was quantitatively eluted within very few pore volumes. This remobilization is easily explained by the displacement of the sorption reaction (desorption) of Hg due to the presence in solution of chloride ions leading to the formation of the non adsorbed anionic species HgCl_3^- and HgCl_4^{2-} .

Natural organics and synthetic multidentate chelators are also very powerful complex formers. For example, the concentration of dissolved organic carbon (DOC) in municipal waste leachates is one of the most important factors involved in the solubilization and subsequent migration of heavy metals through soils (Frost and Griffin 1977; Fuller 1983; Bolton and Evans 1991). The higher the DOC, the faster the rate of migration. In the presence of a synthetic chelator, such as EDTA or NTA, the adsorptive behavior of a heavy metal can be strongly modified, because of the resulting new dissolved speciation of the metal (Bourg and Schindler 1979; Bowers 1982).

2.3 Ternary Species (Co-Adsorption and Co-Precipitation)

If the speciation of heavy metals could be represented as easily as in Fig. 1, geochemists would have it pretty easy. However, even if reactions such as those described in paragraphs 2.1 and 2.2 do occur in natural systems, a variety of more complex reactions can make the overall picture quite complicated.

In some cases co-precipitation can control metal solubility. For example, it has been suggested by Rai et al. (1986) that the solubility of Cr(III) in natural waters is limited by mixed iron(III)-chromium(III) minerals (of the form $(\text{Fe}_{0.99}\text{Cr}_{0.01})(\text{OH})_3$ rather than by $\text{Cr}(\text{OH})_3(\text{s})$).

Moreover, under some conditions, organic complexes of heavy metals can adsorb onto solids and this either through the metal or through the organic ligand (depending on the ternary metal-organic-solid system) (Bourg and Schindler 1978; Davis and Leckie 1978; Bourg 1983, 1988). The solubility in soils of the heavy metals having strong associations with natural organics (e.g., Hg, Pb and Cu) is expected to be closely related to organic matter behavior (solubilization *versus* unsolubilization) (Bourg and Schindler, 1985).

2.4 Kinetics and Reversibility of the Geochemical Reactions Involved in Speciation

The various reactions controlling the speciation of a given metal can be more or less rapid compared to competing chemical reactions or to other non chemical processes (e.g., advective transport, biological absorption).

Quantitative information on the desorption of heavy metals from soils and aquifer solids is not abundant (see Bourg 1988). For example, the degree of reversibility of Cd adsorption by calcareous solids (soil and aquifer solids) decreased with contact time between the Cd aqueous solution and the adsorbate (Fuller and Davis 1987; Bourg and Gadalía 1991). For sandy and loamy soils, the desorption of Cd was quite rapid (a few hours) even though adsorption was faster (equilibrium in less than 1 hour) (Bourg and Gadalía 1991). It seems, therefore, that adsorption would be an efficient attenuating mechanism only in the presence of calcareous solids. Other soils would provide only some retardation (of the chromatographic column type) in cadmium transport. Conversely it can be predicted that decontamination would be less efficient for calcareous soils or aquifer solids.

2.5 General Trends

The situation presented in the two preceding paragraphs leads to a pessimistic outlook for the understanding and prediction of speciation and transport behavior of heavy metals. Some of the speciation is controlled by simple reactions, though, in many cases one is not sure about their states of equilibrium and reversibility. Moreover, for heterogeneous reactions, and especially for those involving organic

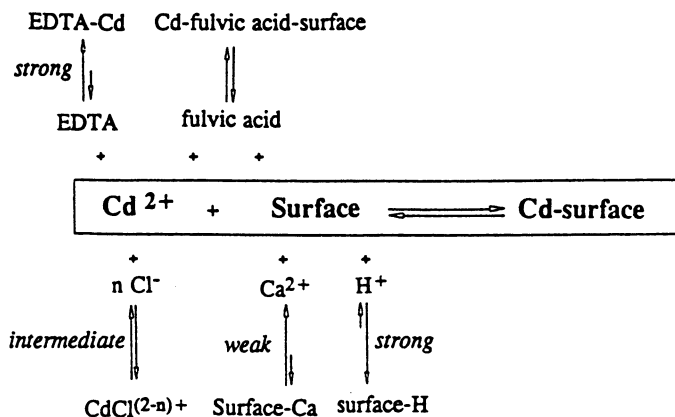


Fig. 3. Summary of chemical reactivity (stoichiometry and strength of reactions) of cadmium in the presence of calcareous aquifer solids (from Bourg et al. 1994)

matter, reliable predictions seem difficult. Semi-quantitative estimations can nevertheless be made, provided that a sufficiently detailed investigation is carried out (Fig. 3).

To illustrate the complexity involved in the determination (or rather estimation) of the speciation, some examples are given in Figs. 3 and 4. Fig. 3 summarizes the results of laboratory experiments and Fig. 4 is from a compilation of literature data.

A very general picture of the speciation of all the elements of the periodic table was presented by Turner et al. (1981) and Whitfield and Turner (1983). Partition coefficients (particulate *versus* dissolved) describing the distribution of the chemical elements between sea water and crustal rock were shown to be related to a number of parameters which reflect the chemical periodicity of the elements: the ionization potential (z^2/r , where z is the ion charge and r , its radius) and a

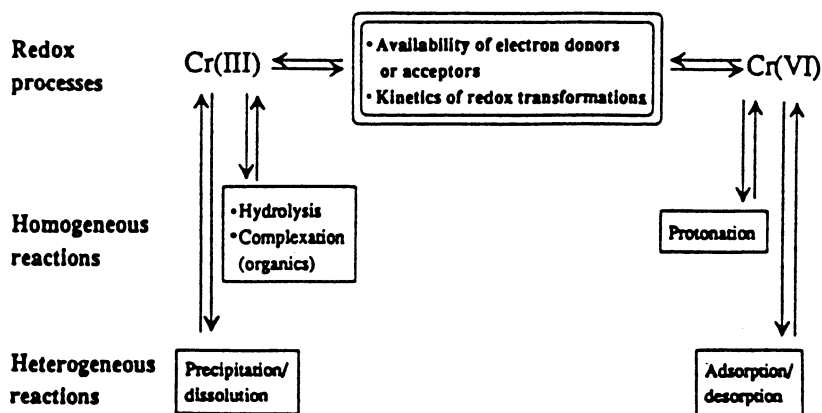


Fig. 4. Major chromium species in the subsurface environment (adapted from Richard and Bourg 1991)

"softness" parameter which is related to the electronegativity of the element. The relevance, and possible peculiarities, of such a classification for subsurface environments should be investigated. A major problem anticipated in the use of this general classification is how to integrate natural organic matter, but Turner et al (1981) do introduce a promising methodology (relating metal-humic acid complexation to metal hydrolysis).

Geochemical computer codes are convenient tools for providing some predictive estimates of the behavior of heavy metals in hypothetical or real situations. Their use would be simplified if the unifying methodology of Turner et al (1981) could be generalized to subsurface systems. However they suffer from several limitations (see below).

3 Methods for Determining the Speciation

To determine speciation, one must have methods available to measure both the total concentration and, selectively, the concentration of the different chemical species including the free ion. The selectivity of such methods depends on the rapidity of the reactions involved in the formation or dissociation of the species to be measured. Criteria need to be defined for distinguishing between kinetically inert and labile complexes (Buffle 1988).

Current approaches used for determining metal speciation have been reviewed by others (e.g., Campbell and Tessier 1987; Buffle 1988) and will not be covered here. We, nevertheless, want to point out, as emphasized by Buffle (1988), that "the classical approach, which consists of isolating and studying each of the constituents separately has two significant limitations": (1) this type of separation is very difficult, if not impossible, to achieve with available methods, and (2) more important, the properties of singled-out components of a complex mixture are not additive "because of the multiple interactions which often exist between them".

A series of computer models have been developed to calculate the speciation of heavy metals, some including adsorbed species and simple minerals (as opposed to mixed minerals). For practical applications such as predictions of the solubility of heavy metals, classical geochemical codes suffer from several limitations: (a) lack of reliable thermodynamic data for relevant species, (b) inadequacies of the equations used to correct activity coefficients for high ionic strength, (c) problems related to the correct definition of the redox status of the system, (d) reaction kinetics can be taken into account mathematically but there is little validation data to be found in the literature, (e) current codes usually assume reversibility of the reactions, (f) difficulties in characterizing the natural adsorbing surfaces and the various dissolved or solid organic substances, (g) complex reactions such as those occurring in ternary systems (co-precipitation or co-adsorption) are not included (even though some semi-quantitative information is available).

4 Predictive Trends: Natural and Provoked Mobility

4.1 Natural Mobility

As water percolates through soils and aquifer solids, it acquires, through heterogeneous geochemical reactions, its intrinsic chemical composition (related to the natural solids encountered). This chemical signature of soil water and groundwater is the result of surrounding biological activity, water-solid interactions and physical water mixing. The resulting chemical composition can thus vary with space and time.

The natural attenuation of heavy metals in the subsurface environment should thus be strongly variable depending on the local biogeochemical properties of the system investigated (Bourg 1993). If we now summarize predictive trends from the processes described in paragraph 2, it is possible to estimate the potential mobility of heavy metals if the water chemistry of a given subsurface system is sufficiently well known (including spatial and temporal variability).

The most important effects of microbiological activity on the behaviour of heavy metals in soils come from the degradative transformation of organic matter and oxydoreduction reactions involving Fe and Mn oxyhydroxides and sulfide. In medium to alkaline pH and oxidizing environments, Fe and Mn amorphous or crystalline solids are strong adsorbents or co-precipitating matrices. Under reducing conditions, heavy metals are removed from solution as sulfide minerals (Fig. 5). When the environment is only slightly reducing or slightly oxidizing and for

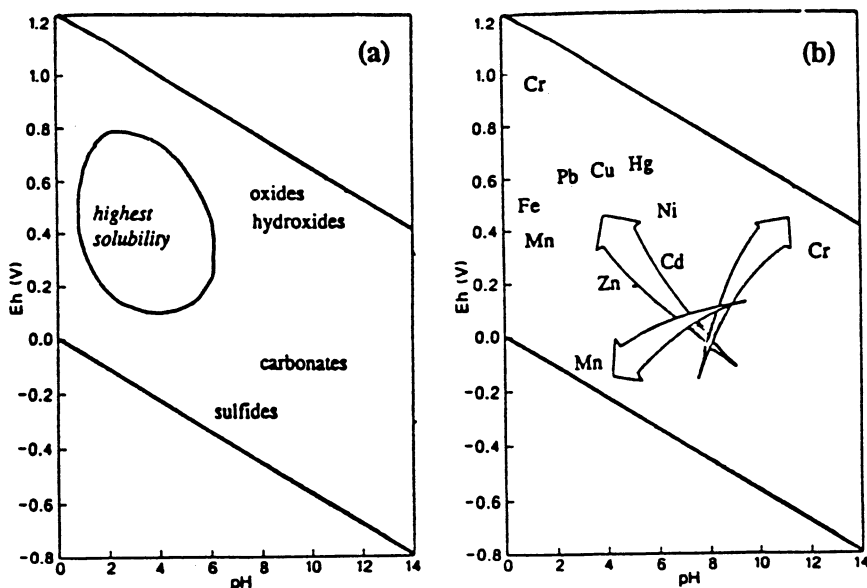


Fig. 5. Trends in solubility of heavy metals in relation to pH and Eh (in the absence of dissolved and solid organic matter) (a) main minerals controlling the solubility of heavy metals; (b) trends of increasing solubility (Förstner, 1987)

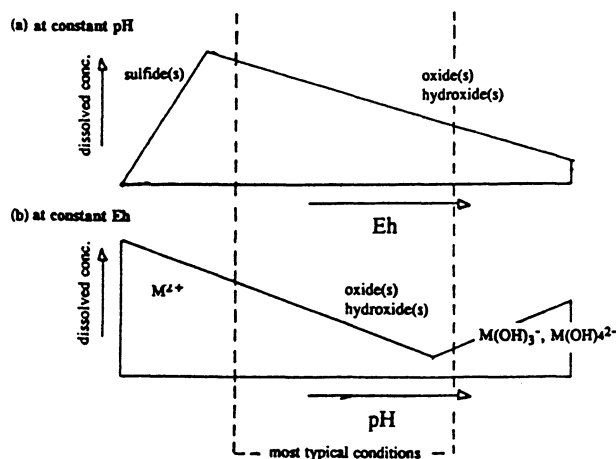


Fig. 6. Effect of Eh (a) and pH (b) on the solubility of heavy metals (from Bourg and Kedziorek 1994)

medium to acidic pH range, the surface reactive Fe and Mn oxyhydroxides are solubilized when Fe(III) and Mn(IV) are reduced to soluble species (Fig. 5). Under these conditions, when the pH is slightly alkaline, Fe and Mn may precipitate as carbonates but these minerals are certainly less adsorbant than the corresponding oxides and hydroxides.

Another simplistic way of summarizing the solubility patterns of heavy metals (and thus their predictive mobility) in the absence of significant metal-organic interactions is given in Fig. 6. As seen also in Fig. 5 (a), environments of low pH and moderate to high redox are the most favorable to solubilization for many heavy metals.

Concerning complexing ability (both as surface and dissolved species), the suite of organic compounds found naturally in soils depends on pE, pH and the attendant microbial ecology (Sposito and Page 1984). Moreover, the lability of organic complexes of heavy metals has strong implications on metal transport. For example, in a field migration experiment (in a sand-groundwater system) cobalt formed organic complexes (mainly with fulvic acid) and, as such, was mobile in the short term (Warwick et al. 1991). However these associations were unstable and were thus unlikely to migrate over long distances.

4.2 Provoked Mobility

The solubility, and consequently the mobility, of solid-bound metals in the subsurface environment can be increased by three major processes which induce changes in speciation (in solution, at the surface or in the bulk of solids): (a) lowering the pH (which can dissolve and/or desorb metals from the solid phases), (b) altering the redox conditions (to induce moderate to high redox potential), (c) increasing

the concentration of inorganic salts (to provide competition by salt cations for heterogeneous reactions and dissolved complexation with salt anions) and of natural or synthetic complexing agents.

One way to evaluate the potential for heavy metals removal (by increasing their mobility, for decontamination purposes) or the perennial nature of their trapping by soils or aquifer solids (to assess their immobilization) is to investigate their solubility during extraction procedures designed to simulate typical possible changes in the subsurface hydrogeochemical environment (e.g., acidification, lowering of the Eh,...). For example, according to Fuller (1983), Cu and Pb are the least mobile heavy metals and the least likely to be extracted by water once sorbed by soils. Because these two metals form very strong complexes with EDTA (see Table 2) they should, however, be easily remobilized in presence of high enough concentrations of this chelator (see below).

As we saw earlier complexation with chloride remobilized sorbed mercury, but the salt concentration involved is large and, moreover, the aqueous solution percolated was synthetic and the porous solid very simple (sand). What would happen in a real system with numerous competitors for complexation with chloride (see Table 2. for the relevant constants)? The use of synthetic chelators, such as EDTA or NTA has been suggested to decontaminate soils or aquifers *in situ*. Even though large amounts of competing Ca and Mg are present in groundwater and at the surface of soil and aquifer solids, one should expect strong chelators to have a significant complexing ability for heavy metals because their complex formation constants are usually many orders of magnitude higher (see Table 2). In a laboratory EDTA percolation experiment involving soil contaminated by long-term (ca. 100 years) land application of sewage (more or less treated depending on the period of application), a significant fraction of zinc, copper, and cadmium was recovered within a small eluted volume (10 pore volumes) even though a lot of the EDTA complexing capacity was used by Ca, Mg, Fe and Mn (Bourg 1994) (Table 3). The pH of the elution experiment is critical because the speciation of EDTA, the charge of the soil surface and the adsorption of metal EDTA complexes are all function of pH (Bourg and Gadalía 1991).

Table 2. Formation constants for ML complexes (as $\log_{10}b$)^a

Ligand	Metal					
	Ca(II)	Mg(II)	Cr(III)	Fe(III)	Fe(II)	Mn(II)
Cl			0.1	1.5		0.6
EDTA	12.4	10.6	26.0	27.7	16.1	15.6
Ligand	Metal					
	Ni(II)	Cu(II)	Zn(II)	Pb(II)	Cd(II)	Hg(II)
Cl	0.6	0.5	0.4	1.6	2.0	7.2
EDTA	20.4	20.5	18.3	19.8	18.2	23.5

^a From Morel 1983.

Table 3. Mass balance of eluted metal^a

Metal	Initial conc. (ppm)	% leached (for 10 pore volumes)
Ca	23 000	0.5
Fe	10 000	0.04-1.0
Mn	155	1-6
Cd	35	3-4
Cu	300	6-8
Ni	35	1-2.5
Zn	1100	10-16

^a From Bourg 1994.

5 Conclusion

The speciation of heavy metals in soils and groundwater is related to their biogeochemical reactivity, which in turn is controlled by the local water, microflora and porous solid properties.

The solubility, and consequently the mobility, of solid-bound metals in the sub-surface environment can be increased by three major processes which induce changes in speciation (in solution, at the surface or in the bulk of the solids): lowering the pH, altering the redox conditions, increasing the concentration of inorganic salts (competition for heterogeneous reactions and dissolved complexation) and of natural or synthetic complexing agents.

Increasing the mobility of heavy metals in soils and aquifers would permit the development of *in situ* remediation operations (see Rulkens et al in chap 15 of this volume). The efficiency (extraction yield) and the cost of such procedures is still to be investigated in the laboratory or on small pilot operations for a sufficiently large number of metals (with the possibility of determining predictive trends according to their chemical reactivity, *i.e.*, their position in the periodic table) and for a variety of geological situations. If *in situ* operations are not economical, chemical extraction (for example, on site but after excavation of the solids) may be an alternative and sometimes actually a more efficient solution.

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3 Diffuse Sources of Pollution by Toxic Metals and Impact on Receiving Waters

Vladimir Novotny

Department of Civil and Environmental Engineering Marquette University
Milwaukee WI 53233 USA

1 Introduction and Definitions

Metals are naturally occurring in nature. In receiving water bodies, metals can originate both from natural and anthropogenic sources. Thirteen metals and metal-loids have been recognized as potentially hazardous to man's health and aquatic biota and have been included on the *Priority Pollutants List (Black List)* by environmental control agencies throughout the world.

Natural and diffuse anthropogenic sources of toxic (priority) metals are described and qualitatively and quantitatively assessed. Urban runoff appears to be the most significant source and most of water quality problems attributed to toxic metals can be found in receiving water bodies in the vicinity of urban centers.

Modeling and description of fate of toxic metals in aquatic systems is complex and requires sophisticated models. Basis concepts of the fate modeling are presented in the paper.

Metals are natural elements that can be naturally found even in unimpacted surface waters, depending on the type of soils or rocks present along the river stream-bed. In small trace quantities, many metals are needed nutrients for aquatic life and human health. Only few metals may be found in aquatic systems in quantities that will exceed the toxicity threshold, and these are typically caused by excessive discharges and emissions of metals from man-made (cultural) sources. Hence, a distinction must be made between the natural and cultural causes of contamination of aquatic systems by (potentially) toxic metals.

Of the original EPA's list of priority pollutants containing in 1993 129 priority pollutants, only 13 items are metals, while the others are organic compounds, pesticides, PCB's and few nonmetallic inorganic compounds (asbestos and cyanides). However, on the EPA list of the most commonly discharged priority pollutants (EPA, 1985), 5 out of 16 pollutants are metals, and their frequency of detection exceeds by far the detection of non-metals.

Among the most frequently discharged metals (from point-sources of pollution), are: copper, zinc, chromium, lead and nickel. In addition, relatively high metal contents are also present in runoff from urban areas. Recent increases in acidity of precipitation have contributed to increased elutriation of metals from the soils and man - made metallic surfaces such as roofs and downspouts in urban areas, making the task of meeting the water quality standards even more difficult.

2 Definition of Pollution and Background Water Quality

The term **pollution** is derived from a latin word (*pollere*) which means " to soil" or " to defile." The terms *pollution*, *contamination*, *nuisance* and *water (air, land) degradation* often are used synonymously to describe faulty conditions of surface and ground waters. Various definitions have been offered to define pollution and other related terms (Krenkel and Novotny, 1980). Probably the most accepted definition of pollution by scientists is " unreasonable interference with the beneficial uses of the resource."

In the United States, the statutory (legal) definition of pollution is included in the Water Quality Act - Sec. 502-19 (U.S. Congress, 1987) :

The term " pollution " means man-made or man-induced alteration of chemical, physical, biological, and radiological integrity of water.

The term integrity means " being unimpaired " , therefore, "alteration of integrity" means impairment or injury. An alternate working definition is then:

Pollution is a change in the physical, chemical, radiological or biological quality of the resource (air, land or water) caused by man or due to man's activities that is injurious to existing, intended or potential uses of the resource.

According to this definition, pollution is differentiated from quality changes of the environment due to natural causes, such as volcanic eruptions, deposition of fly ash from natural forest fires, natural erosion, weathering of rocks and natural

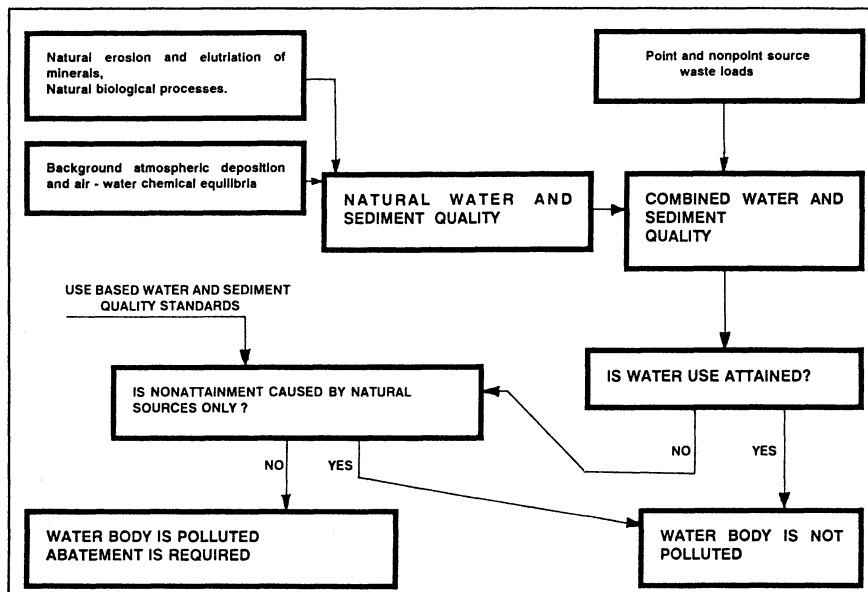


Fig. 1. Concepts of water quality and pollution by metals

elutriation of minerals, and others, even though they may have the same actual or potential adverse impact on uses of water or of a resource as pollution.

Since all metals can be found in nature and are part of the earth's crust distinction must be made whether the metals originate from natural or man-made sources.

This definition and the fact that both natural and anthropogenic sources contribute to water quality content of surface water bodies, have two important consequences. First, if the metal content of a water body, in sediment or water, is due to natural causes it is considered as a background (natural) water-sediment quality. Second, only water-sediment contamination from cultural sources that "impair integrity of the water resource" is pollution. These concepts are shown on Fig. 1.

From the many metals in the periodic table only about a dozen are present in aquatic systems in quantities that can be harmful to aquatic biota and/or human health. In the United States, these metallic elements are a part of a group of potential pollutants which have been included into so called *priority pollutants*. The European Community included such metallic pollutants into its *black list* of contaminants.

3 Distribution and Environmental Mobility of Toxic Metals

Diffuse pollution may be responsible for the major part of contamination of the environment by toxic pollutants. Toxic chemicals and components contaminating the environment are either **inorganic** or **organic**. Inorganic contaminants are mostly in a category of trace metals, which may be both natural or anthropogenic (man-made). Other inorganic nonmetallic toxic compounds detected in the aquatic environments are unionized ammonia (NH_3), cyanides, asbestos, hydrogen sulfide (H_2S) and low or high pH. This paper deals with the diffuse sources of toxic metals.

Table 1. Toxic metals of particular environmental concern^a

Very toxic and readily accessible	Man-induced mobilization Higher than natural rate
As	Ag ^b
Co,Bi	As
Ni,Cu	Cd
Zn, Sn ^b	Cu
Se ^b ,Te ^b	Hg ^b
Pd ^b , Ag ^b	Ni
Cd, Pt ^b	Pb ^b
Ag ^b , Hg ^b	Sb
Tl ^b , Pb ^b	Sn ^b
Sb	Zn

^a From Wood (1975) and Ketchum (1972), quoted in Chapman (1978).

^b Metal alkyls stable in aqueous environment, reported to be bio-methylated in sediments.

The periodic table includes over 90 elements from hydrogen to trans-uranians and all but 20 may be characterized as metals. As many as 59 of these elemental metals can be classified as "heavy metals" and are potentially toxic. However, only 17 of these metals are considered both very toxic and available in places at concentrations that exceed toxicity levels. Of these 17 toxic metals (Table 1) nine are being mobilized into the environment by man at rates greatly exceeding those of natural geological processes (Chapman, 1978; Weiss et al., 1975).

The following thirteen metals have been included in the priority pollutants list by the U.S. Environmental Protection Agency:

antimony, arsenic, beryllium, cadmium, chromium, copper, lead, mercury, nickel, selenium, silver, thallium, zinc.

Table 2. Natural sources of metals and elements on the priority pollutant list

Element	Natural source or metals. Metallic minerals.
Antimony	Stibnite (Sb_2S_3), geothermal springs, mine drainage
Arsenic	Metal arsenides and arsenates, sulfide ores (arsenopyrite), Arsenite (HAsO_2), volcanic gases, geothermal springs
Beryllium	Beryl ($\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{16}$), Phenacite (Be_2SiO_4)
Cadmium	Zinc carbonate and sulfide ores, Copper carbonate and sulfide ores
Chromium	Chromite (FeCr_2O), chromic oxide (Cr_2O_3)
Copper	Free metal (Cu^0), copper sulfide (CuS_2) Chalcopyrite (CuFeS_2), mine drainage
Lead	Galena (PbS)
Mercury	Free metal (Hg^0), Cinnabar (HgS)
Nickel	Ferromagnesian minerals, ferrous sulfide ores, Pentlandite ($(\text{Ni,Fe})_9\text{S}_8$) nickel oxide (NiO_2), nickel hydroxide ($\text{Ni}(\text{OH})_3$)
Selenium	Free element (Se^0), Ferroselite (FeSe_2), uranium deposits, black shales, Chalcopyrite - Pentlandite - Pyrrhotite deposits
Silver	Free metal (Ag^0), silver chloride (AgCl_2), Argentide (AgS_2), copper, lead, zinc ores
Thallium	Copper, lead, silver residues
Zinc	Zinc blende (ZnS), Willemite (ZnSiO_4), Calamine (ZnCO_3) mine drainage

3.1 Natural (Background) Sources

Metals are some of the most abundant elements in the earth's crust. Minerals such as those listed in Table 2 represent the original source of metals found in soils and aquatic environments. Mineral weathering (natural) or mining (cultural) processes are then responsible for the distribution of metals in the terrestrial, aquatic and atmospheric systems.

Soils are weathered minerals enriched by other compounds such as decaying and mineralized organic matter. In soils, metals are a part of soil minerals or exist mostly as particulate complexes of different forms. Table 3 shows metal concentrations in soils of the conterminous U.S.

When toxic metals are added to soils and water (sediments) both from natural and man made sources, they undergo complexation with ligands. Ligands are chemical constituents both organic and inorganic that combine with the metals in a chemical complex. From the basic physical chemistry it is known that metals precipitate as a result of changes in pH, oxidation and other changes of their chemical composition. However, the process of complexation in natural waters is more complex. Major causes for precipitation and metal complexation are (Salomons and Förstner, 1984):

- oxidation of reduced components such as iron, manganese and sulfides,
- reduction of higher valency metals by interaction with organic matter (Selenium, Silver),
- reduction of sulfate to sulfide (Iron, Copper, Silver, Zinc, Mercury, Nickel, Arsenic and Selenium are precipitated as metal sulfides),

Table 3. Metal concentrations ($\mu\text{g/g}$) in surficial materials in the U.S.^a

Element	Geometric means				
	Average Range	Arithmetic Analysis U.S	Conterminous Meridian	West of 97th Meridian	East of 97th Meridian
As		0 - 1000			
Ba	534	15 - 5000	430	60	30
Cd		0 - 20			
Ce	86	<150 - 300	75	74	78
Cr	53	1 - 1500	37	38	86
Co	10	<3 - 70	7	8	7
Fe	25 000	100 - 100 000	18 000	20 500	15 000
Pb	20	<10 - 700	14	18	10
Mn	560	<1 - 7 000	340	389	385
Ni	20	<5 - 700	14	16	13
Hg ^b		0.01 - 0.03			
Cu ^b		2 - 100			
Se ^b		0.1 - 2			

^a after Shacklette et al. (1971).

^b after Lindsay (1979).

- alkaline type reactions (Strontium, Manganese, Iron, Zinc, Cadmium and other elements are precipitated by increased pH usually caused by interaction with alkaline rocks and sediments or by mixing with alkaline waters),
- adsorption or co-precipitation of metallic ions with iron and manganese oxides, clays and particulate organic matter.
- ion-exchange reactions primarily with clays.

In aerobic soils and freshwater sediments the sorption sites are provided by organic carbon, clays and hydrous oxides of iron and manganese. The Fe and Mn oxides have also a limited ion exchange capability. Hydrous iron oxides strongly adsorb chromium, while manganese oxides adsorb nickel, calcium phosphate (also present in sediments) adsorbs cadmium, lead and other metals. Mercury in sediments (in sediments mercury exists mostly as di-methyl mercury $(\text{CH}_3)_2\text{-Hg}$) is strongly adsorbed by organic matter (Langston, 1985). Oxides of iron and manganese are deemed to be more important than organic matter and clays, however, Combest (1991) documented that the Fe and Mn contents correlate with the clay content.

In anaerobic soils and sediments sulfide precipitation is important in complexation of toxic metals (DiToro *et al.* 1989).

It has been found that the free metal ion is the most toxic component for the organisms (Gillespie and Vaccaro, 1978, Salomons and Förstner, 1984, DiToro *et al.*, 1989). Other metal complexes are not bioavailable. Therefore, presence of compounds that will react with the metal ion and cause its precipitation or adsorption on solids (including iron and manganese oxides, sulfides, clay and organic matter) will reduce the toxicity of the metals and makes them less bio-available for organisms. The colloidal and ionic compounds which combine with in a complex with the metal ion are called *ligands* which include organic acids and humic substances, dissolved sulfides, chloride and OH^- ions.

Hence, the adsorbing and complexing compounds for toxic metals include

- particulates
 - * sulfides
 - * iron and manganese oxyhydrates
 - * particulate organic matter
 - * clays
- dissolved
 - * sulfides
 - * humic compounds
 - * organic acids
 - * chloride ion
 - * hydroxyl ion

Dissolved metal-organic (ligand) complexes may be also adsorbed by particulates such as iron and manganese oxyhydrates. On the other hand, some dissolved organic compounds such as detergents may reduce adsorptivity of metals while chlorides may enhance adsorptivity.

From the above mechanisms, iron and manganese oxyhydrates provide the strongest adsorption sites followed by particulate organics and clays. The processes of complexation of metals in soils and sediments will be presented elsewhere.

3.2 Erosion and Enrichment of Overland Flow by Metals

From soils, metals can be transported by erosion caused by both wind and water. During the erosion and overland flow runoff is *enriched* by pollutants.

Enrichment explains the difference in metal concentrations on solids in the parent soil and in runoff (stream flow). The process of enrichment occurs in two phases. First, detachment of sediments and pollutants from the parent soil is selective for dissolved fraction of the pollutants (ionized metals and dissolved complexes in pore water of the soil) and for the fine soil fractions. As pointed out, in soils most of the toxic metals are associated with clay and organic matter. Second, when rainwater reaches the surface horizon of the soil, some metals become dissociated and go into solution, others remain adsorbed and/or precipitated and move with the soil particles. Therefore metals contained in runoff sediments are present in higher concentrations than in the parent soil. The difference is termed *the enrichment ratio (ER)* defined as follows:

$$ER = \frac{C_r}{C_s} \quad (1)$$

where C_r is the metal concentration in the runoff expressed per gram of sediment and C_s is the metal content of the parent soil per gram.

Table 4. Concentrations of toxic metals (in $\mu\text{g/g}$) in unpolluted parent soils and sediments in Rhine River basin*

Metal	Soils	Sub-recent Rhine sediments	Lacustrine sediments
Cd	0.82	0.3	0.40
Co	12	16	16
Cr	84	47	62
Cu	25.8	51	45
Hg	0.1	0.2	0.35
Mn	760	960	700
Ni	33.7	46	66
Pb	29.2	30	34
Zn	59.8	115	118

* Compiled by Salomons and Förstner, 1984.

Table 5. Enrichment of suspended sediment by clay and metals¹

<i>Constituent</i> ²	<i>Soil</i>	<i>Suspended sediment</i>	<i>Enrichment ratio</i>
Clay	27	91	3.4
Lead (Pb)	19	39	2.0
Cadmium (Cd)	0.3	0.31	1.0
Zinc (Zn)	69	280	4.0
Copper (Cu)	25	45	1.8
Aluminum (Al)	22,000	49,000	2.2
Iron (Fe)	21,000	46,000	2.2
Manganese (Mn)	700	730	1.0
Chromium (Cr)	29	56	1.9
Nickel (Ni)	17	45	2.6

¹ from Dong et al. (1983b, 1984).

² Clay is in percent and metals are in µg/g of sediment.

Table 4 shows the differences (or similarities) between the soil and aquatic sediment contents of toxic metals which were not affected by man-made (cultural) emissions. Table 5 then lists calculated enrichment ratios for a small watershed located in south-eastern Wisconsin.

The background metallic content of soils is not highly variable. Agricultural activities do not contribute significant amounts of metals. However, in the past before the widespread use of organic pesticides some metal salts were used for weed control (arsenic).

4 Urban Sources

Pollution of aquatic systems by toxic metals is, by definition, of man-made origin. Urban and industrial diffuse sources of metals have been identified as the primary cause of pollution by toxic metals.

Marsalek (1986) studied distribution of toxic compounds in Ontario. He found that trace metallic element contents in or near urban areas were the most prevalent toxic contaminants in runoff and stream sediments. The most frequently detected elements were zinc (98 % of all water samples), copper (93 %), nickel (87 %), and lead (78%). Similar results were also found by the National Urban Runoff Project (NURP) in the U.S.(Table 6). The frequencies of detection of trace elements in sediments were higher. Urban runoff contained in overflows from storm and combined sewer overflows is a significant diffuse source of pollution by toxic metals.

The origins of these toxic compounds are very diversified. The most obvious industrial operations are foundries, steel mills, metal plating, metal processing and manufacturing, and ore processing plants. These sources are legally classified as

Table 6. Most Frequently Detected Toxic (Priority) Metals in NURP Urban Runoff Samples^a

Detection rate ^b	Inorganic
Detected in 75% or more of the NURP samples	Lead (94%) Zinc (94%) Copper (91%)
Detected in 50% - 74% of the NURP samples	Chromium (58%) Arsenic (52%)
Detected in 20% - 49 % of NURP samples	Cadmium (48%) Nickel (43%)
Detected in 10% - 19% of the NURP samples	Antimony (13%) Beryllium (12%) Selenium (11 %)

^a Source U.S. EPA (1983).^b Percentages indicate frequency of detection, not concentrations.

manufacturing, and ore processing plants. These sources are legally classified as point sources of pollution even though runoff from these complexes is a diffuse source.

In urban zones, traffic, deterioration of infrastructure are major sources and processes listed in Table 7 can be blamed for metal contamination of urban (highway) runoff, receiving waters and sediments. Previously, metallic salts were used for control of algae of lakes and weed control of urban lawns.

4.1 Traffic Sources of Metals

Strecker et al. (1987), summarized data on the quality of runoff from highways obtained in research sponsored by the Federal Highway Administration. Average

Table 7. Sources of toxic and hazardous substances in urban runoff (after US EPA-1990)

	Automobile Use	Pesticide Use	Industrial/Other Use
Metals			
Arsenic		algicide	
Copper	metal corrosion	algicide	paint, wood preservative, electroplating
Lead	gasoline, batteries		paint, lead pipe
Zinc	metal corrosion tires, road salt	wood preservative	paint, metal corrosion
Chromium	metal corrosion		paint, metal corrosion,

Table 8. Average concentration of pollutants in highway runoff according to Strecker et al. (1987)

Constituent	Mean Concentration mg/l	Coefficient of variation ^a
Suspended solids	143	1.16
Lead	0.53	2.01
Zinc	0.37	1.37

^a The coefficient of variation is a ratio of standard deviation to the mean.

Table 9. Traffic emission according to Shaheen (1975)

Pollutant	% of total solids by weight
Lead	1.2
Chromium	0.008
Copper	0.012
Nickel	0.019
Zinc	0.15
Emission rates of total solids	0.671 g/axle-km

concentrations of constituents in highway runoff are given in Table 8. Bannerman (1991) has found that the flow weighed average concentration (so called Event Mean Concentration) of metallic toxic pollutants can be correlated to traffic volume (Fig. 2). Table 9 presents measured emissions of pollutants from vehicular traffic in the Washington, DC area in the 1970's. As far as lead emissions are concerned the emission rate measured by Shaheen in the 1970's corresponds to the

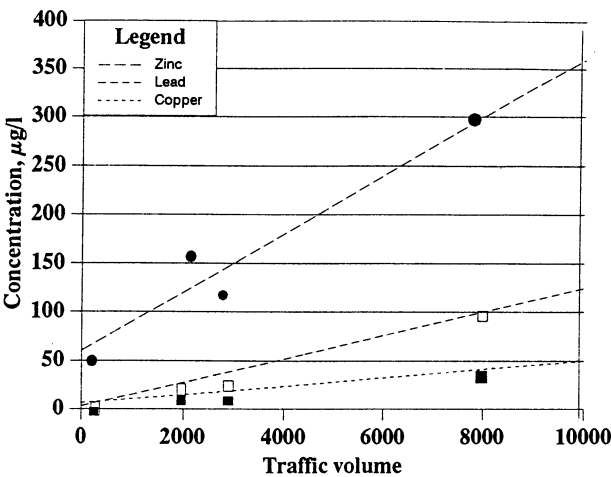


Fig. 2. A relation of concentration of metals in urban runoff to traffic density (After Bannerman, 1991)

period which had no restriction on the use of leaded gasoline, a situation typical for many Central and Eastern European Countries today. Use of leaded gasoline was banned in the U.S. about ten years ago and practically terminated after 1990. Strecker's data from the middle 1980's represent a transitional period where use of leaded gasoline was significantly curtailed.

Automobile manufacturers have also reduced use of metals in production of vehicles. Parts which used to be made of nickel or chromium are now manufactured from plastics. This has also reduced emissions of metals from traffic.

4.2 Other Sources

Other significant sources of pollution by metals in urban areas include metallic roofs, gutters and downspouts, metallic corrugated pipes, old lead pipes, storage areas, parking lots and automobile junk yards, landfills and other solid waste disposal sites (many of them unsanitary and emitting contaminants).

A comprehensive study on toxic contamination of urban runoff and CSO's was prepared for the U.S. EPA by Pitt and Barron (1989). They analyzed about 150 samples of surface runoff (sheet flow) and CSO samples and found that about 15 percent of the samples analyzed were found extremely toxic. The remaining samples were evenly split between being moderately toxic and non toxic.

The CSO samples had the greatest percentage of samples that were considered extremely toxic, followed by parking and storage area surface runoff samples. Roof runoff, urban creeks, and CSO samples had the greatest detection frequencies, while vehicle service and parking areas had the highest observed concentrations of organic toxicants. Roof runoff had the greatest concentrations of zinc, while parking areas had the greatest concentrations of nickel. Traffic and parking associated areas had the greatest concentrations of lead and urban creeks were highest in copper content.

A summary of measured concentrations is presented in Table 10.

Table 10. Concentrations of priority pollutants in runoff from urban source areas (from Pitt and Baron, 1989)

Constituent µg/l	roofs	parking	storage	Source area streets	vehicle service	landscaped area
Cadmium	0.8-30	0.7-70	2.4-10	0.7-220	8-30	0.04-1
Chromium	7-510	18-310	60-340	3.3-30	19-320	100-250
Copper	17-900	20-770	30-300	15-1250	8.3-580	80-300
Lead	13-170	30-130	30-330	30-150	75-110	9.4-70
Nickel	5-70	40-130	30-90	3-70	35-70	30-130
Zinc	100-1580	30-150	66-290	58-130	67-130	32-1160

4.3 Effect of Acidity of Urban Precipitation on Pollutant Loads by Metals

Acidity of urban precipitation caused by local and regional sources of sulphur oxides and mostly local (traffic) sources of nitric oxides is quickly buffered by overland flow (Novotny and Kincaid, 1982). However, this "buffering" capacity in urban areas is provided primarily by the infrastructure, including buildings, pavements, and sewers. During buffering the excess hydrogen ion from acid precipitation is buffered by carbonates, which releases the cations such as calcium and magnesium (primary components in concrete, mortars and soil) into the runoff.

Acids in precipitation also dramatically increase solubility of metals used in cars, zinc gutters and other places. Förster (1990) showed that urban metal roofs and roof and gutter materials (such as zinc) are good buffers for acid rainfall but metals and other pollutants (for example, PAHs from roofs with tar shingles or cover) are elevated in the runoff from these surfaces. Although zinc roof materials provided very high buffering of the pH of the acid rainfall (pH of runoff was near neutral) dissolved zinc content in the runoff was 450 times greater than that in the rainfall (0.005 mg of dissolved Zn/l in rainfall compared to 2.2 mg dissolved Zn/l in roof runoff from zinc covered roofs and gutters) when pH of rainfall was less than 4.

5 Receiving Water Impact and Fate of Metals

In aquatic environments, toxic metals are either in dissolved (dissociated) or particulate fractions. The sediment fractions that may interact with toxic metal compounds are where precipitated metals would reside, include fine (clay - fine silt size) and organic particulates. Clay and organic particulates have a high sorptive capacity for many chemicals and act as the contaminant transport medium in aquatic systems. These sediments are classified as *cohesive* and their behavior in aquatic systems is different from cohesive sediments. Clay and organic matter can effectively adsorb or coprecipitate such pollutants as phosphates, ammonia, a variety of polar and nonpolar organic chemicals, and toxic metals.

Typically, cohesive sediments (mud) in riverine and estuarine systems are composed of clays, silt, and organic particulates. Cohesion of particles (floc formation during settling and consolidation during and after deposition) is more pronounced for clay particles (size $\leq 2 \mu\text{m}$) than for more coarse silt particles (2 to $100 \mu\text{m}$). In fact, Mehta *et al.* (1989) speculated that cohesion of silt particles into larger flocs and compacted matter is by clays.

The process of cohesive sediment movement, deposition and erosion is more complex and more empirical than that of noncohesive sediments. When larger quantities of coarser materials such as sand and larger size organic detritus, are present in the sediment its behavior and interactions become quite complex and are presently not well understood (Mehta *et al.*, 1989).

The fine sediment particles can aggregate during settling and when settled form cohesive deposits. During erosion at low shear stresses fine particles are eroded first leaving coarser particles in the bed. These coarser particles are then bound with the remaining clays, resulting in armoring the bed (Ziegler and Lick, 1988). Consequently, settling and scour of cohesive deposits differ from classic sedimentology of discrete settling of noncohesive sand particles.

5.1 Interaction of Cohesive Fine Sediments with Toxic Substances and Other Adsorbable Compounds

The concentrations of adsorbed and dissolved fractions of the toxic and other adsorbable compounds are in an equilibrium which is typically expressed by the equilibrium-partitioning equation (O'Connor, 1988) i.e.

$$r = \Pi C_d \quad (2)$$

where

r = pollutant fraction adsorbed on the sediment, $\mu\text{g/g}$

C_d = dissolved pollutant concentration, $\mu\text{g/L}$

Π = partition coefficient, l/g .

Considering that m_{ss} is the concentrations of suspended solids that have an affinity for adsorption or co-precipitation of the pollutant and θ is the water content of the water-sediment mixture (volume of water/total volume) the total concentration of the pollutant becomes

$$C_T = \theta C_d + C_a = \theta C_d + m_{ss} r = C_d (\theta + \Pi m_{ss}) \quad (3)$$

For water - sediment transport, the moisture content θ is one. For sediments θ is equated to porosity.

$$\Pi [\text{l/g}] = K_{p0} \times Ss^\alpha \times 10^{-3} \quad (4)$$

An empirical relationship has been determined for the partition coefficient of metals in an aquatic environment, as a function of suspended solids concentrations, as:

where K_{p0} and α are given in Table 11.

It should however be noted that literature reported values show very little or no consistency of K_p values for a specific metal, even in quite similar environmental conditions.

A reasonably reliable model of fate of toxic compounds must include a balance of fine solids. However, while the science of sedimentology is well developed and advanced for noncohesive sand type noncohesive sediments (Vanoni, 1975) the state-of-art of cohesive sediment modeling is still evolving.

Table 11. Partition coefficients for selected metals in streams and lakes (after EPA, 1985)

Metal	Streams		Lakes	
	K_{p0}	α	K_{p0}	α
As	0.48×10^6	0.27	n.d.	n.d.
Cd	4.00×10^6	0.87	3.52×10^6	0.08
Cr	3.36×10^6	0.07	2.17×10^6	0.73
Cu	1.04×10^6	0.26	2.85×10^6	0.10
Pb	0.31×10^6	0.81	2.04×10^6	0.47
Hg	2.90×10^6	-0.14	1.97×10^6	-0.17
Ni	0.49×10^6	0.43	2.21×10^6	0.24
Zn	1.25×10^6	0.30	3.34×10^6	0.32

5.2 Processes Affecting the Fate of Toxic Metals in Water Bodies

The processes that affect the fate of pollutants, both conventional and toxic, in the aquatic environment can be classified into the following four main categories:

- Transport processes** which can occur according to the following mechanisms:
 - Advection. Pollutants, in dissolved, suspended or sorbed (to suspended sediments) form are transported by the hydraulic flow
 - Sedimentation. It affects suspended pollutants and pollutants sorbed to suspended sediments. In addition, sediment deposition rates can affect dissolved pollutants concentration via adsorption/desorption equilibria
 - Precipitation/dissolution. It may be considered a transport process in that it causes a change in the phase of the pollutant and may affect the availability of the pollutant to other transport and transformation processes.
- Transformation processes**, among which are:
 - Biomodification. It is carried on by microbial metabolism. In the case of toxic organic compounds, microbial metabolism may alter the original toxicity of a compound.
- Speciation processes** which include:
 - Acid-base equilibria. They determine the ionic states of acid and bases, and may influence volatility and precipitation/dissolution processes.
 - Sorption. Hydrophobic organic compounds are sorbed to suspended sediments according to sorption equilibria. The fate of sorbed matter is then correlated to the fate of suspended sediment.
- Bioaccumulation.** Bioaccumulation refers to the intrusion of nondegradable, nonassimilable (usually toxic) compounds in the food chain. In this context, bioconcentration refers to the primary uptake of such compounds (i.e. through the gills of the fish), while biomagnification refers to their uptake as part of a

prey/predator food chain scheme (i.e. consumption of "contaminated" food or lower order predators). Bioaccumulation is the final step in the pathway of pollutants in the aquatic environment. It is not considered as part of water quality/waste assimilative capacity determinations; it is, rather, a starting point to determine allowable pollutant concentrations in the water.

The prediction of the fate of pollutants requires :

- a) to know which processes act on which toxicant;
- b) to define the environmental compartments between which the processes occur;
- c) to select (or develop) a model that simulates a process of interest;
- d) to estimate the input parameters and/or coefficients for that model.

Since metals do not generally degrade, volatilize or decay by photolysis, their fate in natural water is mainly controlled by transport processes. In addition, metals speciate into many different forms, and these may differ in relative toxicity and behavior (for example, adsorptivity on sediments). Table 12 lists possible processes involved in transformation and transport of metals in aquatic environments.

Metals in a riverine environment are present in the water column and sediments in both dissolved and particulate form. Consequently, transformations and exchanges between the two phases and forms affect their fate over prolonged periods of time. For example, assume that a stormwater overflow with a high metal content from urban diffuse pollution sources is eliminated following implementation of BMP's. Depending on the bed sediment characteristics and the rate of desorption of the metal therein accumulated in previous years, the actual observed decrease of metal concentration in the water column could prove to be lower than predicted due to gradual release of the metal from the sediments to the water column, once the direct discharge has already been eliminated.

Table 12. Summary of significant reactions involving toxic metals and metalloids

	Anion Exchange	Sorption Potential	Acid- base Hydro- lysis	Complex- ation w/Inorganic Ligands	Complex- ation w/Organic Ligands	Methylation or Redox
Cadmium		x	x	x	x	
Arsenic	x					x
Mercury		x	x	x	x	x
Selenium	x					x
Lead		x	x	x	x	x
Zinc		x	x	x	x	
Copper		x	x	x	x	

The following approaches can be used to describe metal behavior in rivers. These approaches are applicable to a metal that is present in the aquatic environment in a single dissolved species and a single adsorbed species, and are introduced in increasing order of complexity:

1. **Dilution approach.** The variation in dissolved metal concentration is given by loads from both diffuse and point sources, and dilution with river water. This method considers total metal (adsorbed + dissolved) concentration only in the aqueous phase (water column) and treats it as a conservative substance. The hypotheses under which it is reasonable to assume a dilution-based approach include: suspended solids concentration in the water column relatively constant (no significant scouring and deposition occur), and the sources of metals are fairly constant over time. Input variations may induce a driving force for adsorption or desorption to, or from, the sediment bed.
2. **Dilution plus sediment transport.** The exchange of contaminated sediments due to scour and deposition influences total metal concentration (dissolved + adsorbed) in the water column. The hypotheses underlying this approach are: degradation and decay of metal are zero, and partition coefficients in the sediments and water column are the same. While the first hypothesis is almost always satisfied (only elemental mercury volatilizes), the second is justified due to uncertainties in the determination of partitioning coefficients values. The MICH Riv model by the US EPA can be used for simpler simulations of the metal content and simpler speciation.
3. **Dilution plus adsorption/desorption equilibria.** The application of the previous two approaches is justified if the degradation rate of the metal is negligible (usually true), and so is its partitioning between the water column and the sediment bed (i.e. metal concentrations are the same in the two phases and there is no adsorption or desorption between). This latter assumption is equivalent to a steady-state hypothesis, and may be valid in a situation when an existing discharge has been operating for a long period of time and the bedded sediments were not subject to significant erosion or deposition; in the case of a new discharge, however, as dissolved metal in the water column comes in contact with uncontaminated sediments downstream, adsorption phenomena may become significant, depending on the value of the partition coefficient for that metal. Conversely, if the existing discharge is terminated, natural desorption of the metal from the sediments will occur. It should be noted that the time-scale of adsorption/desorption equilibria and resuspension/deposition dynamics affect the water body on different time-scales: while resuspension/deposition phenomena exert their effects at the time scale of hydrologic variations of flow (i.e. high flow following wet periods and low flow during dry periods), adsorption/desorption effects are more likely to be significant over a time frame of months-to-years. Since resuspension/deposition rates fluctuate significantly over time periods of this length, it may be assumed in

first approximation that their effects cancel each other out and can therefore be ignored.

In most cases such complex cases are simulated by mathematical models.

5.3 Effect of Impoundments on Metals in Natural Waters

Settling of metal-contaminated solids has a much higher likelihood of occurring in lakes or reservoirs than along the river channel itself, both during high flow and low flow periods, since in these hydraulic conditions they are more quiescent than in the former, and turbulence effects are smaller. A lake or reservoir along a river channel can thus be imagined to be a sink of metals.

It should be however noted that the reservoir can selectively hold particles of a specific class of solids (usually coarser particles), and this may reflect in a change of the value of the partition coefficient in the influent and effluent water, since finer particles have a larger specific area (area per unit of mass) available for adsorption. The mass balance equations written above should therefore be applied separately to each class of solids.

5.4 Metal Speciation

The analysis previously presented is valid when a metal follows partitioning into one dissolved species and one adsorbed species; however, this is rarely the case, as the actual behavior in an aquatic environment is highly complex. A generic metal may in fact be present in dissolved form as a free ion, or as a complex with other organic or inorganic compounds, and in suspended form as a precipitate.

The major processes affecting metal speciation in an aquatic environment are:

- precipitation/dissolution equilibria
- oxidation/reduction reactions
- dilution
- adsorption.

The latter two processes were discussed in the previous section. It should however be remembered that:

- Dilution effects will most likely alter the "master variables" (pH, ionic strength, temperature) of the original discharge, and may significantly affect their original values in the water body. Both pH and redox conditions may significantly affect the relative distribution of the dissolved species of a metal present in the discharge.
- Adsorption is influenced by pH, concentration of both the metals and the ligand. The following rules-of-thumb apply: generally, at low pH values little metal is adsorbed, while at high pH most of the metal cations are (in natural waters, most metals are present as cations, with some exceptions, such as

CrO₄²⁻ and AsO₄³⁻). Since most of the organic carbon in a water body is usually dissolved, it may be expected that soluble metal-organic complexes can be formed, and this may tend to increase the dissolved fraction of the metal. Usually, dissolved organic carbon levels in rivers vary in the range 1-10 mg/l, while solid or adsorbed organic carbon vary in the range 0.1-1 mg/l. When more than one adsorbable metals are present, and adsorption sites are limited, competitive adsorption occurs, and the adsorption of some ions may be limited by the lack of substrate.

Precipitation/dissolution equilibria are defined by the generic relationship:

$$K_{sp} = [M^{b+}]^a [B^{a-}]^b \quad (5)$$

where

$[M^{b+}]$ = concentration of the metal cation

$[B^{a-}]$ = concentration of the anion, and

K_{sp} = equilibrium constant, or solubility product of the metal.

If the solubility product value for a specific metal is exceeded, then the metal precipitates, forming a solid phase (for example, an hydroxide), which can either remain suspended or settle into the sediment layer, depending on hydraulic conditions and on the degree of precipitation achieved.

Equilibrium constants for metals are fairly well determined, and reported in most chemistry textbooks; the solubility of the metal in natural water body is however complicated by the fact that several solid phases can be present. In an oxic environment, carbonates or hydroxides are predominant, while in anoxic environments, sulfides often prevail; it should be remembered that the magnitude of the solubility product for a given equilibrium does not indicate which is the controlling equilibrium, and more values cannot usually be directly compared with each other. Also, equilibrium conditions may not be reached in every water body, and supersaturation of one or more constituents often occurs.

5.5 Oxidation/Reduction Equilibria

These reactions are conceptually equivalent to acid/base reactions, except for the fact that they occur at a slower rate. Metals change from free ions to ionic species, or from one ionic species to another at a different valence through redox reactions. Oxidants and reducing agents are electron acceptors and donors, respectively. In general, when even a small amount of dissolved oxygen exists in the water body, oxidizing conditions occur.

6 Summary

Metal contamination of aquatic water bodies from diffuse sources should be divided into natural (background) quality and cultural (man made) pollution. Since the term "pollution" in the United states implies a harm or damage to the aquatic ecosystem, public health or impairment of other uses the toxic component of pollution by metals must be also identified. Typically, divalent cation form of dissociated metals are most toxic. Of the 59 metal elements, thirteen have been included into the priority list of pollutants by the U.S. Environmental Protection Agency.

Urban, highway and industrial diffuse sources are the major causes of pollution by toxic metals.

Ascertaining the fate of toxic metals in aquatic environments is difficult since most metals occur in several dissolved (dissociated) and solid (precipitated - adsorbed - complexed) forms. Mathematical models describing the fate of metals are available.

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4 Monitoring of Air Pollutant Effects, Some Principles and Examples

E. Reichrtova

Institute of Ecobiology, Slovak Academy of Sciences, Mlynske Nivy 59,
814 34 Bratislava, Slovak Republic

1 Bioindication and Biomonitoring

The biological methods of ambient air pollution monitoring are based on the principle of the utilization of *biota* as integrators of the environmental exposure. Species of *fauna* and *flora* are utilized for the bioindication of environmental changes (Mejstrik and Pospisil 1988) on account of their sensitivity. The most sensitive species among phytoindicators - lichens are of a special interest because their mineral nourishment is absorbed by their whole body surface. Where lichens do not grow, the method of lichen transplantation is applied (Goodman et al. 1975). Wild growing plant communities can also indicate air pollution. The sensitive species gradually extinguish and only the resistant plants persist. In the areas polluted by magnesite emissions as well as in the surroundings of the chemical factory, only the most resistant plant species occur (Kaleta 1988). A gradual deterioration of the deciduous forests also indicates air pollution. Concerning *fauna*, insects can be referred to as sensitive bioindicators of air and water pollution. The rusty colour of *Daphnia magna* living in standing water adjacent to a nickel smelter dumping-site indicated the increased metal accumulation (Fe, Ni, Cr). This was confirmed by X-ray microanalysis (Foltinova et al. 1988).

Contrary to the bioindication results, which give information on the changes in the quality of the environment, the method of biological monitoring should be understood more as a quantitative approach (Mejstrik and Pospisil 1988). The advantages of it are the acquiring of information on the extent of the accumulation of pollutants, their redistribution within the organism, and also a geographical distribution of the searched pollution. Using *biota* as test-objects, the exposure of organisms is analytically checked. In addition, a dose-response between the concentration of pollutants and the effects resulting from the pollution can be assessed by various methods. Contrary to the bioindication, in the biological monitoring not only sensitive plant and animal species are utilized. The model bioindicative species of the hare (*Lepus europeus* Pall.) which sensitively reacts to air pollution by blood cell count changes (Novakova and Paukert 1973) was replaced by the field vole (*Microtus arvalis* Pall.). Recently, species were selected that are neither rare nor protected. For example *Larus ridibundus* L., living in colonies on islands of the water reservoirs, has been proved to be useful for biological monitoring of the exposure arising from the metal waste originating from a nickel smelter. An in-

creased level of metals (Fe, Ni) in the shells and egg contents has been found when compared to a non-polluted locality (Darolova et al. 1989).

2 Model Biomonitoring of Air Pollutants on Domestic Rabbits

The results of epidemiological mortality studies after air pollution episodes in various countries had their public impact, and governments began to develop strategies for air pollution control. In the mean time, the prevention of chronic effects has become much more serious than the acute toxic effects. Ambient air quality standards were established and permanent control measures introduced. The alternative way of the technical pollution control was the development of biological monitoring methods. A modification of wild animal utilization in biological monitoring of ambient air pollution is a field exposure of domestic rabbits. An advantage of this approach is exposure under semi-defined conditions. A defined set of animals is prepared, divided into test and control groups, and all parameters of the exposure design are selected. Both groups are simultaneously exposed to the polluted and non-polluted regions. Such an experimental arrangement makes it possible to assess the course of pollutants accumulation in body tissues of the exposed animals at various time intervals in comparison with the non-exposed group. It is possible to arrange a prenatal exposure of the filial generation as well as to test the postnatal period. The model on domestic rabbits gives extensive and quantitatively sufficient material choice for analyses, and a chance to perform the specialized investigations concerning air pollutant effects. As a result of new insights into biochemistry, cellular biology, cytogenetics, pharmacology and immunology, increased attention has been paid to the ability of toxic agents individually or collectively to induce response and pathological changes at the cellular level. For this reason the model biomonitoring of the pollutants effects on domestic rabbits is extraordinarily suitable. The animals are kept in special cages designed to enable free circulation of air. Food and water are the same as for the non-exposed group. Animals inhale the air in the same respiratory zone as man. The cages are situated in the direction of prevailing winds from the source of air pollution. For the first time, domestic rabbits were used for biomonitoring environmental exposure to arsenic (Bencko et al. (1968), later to lead, manganase, chromium, cadmium and nickel (Bencko et al. 1981). The animals can be sacrificed in the course of one year at various intervals and tissues analyzed for metal contents to observe the dynamics of their body accumulation. In the vicinity of metallurgical lead plants a field experiment using domestic rabbit exposure was performed. The lead content was assessed by the atomic absorption spectrophotometry (AAS) method in blood, liver, kidneys, spleen, bone and fur. The rabbits were sacrificed in groups of three after exposure lasting 1, 3, 6, 9 and 12 months. The lead content in the exposed group was compared with values in controls from a non-contaminated area. The differing accumulation of the lead in tissues between both of the groups was detected using the method of atomic absorption spectrophotome-

try (AAS). The exposure to lead was also followed in a group of twenty boys between the ages of 7-14 years living in the environment of the plant. The examination used the determination of lead in blood and in hair by the AAS method. The results of analyses were compared to a control group of children. Similarly to the findings in rabbits, increased lead concentrations in the exposed group of children were demonstrated (Bencko et al. 1981).

Model biomonitoring using domestic rabbits was extended to biomonitoring air pollution created by dust particles derived from the magnesite and cement industries, a nickel smelter and also a mercury producing plant. All particles had the same content of macro- and microelements. Besides the domestic rabbits, laboratory Wistar rats were employed in the biomonitoring studies provided in the polluted regions by the cement and magnesite industries (Reichrtova et al. 1980, Reichrtova et al. 1984). The exposure of laboratory rats is supposed to last during the summer time only. In a region heavily polluted by magnesite emissions, we used also herds of cattle for monitoring exposure where the farming had considerably deteriorated (Reichrtova et al. 1984).

Magnesite emissions contain largely magnesium oxide (about 90%) and a mixture of macro- and micro-elements. The biomonitoring studies on domestic rabbits as well as on the other kinds of animals revealed a corresponding increased accumulation of magnesium, iron and other metals in the body organs of the exposed animals. Simultaneously, the magnesium-calcium ratio was distorted in the exposed organisms on account of the biological antagonism. Using the method of neutron activation analysis, an increased accumulation of metals in the fur of the exposed domestic rabbits was shown. The accumulation of magnesium and other metals in the lungs, spleen, liver and myocardium was attended by morphological changes in organ microstructure and ultrastructure, respectively (Vesela et al. 1987). The changes found in the ultrastructure of myofibrils in the exposed rabbits were similar to those reported in cases of hypomagnesemia. They reflected the effects of excessive or deficient intake of magnesium by heart muscle. The specific adenosine triphosphatase (ATP) activity in the exposed heart muscle was found to be diminished (Reichrtova et al. 1987). The observed affinity of myocardium for metal deposition is important with a view to the development of cardiomyopathy (Koltai et al. 1983). The effect of inhalation exposure to magnesite emissions in the open air was evaluated in laboratory rats and domestic rabbits using scanning electron microscopy to study the excisions from the trachea. Cilia were covered by a mucus layer to form crystal-like structures, which had the shape of delicate plates with the cilia built in. These changes resulted in damage to lung clearance from the inhaled particles. Tracheal excisions were examined for the presence of chemical elements by means of X-ray microanalysis. The results have shown the content of iron and magnesium as well as other minor elements. The above mentioned magnesium and iron were accumulated around the sites of morphological lesions of the tracheal relief (Foltinova and Reichrtova 1990). The number of lavaged pulmonary alveolar macrophages (PAM) that are responsible for phagocytosis of the inhaled foreign particles, was increased significantly following the animals exposure. There was a concomitant increase in PAM acid phosphatase activity.

These findings pointed to the enormous load in the deep region of the lungs from the inhaled emissions (Reichrtova et al. 1982). Concerning the effect of inhaled magnesite emissions on the immune response, increased count of B lymphocytes and their lactate dehydrogenase (LDH) activity in the peripheral blood has been shown. Light microscopy pictures of the lungs and spleen of the exposed animals confirmed their defensive response to the presence of accumulated particles. Bio-monitoring aimed at the examination of magnesite emission effects on reproductive ability and embryotoxicity in the exposed animals was carried out utilizing domestic rabbits and laboratory rats. Females were exposed to magnesite emissions for 6 months and mated with non-exposed males following the exposure. It was found that the fertility index of the exposed females was 40% less than of control females and that average litter size was smaller. The mean weight of newborn progeny was the same as in the controls, however, the young weighed less on the 21st postnatal day. The lungs, kidneys and brains of young born to exposed females weighed less, whereas there was no difference in the weight of the livers and spleens, respectively. Magnesium concentration was found to be significantly increased in the lungs and muscles of the exposed young (Reichrtova et al. 1982). The increased content of magnesium in the brain was concomitant with a decrease in calcium content. These findings suggested that distortion of the ratio between magnesium and calcium resulting in the changes in the ratio of other elements may induce changes in female reproduction characteristics. The embryotoxic effect of magnesite dust has been studied in a laboratory experiment using avian embryos. Embryotoxicity as well as potential teratogenicity on the direct administration of a magnesite dust suspension into the eggs during embryonal development has been shown (Reichrtova et al. 1981). On the contrary, magnesium sulphate administration did not evoke a teratogenic effect in avian embryos. The findings pointed to the synergic effect of magnesium and metal components in magnesite emissions.

The biomonitoring method using domestic rabbits was applied also in a region polluted by the waste from a nickel smelter and refinery. Airborne metal particles arise primarily from the works, and secondarily from the waste on the dump. The waste contained about 60% iron and a number of metals, the most dangerous of them being nickel and chromium. By AAS we found preferential deposition of nickel in the lungs and myocardium (as early as after a 3-month exposure), while accompanying increases of chromium were detected in the liver and kidneys of exposed domestic rabbits. After the 6-month exposure, an elevated level of Cr was also found in the heart and thigh muscles, whereas Ni content was increased in the liver. The iron content was already elevated in all organs investigated (Reichrtova et al. 1989a). In an F1 generation of young rabbits 6 weeks old born to the exposed females, elevated levels of chromium were found in the liver, kidneys, heart and thigh muscles. The iron content was increased in the liver and thigh muscle, while the nickel concentration was enhanced only in the brain. Increased mucus secretion was observed on tracheal mucous relief of F1 animals in response to the irritative effect of inhaled needle-shaped particles using a scanning electron microscope, despite their short postnatal exposure. Concerning the morphological changes observed under a light microscope, a hypertrophy of muscular tunic of parenchymal

arteria pulmonalis and foci of atelectasis in the lung tissue was found. Bronchioli showed signs of spastic contraction, in bronchial walls there was focal interstitial lymphocytic infiltration. Using scanning electron microscopy, the pictures of tracheal excisions showed a massive secretion of mucus which has the character of a network or a compact mass with interspersed microparticles engulfed by macrophages. The pictures suggested an impairment of physiological tracheobronchial clearance. These findings were consistent with the histological changes in the lung tissues. All of them have shown an irritation of the respiratory system of the exposed animals to metal aerosol derived from a nickel smelter waste (Reichrtova et al. 1988). The increased count of pulmonary alveolar macrophages lavaged from the exposed female domestic rabbits has proved the load of lung alveoli by the inhaled particles (Reichrtova et al. 1989a, 1989b). The investigation of enzyme activity of PAM revealed an increased activity of lysosomal enzymes. In contrast to their increased phagocytic activity, a significant reduction was found in the antibody-mediated rosette formation by PAM in the exposed domestic rabbits, on account of the impairment of Fc receptors on PAM plasma membrane caused by the ingestion of metal particles. The inhibitory effect of metal particles mentioned above revealed the possible adverse effect of long-term exposure in a polluted area on the immune function of pulmonary alveolar macrophages. Antibody-mediated rosette formation by PAM may be a biomarker for risk assessment of toxic pollutants in the ambient air (Reichrtova et al. 1986b). Concerning the other immune processes examination of animals exposed to metal aerosol derived from a nickel smelter and refinery, increased levels of tissue immunocomplexes were found in myocardium and lungs. In the F1 generation of young exposed both prenatally and 6 weeks postnatally significantly elevated serum circulating immune complexes were detected. Further, in a laboratory experiment on Wistar rats following the chamber exposure to waste metal aerosol, a non-specific transplantation immunity was shown to be decreased. The findings suggested a modulating effect of metal aerosol containing chromium, nickel and other toxic metals regarding non-specific immunity (Reichrtova et al. 1990).

We also used the biomonitoring method utilizing domestic rabbits for impact assessment of inorganic Hg-emissions originating from a mercury producing plant that functions also as a refinery for all mercury wastes collected in the territory of Slovakia. The mercury determination in the animal organism was done spectrometrically using a Trace Mercury Analyser TMA-254 (manufactured in Czechoslovakia). The Hg content increase was found in the lungs, kidneys, liver, brain, heart and bone of the exposed animals following their 6-month respiratory exposure. Histopathologically, the impact of inhaled mercury waste aerosol (including mercury vapor) was seen mostly on the lung, kidney and heart muscle tissues. The histological picture displayed a thickening of interalveolar septa in the lungs on account of cell infiltrates resulting in an apparent reduction of respiratory space in lung tissue. In addition, the thickening of the muscular layer of pulmonary vessel wall leading to a considerable narrowing of the blood vessel lumen was observed, similar to the picture observed in domestic rabbits exposed to metal aerosol derived from nickel smelter (Reichrtova et al. 1990). Striking morphological changes

in the tubular parts of kidneys in the exposed group were found. This seemed to be a result of an enormous elevation of Hg-concentration in the exposed rabbits (Reichrtova et al. 1992). Concerning the metals content in the fur of the exposed rabbits, a significant increase of Hg, As, Cd, W, Cr, Sr and Zn was found, being detected by neutron activation analysis (Reichrtova et al. 1991). According to the increased content of mercury in body organs of the exposed animals, the increased production of tissue immunocomplexes, mainly in the heart and kidneys, was observed (Reichrtova et al. 1991). The pictures of tracheal excisions under a scanning electron microscope proved the tremendous adverse effect of metal aerosol inhaled by domestic rabbits in the vicinity of a mercury producing plant on tracheal mucosa relief (Reichrtova et al. 1993). The character of changes seemed to be quite different from those that had been observed in animals exposed to magnesite emissions and nickel smelter waste, respectively.

3 Human Exposure Monitoring

In spite of receiving much valuable information on exposure to air pollutants using animals, human data is needed for a health risk assessment. Human biological materials that are accessible for sampling include blood and urine, but also hair, nails and deciduous teeth. The feasibility of hair as an indicator of human exposure to toxic metals was reviewed by Bencko (1991). Arsenic determination was carried out on hair, urine, and blood samples taken from groups of 10-year-old boys, residing in a region polluted by arsenic derived from burning coal with high arsenic content (Bencko and Symon, 1977). In all the materials examined, considerably elevated concentrations of arsenic were found. The exposure to lead was followed in twenty employees in a plant producing lead accumulators and people living in the environment of the plant, who were represented by a group of twenty boys at the ages of 7-14 years. The examination used was the determination of lead in blood and in hair by the AAS method. The lead blood level in the venous blood of the children was lower than in the employees, but the average lead concentration in the hair samples of both groups was the same (Bencko et al. 1982). The nickel content in blood plasma and urine of occupationally and environmentally exposed persons was similarly increased (Bencko et al. 1980).

4 Human Health Monitoring

Over the last several years ecoimmunology as a separate branch of immunology has been developed with the aim to define the response of immune system to environmental pollutants (including metals). Immune status is a very sensitive marker of environmental toxicants effect resulting in adverse health consequences. Immune biomarkers (e.g. functions of cells and mediators of the immune system)

represent measurable functional alterations caused by pollutants resulting in direct damage of a part of the immune system, or indirectly by influencing the other systems. Immune biomarkers seem to be useful in the group diagnostics of chosen human populations exposed in polluted areas. In addition, it is of importance to search for various inherited defects of the immune system, especially in exposed children (Vogt 1991). The interindividual susceptibility to various pollutants can determine the final immune response resulting in health effect (irritative and hypersensitivity reactions, allergic reactions, unregulated growth of immune cells, suppression of humoral and cell-mediated immunity, etc.). More and more is becoming known on the significance of antiproteases for immunoregulatory function (Menzoian et al. 1974). Alpha-1-antitrypsin (A1 AT), the major plasma protease inhibitor of elastase, is important in protecting the lungs from proteolytic damage, particularly from the elastase of neutrophils. The inhibitor activity of A1 AT is suppressed in the presence of cigarette smoke or chemical oxidants, which can promote subsequent development of lung emphysema in smokers (Carp and Janoff 1978). Chronic obstructive pulmonary disease in smokers results in part from the uninhibited elastolytic breakdown of alveolar connective tissue (Kuhn and Pierce 1981). In addition to A1 AT, proteases such as elastase, trypsin, and bacterial proteases interact with other plasma proteins, particularly alpha-macroglobulins. The latter compromises alpha-2-macroglobulin (A2 M) in human plasma and A2 M and alpha-1-macroglobulin (A1 M) in rabbit plasma. When proteases are chemically inactivated, interaction with A1 AT and with macroglobulins is prevented (Dolowitch et al. 1975). A1 AT deficiency is a common genetic variant, being found in about 10% of the population (Kueppers and Black 1974). Some A2 AT phenotypes are associated with a variety of inflammatory and immunologic disorders (Breit et al. 1982). In 11-year-old children attending schools in the center of the big city (with heavily polluted air) and from the outskirts of a town (less polluted atmosphere), the activity of antiproteases in blood serum was examined. There were statistically significant increases concerning A1 AT and A2 M levels in serum of children from the city center schools in comparison with the children from the outskirts. In the children examined, 9.82% heterozygote and 0.60% homozygote errors of A1 AT have been discovered (Richter et al. 1980). Salivary immunological indexes (muramidase, salivary immunoglobulin G) were investigated in 473 11-year-old children from schools of the same city divided into two groups according to the degree of air pollution. Muramidase activity was very low in all children investigated, however, in the children in the city center it was significantly lower than in those from the suburban areas. As to salivary immunoglobulin A, the findings were also different with the values being decreased in the children from the city center and relatively higher in those living in the outskirts. There were no differences between boys and girls (Pfeifer and Richter 1979). Coal-fired power plants are frequently sources of emissions of airborne fly ash and sulfur and nitrogen oxides. Besides, the trace element content of coal is known to vary with the specific geological conditions in mines. Burning coal rich in some metal content may create air pollution problems not only in the power plant itself, but also in its vicinity, due to excessive metal concentrations in the ambient air

Table 1. Average concentration levels of A2 M and A1 AT in the serum of children residing in the vicinity of a nickel smelter

Group	n	A2 M [mg.ml ⁻¹]	A1 AT [mg.ml ⁻¹]
A	54	4.82 ± 0.93	4.37 ± 0.82
B	64	4.42 ± 0.89	4.08 ± 0.69
C	48	3.87 ± 0.91	3.80 ± 0.75

A - group of permanently exposed children.

B - group of "less exposed" children.

C - group of control children.

(Bencko et al. 1988). In a pilot study, groups of 9-year-old children residing in villages in the vicinity of a nickel smelter and waste disposal site were checked for the activity of blood serum antiproteases (A1 AT and A2 M). In the children living in the downwind areas were recorded the statistically significantly increased average levels of both antiproteases compared to groups of children residing outside the downwind areas. Findings concerning the antiproteases serum values in another group of children from a village only occasionally polluted, according to wind direction, were very striking. Antiproteases values of these children were between the permanently exposed group and the group from emission-free areas. In addition, decreased production of both antiproteases was found in 9.2% of the children examined (Bencko et al. 1983). The data on serum proteases values of the all groups of children are shown in Table 1.

Statistical evaluation of the differences using the Students t-test has shown the significance as follows: A:C - $p < 0.001$ for both A2 M and A1 AT, B:C - $p < 0.002$ for A2 M and $p < 0.05$ for A1 AT, B:A - $p < 0.02$ for A2 M and $p < 0.05$ for A1 AT, respectively. Through a retrospective epidemiological study regarding the children investigated for serum antiproteases, a 3-times higher occurrence of upper respiratory tract diseases as well as hospitalized pneumonia has been discovered in the group of children permanently exposed in the downwind villages (Chorvatovicova 1983). Similar increase of values of A1 AT and A2 M have been detected in the occupationally exposed people in the nickel smelter combined with other changes in their immune profile (Bencko et al. 1983). Balazova et al. (1985) published the findings on the increased nickel concentration in the biological fluids taken from non-occupationally exposed people residing near the nickel smelter. The authors analyzed also the necroptic materials of people who had been living for a long time in that district. The most striking finding was the high accumulation of nickel in myocardium of people suffering from cardiovascular diseases.

Even from this review comparing the data gathered by various biomonitoring methods using different test-objects it should be clear that air pollution may cause immense suffering of living organisms, including humans. From this point of view, experimental studies focused on the exact investigations aimed at effects of pollutants are needed. Chamber exposure of laboratory animals to toxic aerosols under defined conditions is needed to prove the relation between ambient air pollutants and their effects on health. The laboratory exposure of animals to metal aerosol

created from the waste of the nickel smelter was carried out in comparison to the environmental exposure of domestic rabbits nearby the nickel smelter (Reichrtova et al. 1986a). The adverse effect of metal aerosol on the activity of pulmonary alveolar macrophages of animals exposed under both conditions has been proved. In addition, long-term respiratory exposure of laboratory rats to the same metal aerosol revealed the mutagenic effect on PAM (Chorvatovicova and Kovacikova 1992). The laboratory studies discovered that vitamin C and E play an important protective role against metal genotoxicity (Chorvatovicova et al. 1991).

5 Conclusions for Prevention for Public Health

There is no doubt that much more needs to be learned about the mechanism of diseases caused by environmental factors. One of them is the effect of metals in the ambient air of heavily polluted regions. Biomonitoring methods using animals as test objects may contribute to health risk assessment. Changes in the immune profile of an organism due to inhaling polluted air can result in various diseases. The following measures are recommended:

- to search for susceptible persons (especially children)
- to treat people suffering from an impairment of the immune system -
- to move susceptible children from heavily polluted areas
- to increase the vitamin C supply in susceptible persons.

All these suggestions are aimed at health damage prevention and condition improvement, on decreasing the costs for medical treatment, and intensified measures in contaminated areas.

6 Summary

Risk assessment of the exposure of human organisms to air pollutants can utilize the results received from biomonitoring methods using animals. Markers of exposure identify pollutants within an organism. In contrast, markers of effects express impairments detectable by many methods. Both groups are used in a model biomonitoring method using domestic rabbits. This model gives information on events in an organism exposed to various pollutants. Many findings received from animals were comparable to those encountered in a selected human population examined in the identical regions heavily polluted by heavy metals. The model biomonitoring method using domestic rabbits should be combined with other methods recommended for health impact assessment.

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5 Quality of Information on Contamination of the Environment

W. P. Cofino,

Vrije Universiteit, Institute for Environmental Studies, De Boelelaan 1115, 1081 HV Amsterdam, The Netherlands.

1 Introduction

Society has a great demand for environmental analyses. Decisions on the management of waste materials are based on chemical data. Legislation imposes the acquisition of concentrations of a variety of constituents. Environmental taxes may be based on the concentrations of specific compounds. The need for sanitation measures may be assessed through a programme of measurements. Finally, monitoring of contaminants in air, water, sediments, soils and waste streams is carried out on a large scale for a number of purposes.

It is of utmost importance that information on the environment is reliable. This implies that the design, planning, implementation, evaluation and presentation of the programme of measurements has to be well founded. Inaccurate information may lead to conclusions and measures which endanger human health, which invoke (high) costs for wrong actions, or which threaten ecosystems.

In this paper, a holistic approach to quality management of environmental information is described [1]. The acquisition of data has to be seen in the context of the programme of measurements. Environmental information is the result of a chain of activities. Each tier has to have an adequate strength in order to obtain the information pursued. The management of the quality of this process is described in the second chapter. The remainder of this paper focusses on laboratories. A comprehensive infrastructure for the acquisition of adequate data on the environment is described. Basic in this infrastructure is the presence of qualified laboratories which manage the quality of their output. These laboratories should be supported by accreditation, the provision of standard methods, the provision of reference materials and laboratory performance testing. Each of these activities contributes to improved quality (accuracy, precision) of data. A measurement infrastructure in which these activities are concerted makes use of the full potential thereof.

This point of view is elaborated. In chapter three, quality management in laboratories is discussed. Chapter four deals with accreditation, standardization of methodology, reference materials and laboratory performance testing. In chapter five, the line of reasoning is summarized.

2 Total Quality Management of Environmental Information [1]

The process for the acquisition of information is schematically outlined in the quality circle depicted in Fig. 1 [1,2]. The figure, and following discussion, are based on the standard ISO 9004 [3].

The first step is to analyze critically the information needs and expectations [4]. It is not sufficient to specify which parameters have to be measured in which matrices. Where possible, quantitative criteria should be established, for instance the minimal temporal trend which should be detected ($x\%$ difference in y years with a probability of $z\%$) or limits for the producers and consumers risks when compliance with standards has to be checked. The assessment should include aspects such as the time schedule, data management, and the way the information has to be presented. This step should result in qualitative and quantitative specifications the information has to meet.

These specifications are put into the design phase. The physical-chemical properties of the chemicals have to be considered in order to select the most appropriate compartment for measurement [5] and to establish proper procedures for sampling, preservation and laboratory analysis. Knowledge on chemical, biological and physical processes, on specific local characteristics or on properties of the object of investigation, on analytical methodology and on statistics is employed to devise a programme of measurements. Environmental modelling can provide an important contribution in this respect. Data management has to be accounted for. Quality assurance for field and laboratory work should be considered, including the assessment of quality criteria these activities have to meet. Acceptance criteria for the results are to be established.

The planning phase includes the drafting of protocols for sampling and analysis, and the provision of instructions and requisites to the personnel and laboratories involved. Important aspects pertinent for sampling are the presence of a fully

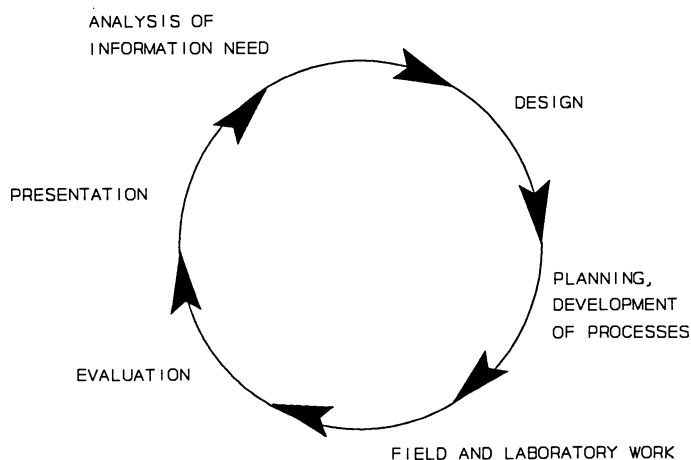


Fig. 1. A quality circle for the process to generate environmental information

documented sampling plan, a system for unambiguous sample identification and arrangements for quality assurance of sampling [6,7]. The sample plan should include among others the objectives, determinants, sampling locations, number and types of samples, identification of the samples, reference to standard operating procedures for sampling and preservation, and required field information (time, weather conditions, depth, and so on). Often, a scheme of inspections can be devised for quality assessment of sampling.

All field measurements and "administrative data" concerning the samples should be noted in logbooks. The sample identification should be such that a proper traceability is assured from sampling to reporting of the data.

When work is contracted out, requirements regarding methodology and quality assurance should be specified.

The field and laboratory work should be carried out within a quality system (e.g. EN 45001 [8], ISO 25 [9]). A more detailed discussion of such systems is given in the next section.

Evaluation of the laboratory data constitutes the next phase. The data should be assessed critically, checks on plausibility should be made. The evaluation should invoke the expertise used to design the programme of measurements.

Presentation ends a cycle. The presentation should tune in to the information need and be clear and timely.

Every stage should include procedures to verify that activities have been done in conformance with previously defined quality criteria. Evaluation of the whole cycle and of experiences of the users of information provides feedback which can be used to ameliorate the process. In this manner, the quality of the information generating process is continuously maintained and systematically improved.

A quality system encompassing the whole process described can be designed using ISO 9001 in addition to ISO 25. In the Netherlands, a standard with a similar scope has been issued by the Netherlands Normalization Institute (NNI, NEN 3417, in Dutch).

In the approach described in this section, the whole process from the analysis of the need for information to the presentation of results is subject of quality management. The information is the result of a chain of activities, and its quality will depend on the strength of the weakest link. Quality control and assurance in the analytical laboratory form a subset of a larger scheme. Quite often, however, a laboratory is commissioned to carry out only a part of the process depicted in Fig. 1. In this case a good communication between the (analytical) laboratory and the customers is essential. Laboratories have to ensure that their methodology meets the requirements put forward by the objectives of the measurement. The expertise of laboratories can be conferred as a service, for instance with respect to the selection of methodology for sampling, sample preservation and analysis and to the design of the sampling programme.

3 Quality Systems for Chemical Analysis

Management of quality is essential for a laboratory. It requires that the level of quality which is to be reached and maintained is critically assessed. This assessment is based upon e.g. the objectives of measurements, requirements put forward by legislation and/or reasons of competitiveness. The implications of this level of quality for personnel, premises and environment, equipment, materials, chemicals and methodology have to be derived. The laboratory has to be designed and operate in such a manner that the quality objectives are met. The entire process of assessing quality objectives, bringing the laboratory up to the level required and implementing and verifying measures assuring that the quality is sustained is encompassed in the development and implementation of a quality system.

Literature on quality management in general is widely available. For laboratories working in the environmental field, the principles of Good Laboratory Practices and the quality systems delineated in the ISO Guide 25 and the European standard EN 45001 are of particular importance. Some papers on quality assurance are given in the list of references [1,10,11,12,13,14,15,16,17].

The concept of Good Laboratory Practice (GLP) has been introduced by the US Food and Drug Administration (FDA) in the mid-seventies. This organization observed serious short-comings during the examination of toxicological tests conducted by animal testing laboratories [18]. In response to these observations the FDA established the principles of GLP, which were accepted in the US in 1976. The importance of the GLP guidelines was acknowledged by the Organization for Economic Cooperation and Development (OECD). The OECD published similar guidelines in 1982, which are applicable for all toxicological research carried out for the risk assessment of chemicals for man and environment [18,19].

GLP has the objective to assure the quality of laboratory data and to achieve transparency of the design, conduct and evaluation of the study. GLP provides criteria for the organization of a laboratory and for the way it should work in order to obtain valid data. GLP does not prescribe specific methodology. The criteria enable third parties to reconstruct the approaches and methods used and the results obtained. Most industrialized nations have incorporated the use of GLP guidelines in their legislation [20].

ISO Guide 25 and the European Standard EN 45001 provide a basis for the establishment of quality systems in calibration and testing laboratories. The framework of these standards will be discussed briefly.

Personnel

A laboratory has to ensure that its personnel has appropriate qualifications and experience for the analyses carried out. On-going training should be arranged.

Environment and Premises

The location, construction and spatial planning of the laboratories should meet the needs to perform the investigations correctly (e.g. without contamination), safely and without danger for the health of the personnel. Areas where incompatible activities are performed should be effectively separated. Good Housekeeping practices should be observed. The laboratory should formulate rules governing access and use of its premises.

Equipment, Materials and Chemicals

A laboratory should establish specifications which equipment, materials and chemicals should meet for a proper execution of their activities. The equipment, materials and chemicals should meet these specifications, as demonstrated by checks. Particular attention should be paid to traceability and calibration (e.g., also for volumetric glassware). Maintenance procedures for equipment should be arranged and documented. Verification procedures should have been established for incidences where malfunctioning of instrumentation occurred.

Storage containers for chemicals should have information on its contents: origin, composition, purity, date of receipt/preparation, latest date for use, storage conditions.

Proper administrative procedures have to be observed (e.g. logbooks for equipment).

Methodology

The performance characteristics of methodology should be adequate in view of the objective of measurement. The methods should be well documented, for instance in standard operating procedures. ISO 25 and EN 45001 state that preferably methodology should adhere to national or international standards. In-house methods are allowed, however. In all cases, particular attention should be paid to the validation.

Validation has been described as 'determining the suitability of methodology for providing useful analytical data'. A method is validated when the performance characteristics are adequate and when it has been established that the measurement process is in statistical control and produces accurate results [21]. A WELAC/EURACHEM guide specifies the performance characteristics : precision, accuracy, limit of detection, limit of quantification, selectivity/specificity, range, linearity and ruggedness [].

In the Netherlands, for environmental analyses it has been recommended to include procedures in methodology which enable a technician to assess a proper functioning of the measurement system. Examples are the determination of metals with ICP-AES by measurement at two different wavelengths and comparison of the results, and the use of internal standards in chromatography. Such procedures

enable a technician to detect analytical problems and/or errors and to take corrective actions timely.

Calculations and data transfers ought to be checked. ISO 25 and EN 45001 also contain criteria with respect to computers and computer controlled systems in laboratories.

Particular attention should be paid to calibration, which has been identified as a major source of systematic error in environmental analysis (e.g. [22,23,24, 25,26]. Errors related to calibration include improper purity, stoichiometry or identity of compounds, dilution errors, the neglect of the density of solvents and of temperatures when preparing standard solutions on a volume basis, inadequate internal standards or errors in their application and bad storage and handling of stock solutions [27,28]. The quality of commercially available standard solutions can be questionable [29]. It is good practice to check the contents of such solutions by the use of an independent standard prepared from pure or stoichiometric compounds ([10,28 34]). The exchange of calibration solutions with other laboratories can prove to be highly instructive. Regularly, dilution, weighing or calculation errors are made in the preparation of standard solutions. Each fresh bottle of standard solution should be checked by comparison with the old bottle. It has been recommended not to prepare a calibration curve by serial dilution from a single solution. The chance of unnoticed mistakes can be reduced by using two or more starting solutions [10].

Management and Organization

The management of a laboratory should ensure that the laboratory has a sufficient number of appropriate personnel, premises, equipment and so on. The personnel should work free of improper influence. A technical manager with a high level of experience should be appointed. In addition, the task of quality manager should be allocated for the development, implementation and maintenance of the quality system. This system should be delineated in a quality manual. Large laboratories may have a full position or a special section for quality management. In small laboratories, the task of quality manager can be combined with other activities.

The management should clearly assign responsibilities to its staff.

The performance of the technicians is an important factor controlling the quality of the output of a laboratory (e.g. [30]). W.E. Deming, one of the founders of quality management, stressed the importance of a stimulating and motivating management. He pointed out the need for a good education programme, warned for parochialism, and made a plea for an atmosphere in which personnel could express themselves. These points have also been stressed by Griepink [14].

Quality Systems: Audit and Review

ISO 25 devotes a special section on this topic. The issues are implicitly present in EN 45001.

A laboratory should maintain internal quality control schemes. These schemes may include the regular use of certified reference materials (primarily assessment of accuracy, usually used with a relatively low frequency) and of laboratory reference materials (not-certified, primarily assessment of statistical control, used with a relatively high frequency), replicate testing of samples, the inclusion of blanks and standard solutions in measurement series, and so on. The participation in inter-laboratory studies is encouraged. The laboratory should audit the quality system periodically. Management should review the system annually.

The criteria delineated in GLP and ISO 25/EN 45001 resemble each other in several topics, e.g. personnel, facilities, the use of standard operating procedures and the management of equipment and chemicals. ISO 25 and EN 45001 elaborate considerably more than GLP as regards the technical contents.

GLP and ISO 25/EN 45001 differ in approach. The purpose of the OECD principles of Good Laboratory Practice is described as to promote the development of quality test data. GLP does not make reference to a quality system as delineated in ISO 8402 [31]. Instead, a quality assurance programme is introduced, defined as an internal control system designed to ascertain that the study is in compliance with the GLP principles. ISO 25 and EN 45001 provide criteria for the establishment of a quality system. The top management has to set out a quality policy in which it expresses the objectives, expectations and commitments. Resources have to be made free to develop and implement a quality system. The latter task is allocated to the quality manager. The quality manager has an on-going task ensuring that the quality system and the methodology meet the specifications and verifying a proper functioning of the laboratory. ISO 25 and EN 45001 entail much more pro-active quality management in laboratories.

4 A Measurement Infrastructure for Sustainable Quality of Environmental Analyses

Environmental management is carried out by a variety of international, national and local authorities and industries. As a consequence, a large number of different laboratories provide data. Environmental management can only be effective when a measurement infrastructure is created in which the laboratories operate. The development of such an infrastructure is a shared responsibility of authorities and laboratories. The infrastructure entails accreditation, standard methods, reference materials and laboratory performance studies, and supports the laboratories with respect to the development and operation of their quality systems. The elements of the infrastructure will be described subsequently.

4.1 Accreditation

ISO 25 and EN 45001 represent international standards for the design and operation of a quality system in calibration and testing laboratories. Laboratories which have implemented such a system can opt for accreditation for several reasons:

- Accreditation may be mandatory in legislation;
- Laboratories may have to be able to provide a guarantee of quality to third parties, e.g. in the case of legal arbitrations;
- Accreditation enhances the competitiveness of laboratories as it provides customers confidence in their results;
- Accreditation may be necessary in view of product liability.

Through accreditation a laboratory receives recognition that its quality system conforms to an (internationally) accepted levels. Customers of laboratories may demand accreditation for this reason. Accreditation is a tool to induce quality among a group of laboratories. This tool is most effective when there is agreement between (representatives of) customers and the laboratories about the quality objective (methodology, performance characteristics).

In Europe, accreditation bodies cooperate in the Western European Laboratory Accreditation Cooperation (WELAC). WELAC has the objective to harmonize Western European accreditation practices and to establish a scheme of mutual agreements, so that an accreditation granted by an affiliated body is recognized by all other bodies which have entered the agreement scheme. Worldwide, harmonization of accreditation practices is pursued by the International Laboratory Accreditation Conference (ILAC). Mutual agreement schemes turn accreditation into a powerful tool facilitating for instance (inter)national trade and environmental policy and management, as it prevents long, sometimes improper discussions about analytical data.

Three phases can be distinguished in the accreditation process. The first phase involves registration of the laboratory. The laboratory obtains an information and registration package at the accreditation body. Registration is accomplished by completing forms which request data on the type of laboratory and the tests being conducted and by sending this material to the accreditation body along with a copy of the quality manual. This material is assessed. If the quality manual is considered sufficient, the second phase begins. A team leader for the accreditation audit is appointed. A representative of the accreditation body and the team leader will pay a first visit to the laboratory. The accreditation procedure will be discussed and a preliminary assessment will be made. On the basis of this visit the assessment team will be completed. The team will consist of an expert in quality management and of technical experts in the fields of testing for which accreditation is sought. The third phase consists of the actual audit. It is established whether the quality system is truly operational. The administration of the laboratory, all procedures and the methodology are scrutinized. Particular attention is paid to the validation of methodology and to internal quality control measures. It is verified that the stated performance characteristics are met. After accreditation has been granted, surveillance

visits are conducted yearly. A full reassessment takes place after every fourth year [10].

4.2 Standard Methods

The value of standard methods is generally acknowledged. Standard methods issued by authoritative national or international organizations are the product of a time consuming process in which the methodology is carefully developed and tested by a number of experienced laboratories. Increasingly, method-performance studies are incorporated in this process to validate methodology. As a consequence, (most) standard methods represent well characterized, validated procedures, the use of which may save a laboratory considerable development time.

Different opinions exist about the role which standard methods should play in society. In some cases it is argued or it is even inevitable, that specific standard methods should be prescribed. Such situations occur in, for instance, international trade and lawsuits. The development of standard methods lags considerably behind developments in instrumentation and analytical methodology. Prescription of standard methods which detail methods in full may hamper the implementation of more accurate and/or precise methods and of more efficient methodology. In addition, prescription of a standard method may improve comparability between laboratories to some extent, but will in general not give rise to the improvement pursued without the additional measures included in the measurement infrastructure outlined earlier.

National environmental management in the Netherlands tends to prescribe standard methods for parameters which are empirically defined (the value of which is thus method dependent), and to define performance characteristics which have to be met in other cases. For the latter parameters, standard methods are indicated (when available) as examples of methodology which meet the specifications [32].

4.3 Reference Materials

Key issues in the validation of methodology are the assessment of accuracy and statistical control. Reference materials are indispensable for these purposes. A certified reference material (CRM) is defined as a reference material one of more of whose property values are certified by a technically valid procedure, accompanied by, or traceable to, a certificate or other documentation which is issued by a certifying body [33]. By measuring CRMs, a laboratory obtains direct feedback with respect to the performance of its methodology. A laboratory has to investigate its procedures if a significant difference between its results and the certified value is observed.

In the ideal case, a number of CRMs with a perfect matrix match spanning the concentration range of interest would be available. In reality, the choice is usually restricted to a limited amount of CRMs. The analyst has to consider the matrix

characteristics and concentration levels and find a reasonable compromise. CRMs fulfil an major role in environmental analysis. The expertise of experienced, highly qualified laboratories is used to establish the certified concentrations. All laboratories which measure these samples compare their results with this expert judgement. Through CRMs, accuracy is transferred among laboratories, contributing in this manner to measurement compatibility [34].

Information on existing reference materials is assembled in the COMAR database [35]. Not all CRMs are validated to the same standard. The user of CRMs should consider the expertise of the producer and information on the preparation of the material, the results of homogeneity and stability tests, the number of different methods used to certify the material, the concentration levels, the matrix characteristics and the uncertainties in the stated values [17]. CRMs enable the assessment of a major part of the analytical process and laboratories should make use of these materials wherever possible.

Laboratory reference materials (LRMs) constitute another important tool for laboratories. LRMs are primarily used to assess statistical control by measuring these materials periodically and monitoring the results with control charts. Certified reference materials can be used, but their application is not recommended owing to the restricted availability and the costs [14]. A laboratory can prepare a batch of reference material itself. The material should be sufficient for a prolonged period of analysis. It has to be verified that the homogeneity and stability are adequate. The preparation of a large batch of material which is stable and homogeneous is not a simple undertaking. Low quality materials may even have a negative effect on the quality of the output of a laboratory [36]. It can be a good policy to obtain these materials from expert organizations, or to produce these materials in cooperation with other experienced laboratories.

4.4 Laboratory Performance Studies [1]

Laboratories have to verify the effectiveness of their quality system. Three levels can be discerned for verification practices with respect to the operational measurement systems [37]. The first level entails the technicians and managers of laboratory sectors. The results of quality control samples (e.g., blanks, recoveries of internal standards or spikes, difference between duplicates, reference materials) should be examined critically. Action should be taken when the results are out of control. Control charts play an important role here.

The second level encompasses internal checks on laboratory performance. To this end, control samples can be provided to the laboratory by the quality manager. The nature of these samples should not *a priori* be disclosed to the laboratory staff.

Laboratory performance studies constitute the third level. These samples should not be given special care. The results of laboratory-performance studies provide independent, objective assessments.

Laboratory-performance studies may be realized in various ways. In a number of cases there is a fixed scheme according to which the laboratories are offered

samples for analysis. The tests are of a routine nature and constitute an integrated part of the quality control programme of a laboratory. These studies are commonly denoted as proficiency tests. Laboratory-performance studies may also be incidental exercises, e.g. in order to assess the comparability of laboratories.

Laboratory performance studies provide feedback on three levels []:

1. The individual laboratories obtain information on their performance. Each laboratory should evaluate the findings of the study and look into its methodology if its results exhibit unacceptable deviations.
2. Third parties as accreditation bodies or managers of monitoring programmes obtain information on the performance of individual laboratories. This information can lead to inquiries about poor performance or to more far-reaching measures.
3. The whole sector is informed on the state of the art with respect to analytical proficiency. Poor overall performance points to the need of harmonization of methodology, validation of harmonized methods via method-performance interlaboratory studies, and/or the preparation of (certified) reference materials. Poor overall performance may also point to inadequate design of for instance monitoring programmes owing to insufficient specification of analytical methodology.

The assessment of the performance of a laboratory on the basis of the results of a laboratory performance study is not as straightforward as it may seem [40]. Not all interlaboratory studies are carried out to the same standard. A laboratory must make its own evaluation as to whether the organization and realization of the interlaboratory study justifies the drawing of conclusions with respect to its performance. Factors which must be taken into consideration are:

- the number of participants and their experience with the methodology tested;
- the origin and representative nature (e.g. character) of testing samples;
- the number and types of methods which have been used in the interlaboratory study;
- the organization of the study (e.g. the statistical model, the number of replicas, the parameters to be measured, the manner of execution);
- the arguments used in the evaluation of the participants' position.

It is important that the organizer adopts a sound procedure to establish the assigned value (the estimate of the true value) [1].

The statistical handling of the results by the organizers of the interlaboratory studies must be viewed as an aid to self-evaluation. In relation with this, attention must be paid to the results of the individual parameters for each sample and to the results of all parameters in relation to the nature of the samples. Furthermore, the laboratories' own performance must be considered in the light of the results of the quality control measurements and the interlaboratory studies in which it has previously participated [38].

Laboratory-performance studies can play an important role in quality improvement programmes. In such programmes, the laboratories collectively approach a

particular analysis problem under the leadership of a project team. The analytical procedure is decomposed in a number of steps, e.g., calibration, sample work-up, and instrumental analysis. Each step is consecutively assessed. For instance, for organic contaminants, respectively a standard solution, a cleaned extract, a row extract and a real sample may be distributed. A method is not presented. A method is not presented. After each step a workshop is organized in which the participants and experts discuss the results. A step is repeated if the results are not satisfactorily. The EC-Community Bureau of Reference (BCR) has developed this method with great success [27,39,40].

5 Summary

In this paper, the need for quality management is indicated. It is emphasized that the quality of information, and not merely the quality of data, should be assured. This requires a holistic approach to quality, starting at the assessment of the information need and extending to the presentation of information.

Laboratories producing data which meet the necessary performance characteristics in a controlled manner are a prerequisite. These laboratories should manage their quality by designing and implementing a quality system. This system can be based on ISO 25 or EN 45001. Basic elements of these systems are discussed.

Environmental management uses data from a large number of laboratories. Laboratories and representatives of their customers (e.g. national authorities) should establish a measurement infrastructure for the dissemination of quality among laboratories. Such an infrastructure encompasses accreditation and the development or dissemination of information on standard methods, reference materials and laboratory-performance studies.

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6 Soil Protection in The Netherlands

J. J. Vegter

Technical soil protection committee, Postbus 30947, 2500 GX The Hague,
The Netherlands

1 Introduction

Environmental policies concerning air and water quality were well developed before soil protection became an important political issue. One of the reasons for this might have been that effects of poor air and water quality are clearly visible, whereas effects of soil pollution can remain unnoticed for quite a long time. Very often effects of a bad or even dangerous soil become apparent only during land reclamation or other major changes in land use.

Some awareness of accumulation of toxic substances and soil degradation has always been present in the Netherlands, but soil protection gained much impetus with the first attempts to give it a legal basis in 1971. However, real clean-up activities had to await major complaints of residents of recently urbanized areas that were built on former waste dumps, like in the town "Lekkerkerk" in 1980. This public concern set the stage for a large soil clean-up operation, which has its legal base in the Soil Clean-up (Interim) Act. The interim act was meant to give a legal basis for soil clean-up only. It will be incorporated in the more general Soil protection Act, which came into force in 1987. This way prevention of soil pollution and clean-up of polluted sites will have the same legal base, permitting an integrated soil protection policy.

The present paper will give a general view on the development of soil protection in the Netherlands. Special attention will be given to the development of soil standards and to their use in the assessment of heavy metal pollution in soils.

2 Outline of Soil Protection in The Netherlands

In order to formulate a soil protection policy (which in the Netherlands includes restoration of polluted soils) one needs legal instruments, objectives and a set of rules and regulations to manage human activities. These aspects will be reviewed in this section.

Table 1. Current state of General Administrative Orders based on the Soil Protection Act

In force now:

- Order concerning the application of animal manure
- Order concerning the application of other organic fertilizers
- Order concerning dumping of liquid waste materials
- Order concerning dumping of solid waste materials
- Order concerning storage of petrochemical products in underground tanks

In 1993:

- Order concerning the application of bulk waste materials in construction work
 - Order concerning obligatory investigation of soils at industrial sites
 - Order concerning artificial infiltration of surface water
-

2.1 Legal Instruments

At present there are two main laws dealing with environmental aspects of the soil, the Soil Protection Act and the Soil Clean-Up Interim Act. The latter will be incorporated in the Soil Protection Act in 1993. The Soil Protection Act is however by no means a fully fledged set of rules covering all aspects of land use. It is only a skeleton that is gradually filled in with general administrative orders (GAO's). At present only a few administrative orders are in force but there are more to come (see Table 1).

2.2 Objectives in Soil Protection

The guiding principle in the Dutch Soil Protection Act is the maintenance or the restoration of soil "multifunctionality". The principle implies that the way a parcel of land is used at present should not affect its utility, that is its fitness for all potential kinds of land use that may be possible given the natural constitution of the soil. Every soil can have various functions, for instance an agricultural function, an ecological function, a carrying function, a function as drinking water supply, etc. According to this principle the number of functions that a soil can have should not be reduced by human activities. Of course it should be realized that in some soils some of the functions might be absent due to natural causes. Serpentine soils might be unfit for agriculture and a soil in a marsh lacks a carrying function.

There are a number of reasons why the principle seems almost unavoidable in the Netherlands:

1. The soil in the Netherlands, which is one of the most densely populated countries of the world, is becoming scarce and by consequence a very valuable resource.
2. Soil, including groundwater, is used very intensively and in many different ways by man and plays an important role in terrestrial and aquatic ecosystems.

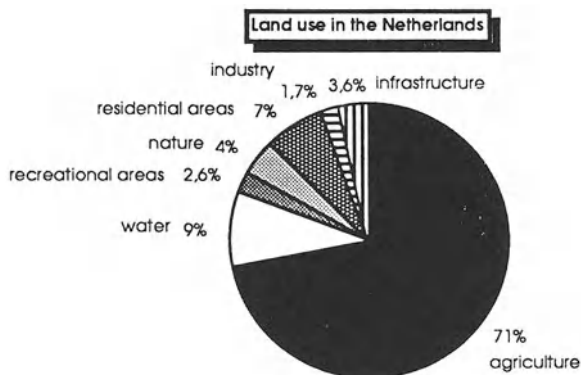


Fig. 1. Land use in the Netherlands

3. Groundwater is the main source of drinking water in the Netherlands. Surface water and rain are unfit due to air and water pollution. Because the groundwater table is very high, there is a high risk of pollution if activities on the soil surface are not restricted. Some of our sources for drinking water are under cities and even industrial areas, and most of our sources are in agricultural areas where large amounts of manure, fertilizers and pesticides are applied to the soil.
4. Land use is changing. Former gasworks, former waste dumps and mining areas have to be cleaned up because these areas are needed now for other purposes like housing. It is estimated that each year on the average 2% of the soil in the Netherlands undergoes a change in use. Major changes can be foreseen in the next century, when overproduction in agriculture and cattle farming will have dropped significantly. The present distribution of various types of land use in the Netherlands is illustrated in Fig. 1.
5. Soils and sediments are sinks for a large number of pollutants. A change in climate, geohydrological conditions or land use can turn this sink into a source. In recent studies published by IIASA these phenomena are referred to as chemical time bombs (Stigliani 1990). An appropriate soil protection policy should therefore anticipate long term change in the capacity of soils to store chemicals and not limit itself to short term effects of soil pollution and present use of an area.
6. Since the principle of "sustainable development" as set out in the report of the Brundtland Commission of 1987 is now widely accepted as fundamental to environmental policy, it can be argued that the number of functions of the soil should not be reduced for the next generations to come.

Of course other countries might make other political choices. Larger countries with a small number of inhabitants, deep and well protected groundwater and little industry are in a luxurious position as they can easily avoid the multifunctionality axiom and still afford some derelict land.

In the Netherlands the principle of multifunctionality is criticized sometimes for being too idealistic. Most of the time this criticism is caused by a misinterpretation of the term "multifunctional", including the so called "ecological function". Multifunctionality is not "back to paradise" or back to pristine conditions from prehistoric times. Nor is it a wish to have nature and industry at the same site. What is meant by "maintaining the multifunctionality of the soil" is "keep all options for future land use open". The word "function" in multifunctionality refers to a set of properties or attributes of the soil that is essential for a certain type of land use. For instance for agriculture the soil must have some water holding capacity and must be free from toxic substances that affect plant growth or make the crop unfit for consumption. Along the same lines an ecological function can be defined: The ecological function is present if the soil is fit as a living place for soil organisms and can function without restrictions in natural cycles. It is well realized that intensive land use sometimes precludes the presence of a natural soil flora and soil fauna, but as long as the site can be recolonized, multifunctionality remains untouched.

From a scientific point of view "multifunctionality" is a complex and abstract concept, that might be difficult to translate in general and quantitative chemical, physical and biological characteristics: as a multifunctional soil is a soil where all options are kept open, the concept does not pertain to the quality of the soil in general but to the quality of its recent history under influence of human activities. One might also state that each individual soil has its own specific multifunctionality. For instance the number of functions that a sandy soil can have is different from a marsh soil, the latter lacking a carrying function and be also different from a peaty soil, which is unfit for growing corn. Notwithstanding these limitations, by definition soils are considered multifunctional as long as the potential number of functions is left untouched by human activities. This in spite of the fact that they do not have the potential for all the conceivable number of functions. In brief: multifunctionality does not imply "omnifunctionality". Hence a complete, general description of a multifunctional soil in terms of quantitative chemical, physical and biological characteristics might be an almost impossible task. Fortunately the development of a soil protection policy does not fully depend on a complete description. This situation can be compared with medicine and human health. Advancement of medical science and human health care does not depend on a complete quantitative description of a healthy person in chemical, physical and biological terms.

2.3 Source Oriented Soil Protection

For the development of soil protection policy based on the multifunctionality principle it will be obvious that human activities that have irreversible effects on the structure and composition of the soil deserve special attention, especially if they endanger any future utilization of the soil by human beings, plants or animals.

Therefore much priority is given to activities that might lead to accumulation of persistent toxic substances in soil and groundwater.

Quite a large number of activities can be regulated without any quantitative description of a multifunctional soil. In the Dutch soil protection concept these are labeled local sources. Examples of local sources are waste dumps, industrial process plants, in general activities that do not depend on the input of chemicals in the soil system. Therefore a policy can be formulated without any reference to the actual quality of the soil. Local sources of soil pollution can be eliminated by an appropriate Isolate, Control and Monitoring (ICM) strategy.

In diffuse sources of soil pollution a simple isolate control and monitor strategy will not do. Atmospheric deposition and sedimentation processes in aquatic systems cannot be isolated, and agriculture would be impossible without application of fertilizers. To preserve the quality of the soil, the input of substances into the soil system must be balanced by its natural or agricultural output. Some quantitative soil quality criteria are needed here, because if the balance between input and output is reached at higher concentrations of a chemical in the soil, the multifunctionality of the soil might be endangered. These soil quality criteria consist of reference values for concentrations of the most important polluting substances, to be used in conjunction with source oriented measures. In regulations concerning the application of animal manure on the soil, the maximum dosage of for instance phosphate and nitrogen compounds on the soil has to be related to an acceptable concentration of these substances in soil and groundwater and the rate at which these substances leave the soil system through the harvesting of crops and the hydrological cycle.

Reference values for a good quality soil have been published in 1987 and have been revised in 1991. The derivation of these values will be discussed in Section 3.

With reference values, it is now -at least in theory- possible to compute the acceptable input of substances into the soil, if output rates are known. However in practice the relation between input, output and reference value has never been worked out in detail. The input from most sources is at present much larger than the output and many substances in the soil tend to accumulate. So the first aim in many regulations in soil protection will be to establish a balance between input and present output. In the GAO on animal manure for instance the target value for the dosage is set equal to the rate at which phosphates are taken up by crop plants. Due to technical and economic and by consequence political problems the excessive application of animal manure can only be brought down step by step, and the target will only be reached in the next century.

In a GOA regulating the application of sewage sludge and compost in agriculture, the tolerable input of heavy metals is set equal to average uptake by crop plants. Although some balance is achieved, no equilibrium relation between input, concentration in the soil and output has been used to compute tolerable input. Given the complexity of the soil and mineral uptake mechanisms by plants a general model that might do the job is still lacking. Instead a pragmatic approach is followed: The application of sewage sludge and compost is prohibited if reference values are exceeded.

Table 2. Extent of soil contamination in the Netherlands

Category	Number	Costs (DFL x mln)
Former gasworks	234	700
Landfills	3300	900
Car breakers yards	2100	500
Former industrial sites	80000	32500
Current industrial sites	25000	11000
Aquatic soil		1000
Other categories ^a	pm	pm
Total	110000	50000

^a groundwork, sewerage, underground tanks, diffuse deposition.

2.4 Clean-Up of Contaminated Land

The general trend in the Netherlands with respect to polluted sites is an increase and a diversification of the problem. In particular the problem of polluted sediments (aquatic soils) is larger than anticipated and difficult to tackle from the point of view of risk analyses and clean-up technology. Some studies published in 1990 estimated the number of locations to be cleaned up in the Netherlands (see Table 2).

When only a few sites have to be dealt with ad hoc approaches based on expert judgment and site by site negotiation and decision making will do. If the number of sites is larger, a programmatic approach is generally recommended.

There has been considerable discussion whether a programmatic approach should consist of predetermined standards or a more versatile site specific modeling and risk assessment methods. Of course simple testing of measured concentrations in soil and groundwater against predetermined standards is rather straightforward and by consequence less expensive than more elaborate risk assessment methods. However clean-up of contaminated sites is very expensive, especially for larger areas. Before deciding about the investment of large amounts of money in clean-up, it might be expedient to invest in more advanced site specific risk assessment. So a combined approach, using standards to streamline the preliminary stages of an investigation and using site specific exposure and risk assessment to achieve some fine-tuning in later stages of an investigation, may be the most appropriate. In fact the different approaches seem to converge to this combined approach as experience with clean-up of contaminated land increases (Siegrist 1990, WEF 1993). In the United States more emphasis is given to formalized site specific risk assessment methodologies, especially for sites on the national priority list (Superfund program), whereas in the Netherlands assessment of soil contamination started as a more standard based approach. In the new guideline for soil clean-up, that is incorporated in a more general soil protection guideline, more emphasis will be given to assessment of exposure to soil contamination.

2.5 Clean-Up Goals

In the Netherlands the possible solutions for a given soil problem are explored in a "clean up investigation" and related to the costs and other technical and environmental aspects (emissions by treatment plants for instance) of clean up technologies. The Dutch government states that total clean-up should be aimed at unless costs or technical problems make a total clean-up impossible in practice. When total clean-up is impossible, which has to be substantiated by the results of the clean-up investigation, a different type of solution is adopted, which aims at reducing exposure and further contamination of surrounding areas by appropriate isolation measures and control and monitoring strategies.

This dichotomy is an important issue in discussions about soil pollution today. If the total clean-up solution is chosen, there is no soil pollution left and by consequence there are no limitations to land use. If isolation is chosen, there are important restrictions to land use. Some people feel for instance that sites where soil pollution is controlled by isolation are unfit for building and advocate a closer link between the type of remedial action and the current use of the soil, especially in urbanized areas. Central to this problem is the perception of soil pollution problems: People advocating land use dependent clean-up goals do not consider soil pollution itself as the main problem but the restrictions on present land use that result from it.

The two different objectives in soil clean-up - either a full restoration of soil multifunctionality or isolation of soil pollution if technical or financial problems make a full restoration of multifunctionality impossible in practice- have their parallel in source oriented soil protection. If the effects of soil clean-up are neutralized by isolation the case of soil pollution is treated as a local source. If restoration of soil quality is aimed at, which is of course the preferential solution, the same target values for soil quality that are used in the diffuse pollution approach are used as clean-up targets.

The coupling between preventive goals and targets in soil clean-up is very attractive from a policy point of view, but there are some practical difficulties. In the beginning total clean-up and restoration of soil multifunctionality could only be achieved by excavation of the polluted soil and dumping it elsewhere, often on rather primitive dumping sites for household waste. This is of course not a very desirable situation. Therefore the development of clean-up technologies was intensively stimulated by the government. This started in 1982 with thermal and extraction methods and included the development of in situ microbiological techniques by 1984. More fundamental research on cleaning technologies started in 1986 in an integrated soil research program.

Even with modern technologies, it is still not possible to clean every soil up to target levels (A-values), but good results can be obtained by using the best technology for the type of soil pollution at hand. Such an optimal match between problem and technological solution could not be achieved by individual soil cleaning enterprises. They experienced a number of logistical problems because supply of polluted soils that can be cleaned with a given technology, and the de-

mand for clean soil as a product were difficult to match. To solve these problems a Service Center Soil-Purification was founded in 1988, to smooth the irregularities in supply and demand experienced by the soil cleaners and to optimize the match between technology and type of soil pollution.

In view of the technical and financial problems of cleaning soils up to A-values, it has been argued that the well known question "how clean is clean?" should be changed to: "how clean is clean enough?" In other words can we relate soil quality to land use and is it possible to design specific soil standards for a number of common forms of land use, such as residential areas with or without gardens, agricultural land, industrial land and nature areas. The answer depends to some extent on the function of standards in clean-up policy. Soil standards can have two functions. Standards can be used in standard based risk assessment and as clean-up goals.

Standard Based Risk Assessment: In risk assessment a comparison of measured concentrations of soil contaminants with soil quality standards is often used as a first step, to see whether assessment of actual exposure (involving more complex investigations of indoor air for instance) is needed. The soil standard is only used as a trigger value, because in most of the cases a prediction of actual exposure based on concentrations of chemicals in the soil is very unreliable. If standards are used as trigger values for further investigations, there is no objection to land use related standards as long as the limitations of these standards are well understood.

Standards as Clean-Up Goals: If soils are either completely cleaned or isolated the soil pollution problem is solved. Partial clean-up in relation to land use is of course possible in theory, it is mainly a political choice. However land use dependent soil standards will not be very helpful in this approach. Predetermined soil standards are bad predictors of the risks of the remaining pollution, especially after a change in land use. Moreover partial clean-up might have changed the geohydrological situation and other important soil characteristics governing the behavior and the availability of contaminants. So from a scientific point of view land use dependent clean-up targets are not advisable, unless there is a very large difference in exposure to soil pollution between various types of land use. For instance for heavy metal pollution a distinction can be made between agricultural land and areas where growing vegetables is impossible or prohibited. Another possibility might be to combine partial clean-up with a monitoring program to control whether exposure to the remaining soil pollution is acceptable from a toxicological point of view. In view of public concern about soil pollution, it might be very difficult to put the latter idea into practice.

3 Recent Developments in Soil Standards for the Assessment of Soil Pollution

3.1 Introduction

The well-known Dutch ABC list is often considered to be the starting point in the development of soil standards. However, the rather primitive ABC trigger value system was not designed to meet the requirements of an integrated soil protection and restoration policy. Therefore generic soil quality standards had to be developed. The A-values from the soil clean-up guideline were the first to undergo major changes. In 1986 a discussion paper was published by the Dutch government proposing so-called reference values for a good quality soil. These values, which replaced the A-values, were still based on background levels for metals and on rather limited toxicological information for other substances. Recently these values have been evaluated in the light of ecotoxicological data and extrapolation methods for standard setting outlined by the Dutch government (Denneman & Robberse, 1990). Because all standards had to fit in the terminological framework for environmental standards, the A-values or reference values should be labeled target values (see Table 3).

According to the new terminology the C-values, which indicate a level of soil pollution where clean-up might be needed, are named "intervention values". This is not merely a change in terminology however. The soil clean-up guideline (now called Soil Protection Guideline because it will deal with soil protection measures as well), including the new C-values, will be rewritten this year. C-values will be more explicitly based on toxicological and ecotoxicological knowledge than their forerunners. Other improvements include a better linking between spatial scale of soil sampling and the C-values, and a clearer distinction between the necessity to clean-up a site and the urgency of the clean-up. If contamination is not mobile and there is no exposure, clean-up might still be necessary but there is a low priority for doing so.

The analysis of soil protection and clean-up policies presented in the previous section showed that two different types of generic soil quality standards are needed. First standards for a good quality soil are needed for the formulation of the source oriented balance approach for diffuse sources of soil pollution. The same standards can be used as target values (A-values) for clean soil in soil clean-up. Second, standards for a "bad" soil might be needed, to indicate the necessity for clean-up. The need for the second type of standards can be questioned, at least in theory. If we were able to give a perfect and unambiguous description of a good

Table 3. Standards and risk levels

Type of standard	Risk level in soil policy	Existing standard
Intervention value	Serious threat	C-value
Limit value	Maximum permissible level	
Target value	Negligible level	Reference value

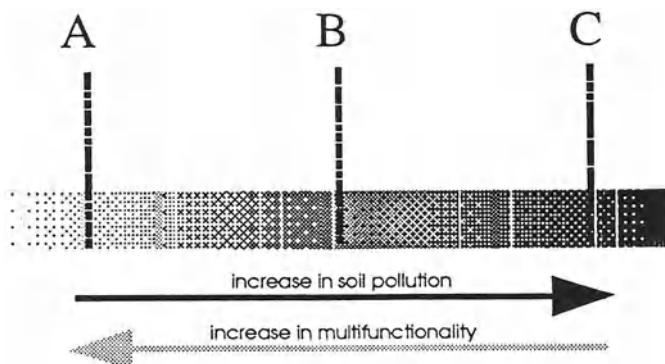


Fig. 2. ABC values as related to soil pollution and soil multifunctionality

quality soil, the boundary between a good quality soil and a polluted or non-multifunctional soil could be defined very sharply.

Advocates of an idealistic environmental policy would perhaps like to state that clean-up should begin where multifunctionality ends and that therefore only A- or target values are needed. There are however many uncertainties in the description of a multifunctional soil, because knowledge about speciation, bioavailability, exposure and adverse effects of many substances is lacking. Moreover, as was stated in Section 2.2, every soil has to some extent its own multifunctionality, so general soil quality criteria can only serve as an approximation. By consequence the boundary between a good or a bad soil will never be very sharp, there will always be a large "gray zone" between them. This situation is depicted in Fig. 2.

At concentrations of chemical substances below A (target value) any use of the soil is considered to be possible. In the zone between A and C, it is uncertain whether the soil is still multifunctional, but on the other hand it is also uncertain whether soil quality is so badly affected that clean-up has to be considered. Above C clean-up might be necessary. The B value divides the zone of uncertainty into two parts. Above B further investigations of soil contamination are considered necessary.

In Fig. 2 the A- and C-values are treated as true soil standards, in line with the use of these values in practice. Because the ABC list in the original soil clean-up guideline was never intended to be used as a set of soil standards (only as trigger values for investigations) the A- and the C-values had to be revised. The B-values still have their original function as a tool for decision making. To avoid confusion with the new meaning of A- and C-values, the B-values will disappear and will be replaced by a new trigger value for decision making.

3.2 From A-Values to Reference Values

The development of soil standards for a good quality soil or in other words the evolution from A-values to target values is characterized by an iterative procedure.

The procedure starts with provisional values and allows for subsequent refinements. The interplay between science and policy makers is very important in this.

First it was realized that the original A-values, a set of values to be used to trigger investigations and remedial action on contaminated sites, could not be used as universal soil quality criteria. The relation between these values and soil multifunctionality was rather ambiguous, they were the same for all soil types and not based on toxicological and ecotoxicological evidence.

In order to derive better values the following working definition of a multifunctional soil has been used:

A good (multifunctional) quality soil:

- Poses no harm to any use by human beings, plants and animals.
- Can function without restriction in natural cycles.
- Does not contaminate other parts of the environment.

This definition set the stage for scientific discussions about chemical, physical and biological soil quality criteria. In view of the importance of soil pollution in the Netherlands, much priority is given to the development of chemical criteria. A complete (eco)toxicological analysis of the effects of the substances involved on man, plants, animals and ecosystems was considered not feasible in view of the lack of knowledge in this field and the urgency by which soil quality criteria were required. Instead, a choice was made to start with provisional values first and to incorporate (eco)toxicological aspects later on.

These provisional values were mainly based on the third element of the definition, by examining soil quality requirements resulting from other areas of policy such as the standards for drinking water, the standards for surface water, the (draft) standards for food and the Dutch government's objectives with respect to nitrates and phosphates. Some of these requirements are based on toxicological principles. One of the more important implications of this line of reasoning is that in a good quality soil, groundwater should meet the requirements for drinking water and surface water. If the lowest value in this set of requirements is used as a reference value (A-value, target value) for groundwater, reference values for the solid phase of the soil might be computed with an appropriate equilibrium partitioning model. The model that has been used in the derivation of reference values is quite simple: the concentration of an organic substance in the solid phase of the soil is considered to be linearly dependent on the concentration in the soil solution, the concentration of organic matter in the solid phase of the soil and the octanol-water partitioning coefficient of the substance in question.

For heavy metals another approach had to be adopted. Because equilibrium models for heavy metals must account for quite a large number of factors that control adsorption and desorption of soils, no general reference values for the solid phase of the soil could be derived from surface water or drinking water criteria. Since a reliable relation between uptake of heavy metals in vegetable crops and the concentration of heavy metals in the soil is also lacking the derivation of soil quality criteria using the standards for food was not possible either. Therefore empirical relationships between concentrations of heavy metals and the percentage clay

and organic matter observed in soil samples from unpolluted agricultural soils and nature reserves have been used to derive reference values. A provisional list of reference values was defined accordingly.

The provisional list was discussed and criticized by experts in a discussion that was organized by the Technical Soil Protection Committee (TCB), an advisory board for the Minister of Housing, Physical Planning and Environment. The discussion resulted in a number of modifications to the provisional list. A new list was published in 1987 and could be considered to reflect the state of the art at that time, as far as adverse effects of pollution in the soil were concerned. Reference values can be differentiated with respect to soil type by using simple formulae that relate the reference value to organic matter content and the clay content of the soil. As a reference, values are also given for a so-called "standard soil" (average soil) with 10% organic matter and 25% clay.

3.3 List of Soil Quality Reference Values (1987)

The list consists of two tables, the first for inorganic compounds (Table 4), the second for organic compounds (Table 5). They should be used only with reference to the commentary given below.

Inorganic Compounds: Reference values for heavy metals, arsenic and fluorine can be calculated for all soil types with the formula presented for each substance. In these formulas, the reference value is a function of the clay fraction and/or organic matter content. The clay fraction is defined as the percentage of mineral elements smaller than 2 μm in the dry weight of the mineral fraction of the soil. As an example, the reference values have been presented for a standard soil with 25 percent clay and 10 percent organic matter. Except for phosphate and ammonium compounds, the reference values for groundwater in the saturated zone are independent of the soil type.

Organic Compounds: The values presented in the table for organic compounds belonging to the black list as published in the Environmental Program of The Netherlands 1986-1990 apply to a standard soil with inorganic matter of 10% ($H=10$). In evaluating the quality of a soil, the values presented should be divided by 10 and multiplied by the organic matter content of the soil. In soils with $H>30$ and $H<2$ the equilibrium partitioning model underlying the reference values is less reliable. For these soils H values of respectively 30 and 2 are used.

It is expected that the detection limits for many black list substances in soil are not exceeded when groundwater concentrations equal the norms in the 1984 Decree on Water Supply, the surface water quality objectives for preparing drinking water, or values based on effect and risk considerations (WHO drinking water guidelines, EPA water quality criteria). Therefore, separate values for these substances have not been included in the table. When the prevailing detection limit for organic compounds is exceeded, it may be seen as a signal for groundwater pollution (saturated zone). Of course, this is also true with respect to organic black list

Table 4. Reference values for inorganic compounds (see commentary for use of the table)

	Soil	Groundwater	
	Soil reference value Formula	Standard soil reference value (H=10/L=25)	
Chromium	(Cr)=50+2L	100	1 µg/l
Nickel	(Ni)=10+L	35	15 µg/l
Copper	(Cu)15+0.6(L+H)	36	15 µg/l
Zinc	(Zn)=50+1.5(2L+H)	140	150 µg/l
Cadmium	(Cd)=0.4+0.007(L+3H)	0.8	1.5 µg/l
Mercury	(Hg)=0.2+0.0017(2L+H)	0.3	0.05 µg/l
Lead	(Pb)=50+L+H	85	15 µg/l
Arsenic	(As)=15+0.4(L+H)	29	10 µg/l
Fluorine	(F)=175+13L	500	-
Nitrate ^a		-	5.6 mgN/l
Sulfate ^b		-	150 mg/l
Bromides		-	300 µg/l
Chlorides ^b		-	100 mg/l
Fluorides ^b		-	0.5 mg/l
Ammonium compounds ^b		-	2/10 mgN/l ^c
Phosphate (total) ^a		-	0.4/3 mgP/l ^c

() Concentrations in mg/kg on a dry matter basis.

H = weight percentage of organic matter on a dry matter basis in the soil.

L = weight percentage (dry matter) of the clay fraction in the (mineral) soil.

^a lower values can be required for protection of nutrient poor regions.

^b higher values appear naturally in regions with a strong marine influence (salty groundwater).

^c the lower values apply to groundwater in sandy regions; the higher values apply to groundwater in regions with clay and peat soils.

compounds which have not been presented for the solid phase for the reasons mentioned above.

Use of the Tables: In general, when concentrations are less than or equal to the values presented in the tables, the soil can be considered multifunctional according to current insights, which means that the substance involved is not expected to cause effects which can be considered detrimental. A technical manual is in preparation which should be used in evaluations of soil quality. Concentrations in excess of the reference values do not necessarily mean that the soil is no longer multifunctional. Locally higher contents may be of natural origin. If there is reason to evaluate the soil's multifunctionality further, more information is needed about these local circumstances and about the prevailing environmental factors which may influence possible human, animal or plant exposure routes. Where reference values are exceeded as a consequence of human soil use, it is also important to

3.4 From Reference Values to Target Values

Recently the reference values for a good quality soil have been evaluated in the light of recent ecotoxicological data and extrapolation methods for standard setting outlined by the Dutch government. As was stated earlier they are now labeled target values in order to fit in the general terminological framework for standards (see Table 3).

Before results of toxicity tests on soil organisms could be used in standard setting, some procedure must be agreed upon how to derive standards from this type of data. After some discussions the method of Van Straalen and Denneman (1989) is adopted as a general procedure. The method is based on the average value of No Observed Effect Concentrations (NOEC) for species of soil organisms and their variability. The standard that is derived with this method is lower if average sensitivity of species is higher and variability in sensitivity is large. The latter point seems reasonable: the more variable the data the less certain we are about effects on soil organisms. Hence a lower value must be proposed in order to protect the majority of species. The method proposed by Van Straalen and Denneman combines the average value and the variability of NOEC's in an elegant statistical approach. Usually NOEC's tend to show a symmetrical or normal frequency distribution on a logarithmic scale. This distribution can be described mathematically with two parameters, the mean and the standard deviation. If the value of these parameters can be estimated from laboratory data and it is assumed that these estimates are unbiased (that is: laboratory data on different species can be considered as a random sample from all species) the frequency distribution of NOEC's can be estimated.

Van Straalen and Denneman give the following formula for the fraction of species q that is exposed to a hazardous concentration when the environmental concentration equals C .

$$q = \frac{1}{1 + \exp \left\{ \frac{\pi^2 (X_m - \ln C)^2}{3 \times s_m^2 \times d_m} \right\}}$$

X_m : mean of log-transformed NOEC's for m species

s_m : standard deviation of log-transformed NOEC's for m species

d_m : correction factor for errors in estimation procedure

It is agreed that the 5% percentile value of the frequency distribution of the logarithm of NOEC values can be used as an indicator of an acceptable ecotoxicological risk. This means that the effects of a concentration of substance in the soil are still acceptable if in theory only 5% of the species experience an exceeding of their NOEC ($q_{0.05}$, see formula). Target values however correspond to a negligible risk level (Table 3). According to the principles of the risk assessment strategy of the Dutch government, outlined in "Premises for risk management" (VROM

Table 6. Target values for soil and water. Values for water in µg/l, for standard soil (10% organic matter and 25% clay). in µg/kg dry matter, unless otherwise stated. (VROM 1991)

	Soil	Ground water
<i>Metals</i>		
Cadmium	0.8 mg/kg	0.4
Mercury	0.3 mg/kg	0.05
Copper	36 mg/kg	15
Nickel	35 mg/kg	15
Lead	85 mg/kg	15
Zinc	140 mg/kg	65
Chromium	100 mg/kg	1
Arsenic	29 mg/kg	10
<i>PAH</i>		
Naphthalene	15	0.1
Anthracene	50	0.02
Phenanthrene	45	0.02
Fluoranthene	15	0.005
Benzo[a]anthracene	20	0.002
Chrysene	20	0.002
Benzo[k]fluoranthene	25	0.001
Benzo[a]pyrene	25	0.001
Benzo[ghi]perylene	20	0.0002
Indeno[123cd]pyrene	25	0.0004
<i>Chlorophenols</i>		
Monochlorophenols	2.5	0.25
Dichlorophenols	3	0.08
Trichlorophenols	1	0.025
Tetrachlorophenols	1	0.01
Pentachlorophenol	2	0.02
<i>Pesticides</i>		
Dieldrin	0.5	0.02 ng/l
γ-HCH (lindane)	0.05	0.2 ng/l
Azinphos-methyl	0.06	0.7 ng/l
Parathion-ethyl	0.04	0.05 ng/l
Diazinon	0.07	0.9 ng/l
Malathion	0.02	0.04 ng/l
TBTO	0.1	0.1 ng/l
Atrazine	0.05	7.5 ng/l

1989), the negligible risk level is obtained by dividing the 5% percentile value of the distribution by 100.

After many rather technical discussions about the statistical basis of this method and the type of frequency distribution to be used, the method resulted in a number of modifications in the list of reference values. The revised values (target values) given in Table 6 were published in a memorandum entitled "Environmental Quality standards for soil and water" (VROM 1991). Changes were only implemented for organic substances. The results of the procedure outlined by Van Straalen and Denneman for metals yielded values lower than natural background concentra-

tions, which is not workable from a policy point of view. Therefore the reference values for metals were implemented as target values, except for zinc and cadmium in groundwater. The new values for zinc and cadmium in groundwater are based on new data about normal concentrations in unpolluted groundwater.

3.5 New C-Values

After ten years of experience with soil cleanup, some revision of the Dutch soil cleanup guideline for investigation and restoration of polluted sites was considered necessary. The new guideline, especially the new C-values, will be more explicitly based on exposure routes and toxicological criteria. Also the spatial scale for the estimation of average concentrations of polluting substances in soil and groundwater is specified (van den Berg and Roels 1991, TCB 1992). Because the spatial scale of soil sampling schemes can be related to the spatial scales most relevant for exposure, a more consistent approach is achieved. Standardized sampling procedures to be used in the various stages of investigations are under development.

Another important aspect of the new guideline is the distinction between the necessity for soil clean-up and its urgency. Clean-up is considered necessary if the sum of the contributions of all exposure routes that are possible on a given site exceed a toxicological or ecotoxicological limit value. The C-values are developed to describe this situation. Therefore soil clean-up is considered necessary in the Netherlands if C-values are exceeded. The urgency for cleanup however is dependent upon the actual exposure, which of course is less than potential exposure in the case of only a few exposure routes being present.

There has been some discussion regarding the most appropriate method for assessing the risks associated with contaminated land. In particular the use of predetermined standards versus site by site modeling and risk evaluation procedures. The difference between these approaches is however much less if it is recognized that soil standards can be derived by a reverse risk assessment process. In risk assessment the daily intake of some substance is estimated by summing the contributions of different exposure routes. So, intake can be computed from concentrations of substances in the soil with appropriate exposure models, and compared with some toxicological threshold value, like Acceptable Daily Intake (ADI as defined by World Health Organization for contaminants in food) or a more general TDI-value (tolerable daily intake), (see Fig. 3). By reversing this computation one can derive a critical concentration (C-value) for soil from toxicological TDI criteria.

Based on a large survey of the toxicological literature, TDI's were proposed for a large number of soil pollutants, using methods comparable to the derivation of ADI's by WHO. For genotoxic carcinogens the conventional risk level of 10^{-4} death per lifetime (10^{-6} /year) has been used as toxicological limit value. The next step was the development of exposure models. Various models for individual exposure routes were combined to yield what is now called the CSOIL/HESP model. The model is a joint venture of RIVM, one of the major governmental research

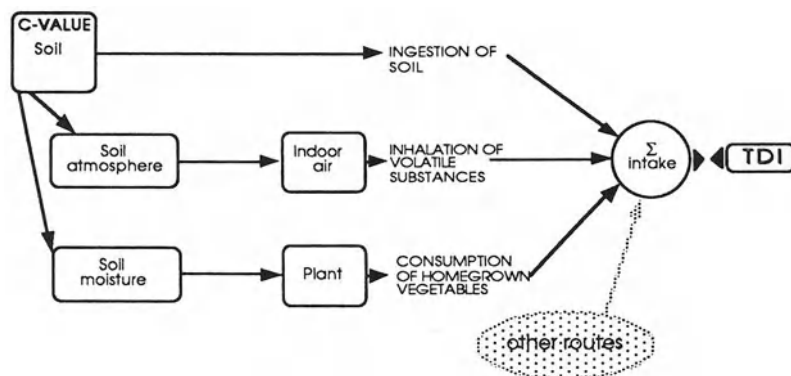


Fig. 3. Major routes of human exposure on contaminated land

organizations in the Netherlands and two major industries, Shell and DSM. A PC-version is now commercially available¹. The model merely consist of a large set of formulae and parameters and does not use any advanced mathematical operations. A description of the model is given in van den Berg (1991) and in van den Berg and Roels (1991). Some comments on numerical details of the model have been given by the Technical soil protection committee (TCB 1992). It is in fact quite easy to build the model by entering the formulae and the appropriate data in a spreadsheet program.

By using a standardized set of exposure routes C-values could be computed by using TDI values as input in the model, which means that a concentration of a substance equal to C will lead to a daily intake equal to the TDI. Although a larger number of exposure routes were used in the model, only the three routes mentioned in Fig. 3 appeared to be really important (>90% of total exposure). Other routes that were considered :

- Inhalation of soil and dust
- Contact with skin
- Consumption of meat and fish
- Drinking water
- Bathing and showering

It should also be noted that an estimated daily intake larger than TDI is considered to be an indication that clean-up is needed. This is of course a political choice and not a result of the model. The results of the approach are presently discussed in the Netherlands and a final decision on the new C-values by the Dutch government will be made in 1993. It is beyond the scope of this paper to deal with the discussion in depth. The description the development of the new C-values for metals given below might further illustrate some of the issues.

¹ The pc version can be obtained at SIMP/HSEO (ms S. van Kooten) Postbus 162; 2501AN; Den Haag; The Netherlands.

Table 7. TDI, Safety factor used in the derivation of TDI and normal daily intake of metals in the Netherlands (Vermeire et al, 1991)

	TDI µg/kg(body-weight) per day	Safety factor used in TDI	Daily intake µg/kg (body-weight) per day
arsenic	2.1	1	0.7(max.)
barium	20*B	10	9(max.)
cadmium	1	1	0.28(avg.)
chromium(III)	5	500	2.9(max.)
chromium (VI)	0.0007	-	0,0004(max.)
cobalt	1.4	100	0.7(max.)
copper	140	50	140(max.)
mercury	0.61	10	0.14(avg.)
lead	3.6	1	1.2(avg.)
molybdenum	10	100	4(max.)
nickel	50	100	4(avg.)
zinc	1000	3	300(max.)

B = [total Ba]/[soluble Ba].

(max.)= maximal daily intake in the Netherlands.

(avg.)= average daily intake in the Netherlands.

3.6 C-Values for Metals

The toxicological criteria underlying the new C-values for metals are given in Table 7. These values were used as input in the C-SOIL exposure model described by van den Berg (1991) and van den Berg and Roels (1991).

For metals exposure due to consumption of home-grown vegetables turned out to be very important. In the CSOIL model uptake of heavy metals from the soil in plants is estimated on the basis of empirical relations between BCF (bio-concentration-factor) and Kd (soil-water partitioning coefficient) published by Baes (1984) or by BCF values published by Sauerbeck (1988). Concentrations of heavy metals in plants due to atmospheric deposition of polluted soil particles is estimated with the method of Hetrick and McDowell-Bayer accumulation of metals in plants and will never obviate the need for measuring the actual concentrations of metals in food plants in risk assessment. The percentage of vegetables in the diet of a person that contributes to exposure can vary from 0 to 100%. In the model the contribution from home-grown vegetables in the diet was set at 10%. If this percentage is allowed to vary it has a dramatic effect on the "C-value", as can be seen in Table 8. If exposure from the consumption of vegetables grown at the polluted site does not occur, exposure is mainly due to ingestion of soil (150 mg/day for children and 50 mg/day for adults). So the column CO% gives the concentration of metal in the soil that would result in exceeding the TDI due to soil ingestion (since other exposure routes are unimportant for metals). This table also

Table 8. Effect of % consumption of homegrown vegetables cultivated on polluted soils (100% = all vegetables are grown on the polluted site) on the "C-value" for a (Dutch) standard soil (10% organic matter and 25% clay). 'A' is the reference value for a good quality soil; 'LAC' is signal value for agricultural soils. At concentrations higher than this value, the quality standards for food might be exceeded in some crops.

	C0% mg/kg	C10% mg/kg	C50% mg/kg	C100% mg/kg	A mg/kg	LAC mg/kg
arsenic	1389	487	135	71	29	
barium	13230	1302	283	143	-	
cadmium	662	4	1	0.36	0.8	0.5-3
chromium(III)	3308	1160	323	170	100	
chromium(VI)	0.46	0.16	0.05	0.02		
cobalt	926	325	90	47	36	30-80
copper	92612	4799	1001	503	10	
mercury	404	142	39	21	0.3	
lead	2381	835	232	122	85	100-200
molybdenum	6615	36	7	4	5	
nickel	33076	1714	358	180	35	
zinc	661513	3600	723	362	140	100-350

shows that metal concentrations in agricultural soils must be close to reference values in order to yield toxicologically safe vegetables (C100%). Noting that the C-values for Cd are remarkably low, one is tempted to conclude that the model is not very realistic. However, in the southern part of the Netherlands, where cadmium contamination occurs in acidic sandy soil with low organic matter content, the first signs of excretion of low molecular weight proteins in urine due to the effect of Cd on the kidney have been observed in people with vegetable gardens at Cd concentrations as low as 2.5 mg/kg

Ecotoxicological Aspects: Human exposure is not the only motive for the restoration of contaminated sites. C-values have to indicate "a serious threat to the environment" as well. This started a discussion about the derivation of ecotoxicological C-values. Because target values are now in principle based on the 5% percentile of the frequency distribution of the logarithm of NOEC's it seemed expedient to use the same data and use some higher percentile as a C-value. Ecotoxicologists agreed that the average value of the logarithm of NOEC's of different species for a given substance would be appropriate as a C-value. So, from an ecological point of view clean-up might be needed if the concentration of a chemical substance in the soil is higher than the NOEC of 50% of the species. Apart from effects on soil animals and plants some NOEC values for effects of pollution on soil microbial processes were also available. The TCB proposed to compute the median of the NOEC's for processes (MED NOEC Processes) and to choose the lowest value of either species or processes as an ecotoxicological criterion (see Table 9).

Table 9. Ecotoxicological criteria used in the derivation of C-values for metals. Values are in mg/kg

	MED NOEC Species	MED NOEC Process
arsenic	37	530
barium		356
cadmium	12	115
chromium(III)	315	157
chromium(VI)		1040
cobalt	92	290
copper	170	238
mercury	6	53
lead	282	1046
molybdenum		480
nickel	71	220
zinc	1414	166

Integrated C-Values: So far the procedures described above resulted in two sets of C-values - ecotoxicological and toxicological- that have to be combined to yield a single C-value in order to fit in the framework of soil clean-up policy. The simplest way is to choose the lowest value. In view of the large differences in reliability of the results, the reliability of C-values should also be taken into account. The lowest value is not always the best value. Finally political arguments might also influence the choice of C-values.

C-values for groundwater are derived from C-values from soil. First the expected concentration of a pollutant in the soil solution is computed assuming that

Table 10. Standards for metals in groundwater and drinking water

Metal	C-value ^b	WHO	Dutch Drinking water	Target or A-value
arsenic	40	50	50	10
barium	600		500	50
cadmium	6	5	5	0.4
chromium(III)	15	50	50	1
chromium (VI)				
cobalt	90			20
copper	35	1000	100 ^a	15
mercury	0.3	1	1	0.05
lead	50	50	50	15
molybdenum	185			5
nickel	40		50	15
zinc	300	5000	100 ^a	65

^a After 16 h in metal pipe: 300 µg/l for Cu and 5000 µg/l for Zn.

^b Proposed by van den Berg & Roels (1991).

the soil solution is in equilibrium with the solid phase of the soil. However this equilibrium might not apply to groundwater. Compared to the water that occupies the pore spaces in a polluted top soil, the groundwater is likely to have lower concentrations. Therefore C-values for groundwater have been set at 10% of the equilibrium value. The values proposed by van den Berg and Roels (1991) are given in Table 10. In addition drinking water standards and A-values are given as a reference.

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7 Mathematical Modeling for Assessment of Soil Pollution

J. G. C. Smits and N. M. de Rooij

Delft Hydraulics P.O. Box 177, 2600 MH Delft, The Netherlands

Abstract

Several mathematical models have been developed in the Netherlands for calculating the transport of pollutants into the environment of polluted sludge or soil. Applications of these models, CHARON in particular, have contributed to the setting of priorities for the cleaning up of polluted sites and to the assessment of alternatives for the storage of polluted sludge. CHARON is based on the principles of both equilibrium chemistry and process kinetics. The model applications in the Netherlands have focussed on the chemistry of heavy metals and organic micropollutants in chemically reduced systems. Adaptation of the input for the equilibrium chemistry may be necessary for application of the models to polluted sites with other (oxidized) soil systems in Central and Eastern Europe.

1 Introduction

The high level of industrial and agricultural activity in the Netherlands and its location downstream of important industrial regions in neighbouring countries have caused large scale pollution of the soil with heavy metals, organic chemicals and nutrients. The pollution problems concern the land as well as water bottom sediments. Consequently, the related environmental problems have been studied intensively, particularly in the past fifteen years. The assessment of the nature, extent and effects of the pollution requires, among other things, tools to quantify the transport of pollutants into the environment of polluted sites. These tools include chemical models as well as transport and hydrological models. The development of these models has reached the point where they can be used for the assessment of a broad variety of soil pollution cases.

This paper aims at presenting the possibilities and the significance of modeling for the management and control of soil pollution. An overview is given of management questions, which were raised in the Netherlands concerning soil and sediment pollution. A review of available models and some examples of applications follow a summary of important principles concerning the speciation, remobilization and fate of pollutants, heavy metals in particular. Finally, some conclusions are drawn

regarding the use of these models for soil pollution assessment in Central and Eastern Europe.

2 Soil Pollution Problems in The Netherlands

A distinction can be made between the pollution of landsoils and of water bottom sediments. The former is usually caused by one local source, whereas the latter typically results from numerous industrial and domestic discharges along a river. The bottom sediments of estuaries and lakes are therefore usually polluted with a wide variety of substances in relatively small concentrations, whereas soil on land may be polluted with only a few substances in relatively high concentrations.

The pollution of the bottom sediments with heavy metals and organic substances has reached dramatic proportions in the Netherlands, especially in the estuary of the rivers Rhine and Meuse, but also in many canals. The presence of toxic pollutants in the bottom sediments has adverse effects on aquatic organisms, resulting in overall degradation of aquatic ecosystems. Due to dredging for maintenance of waterways and clean-up of the water bottom, large quantities of polluted sludge have to be stored in depots on land or in deep pits under water. Solid wastes from water treatment plants, drinking water plants and waste incineration plants must also be stored in depositories. When no precautions are taken pollutants can seep from the stored sludge and waste into groundwater aquifers, which in some cases may lead to the pollution of drinking water sources. The horizontal flow in aquifers transports the pollutants to upwelling regions where they may resurface and accumulate, a process which may last thousands of years.

Many sites on land have been heavily polluted by chemical plants, factories and other industries. Especially those sites that are destined for town expansion must be cleaned up in order to protect public health and to prevent the dispersion of toxic substances into surface water and groundwater systems.

The governmental policy is to prevent as much as possible the dispersion of pollutants into surface water and groundwater in order to safeguard the natural resources for future generations, and to allow sustainable development of the Netherlands. However, considering the number of polluted sites, priorities have to be set regarding the order in which sites are to be cleaned up or isolated. Alternative options for sludge depots and the storage of polluted soil also have to be assessed.

3 Processes in Soil-Groundwater Systems

The remobilization and the transport of pollutants, heavy metals in particular, within soil-groundwater systems is subject to a large number of processes. A distinction can be made between slow processes and (near-) equilibrium processes. The slow degradation of organic matter in dredging sludge or soil and the slow flow of groundwater with a non-equilibrium composition are the driving forces in the diagenesis of soil-groundwater systems. These processes affect the chemistry of a system on the basis of the chemical composition of the soil particles. Macro-chemical parameters such as pH, alkalinity and calcium concentration on one hand and the presence of iron(III) hydroxydes and calcite on the other affect the processes that determine the partition of heavy metals among the fluid and solid phases. Relevant processes are adsorption, desorption, precipitation, dissolution, redox processes and complexation processes. Considering the long time scales involved, an equilibrium approach is allowed for these processes in many cases.

The concentration of heavy metals in groundwater in an oxidized environment is determined by a complex interaction of adsorption and complexation. Clay, hydroxides such as iron(III) hydroxides and organic matter contribute to the adsorption capacity of soil particles, usually expressed as cation exchange capacity. The adsorption of a heavy metal to soil is also affected by such parameters as pH and ionic strength, as well as the concentrations of cations (calcium, potassium, etc.) and complexing ligands (bicarbonate, chloride, sulfate, etc.) in the solution. In an oxidized environment, adsorption is the dominant process controlling the dissolved concentration of most heavy metals. Metal precipitates are usually not formed (except for chromium), and the dissolved metal concentration is therefore proportional to the concentration adsorbed to the solid matter.

The degradation of organic matter may result in a chemically reduced environment. Under reduced conditions, most heavy metals (Cd, Zn, Cu, Hg, Pb, Ni) precipitate as sulfide minerals under reduced conditions, chromium as hydroxide. The dominance of precipitation implies that the dissolved heavy metal concentration is limited by the solubility product of the mineral and the presence of complexing ligands (sulfide, chloride, etc.). The dissolved concentration is small, rather constant and independent of the concentration in the solid matter.

The dissolved concentration of arsenic, which is not a heavy metal but is usually studied together with heavy metals, is determined by adsorption mainly to iron(III) hydroxide and organic matter. Under reduced conditions, little iron(II) hydroxide may be present, as it is transformed into iron(II) sulfides and carbonates. This results in less adsorption of arsenic.

Under oxidized conditions, a pollution front of heavy metals in groundwater is retarded relative to the water flow due to adsorption. Under reduced conditions, little retardation may occur under reduced conditions as the dissolved metal concentration is in equilibrium with a precipitate. Dilution of the heavy metals in

groundwater may occur when polluted groundwater intrudes an aquifer, in which the water flow is relatively fast.

4 Available Models

A variety of mathematical models has been developed by Delft Hydraulics for calculating pollutant transport in soil-groundwater systems. At the core of these models is CHARON, which is composed of a chemical equilibrium module, a slow reaction kinetics module and a mass transport module (de Rooij 1991). The equilibrium module is based on mass conservation and the mass action law (Clasen 1965). CHARON needs as input the Gibbs free energies for all substances

Table 1. A chemical system definition for the water-carbon dioxide equilibrium

Constituent	Components		
	H+	OH-	H ₂ CO ₃
H+	1	0	0
OH-	0	1	0
H ₂ O	1	1	0
CO ₂	-1	-1	1
HCO ₃ ⁻	-1	0	1
CO ₃ ²⁻	-2	0	1

Table 2. The mathematical formulations for CHARON

1.	$\sum_j a_{ij} \cdot x_j = b_i$	a_{ij} : stoichiometric constr. x_j : moles of constit. j b_i : moles of component i
2.	$F = \sum_j x_j (c_j + \ln(xf_j))$	F: total G. free energy c_j : G.F.e. paramter of j xf_j : mole fraction of j
3.	$K = \frac{(A) \cdot (B)}{(C)}$	K: equilibrium constant
4.	$c = \Delta c = -\ln(K)$	c: G.f.e. parameter of C
5.	$\frac{dx_i}{dt} = k1 \cdot x_j + k0$	x_i : slow reactant i x_j : a constituent k1: f.o. rate constant k0: z.o. rate constant
6.	$\Delta M_i = \sum_j (QI \cdot C_{ij}) - \sum_k (QO \cdot C_{ik}) + \sum_l (D \cdot O \cdot \Delta C_i / L_i)$	ΔM_i : total net mass flow of const. i QI: flow rate in QO: flow rate out D: dispersion coeff. O: surface between two segments ΔC_i : concentr. difference between two segments L: distance between centers of two segments

present in the simulated equilibrium system. It builds up substances from components in such a way that the Gibbs energy of the system is minimized. The slow reaction module is mainly used to simulate the degradation of organic matter. The degradation leads to the production and consumption of components, and consequently to the changing of the chemical equilibrium. Adsorption is included as an equilibrium process by including the adsorbent and the adsorbed metal as substances with Gibbs free energies. Table 1 presents a simple example of how an equilibrium system is defined in CHARON. Table 2 summarizes CHARON's basic

Table 3. The definition of the chemistry for heavy metals in a groundwater-soil system

Constituent ^a	C parameter (reference)	Components and Stoichiometric Constants				
H ⁺	0.0	1 H ⁺				
OH ⁻	0.0	1 OH ⁻				
H ₂ O	-40.27 (8)	1 OH ⁺				
CO ₂	-6.26 (8)	1 H ₂ CO ₃	-1 H ⁺		-1 OH ⁻	
HCO ₃ ⁻	-27.78 (8)	1 H ₂ CO ₃	-1 H ⁺			
Ca ²⁺	0.0	1 Ca ²⁺				
CaHCO ³⁺	-34.72 (8)	1 Ca ²⁺	1 H ₂ CO ₃		-1 H ⁺	
CaCO ₃	-11.38 (8)	1 Ca ²⁺	1 H ₂ CO ₃		-2 H ⁺	
F ₃ ²⁺	0.0	1 Fe ²⁺				
FeHCO ³⁺	-35.43 (9)	1 Fe ²⁺	1 H ₂ CO ₃		-1 H ⁺	
FeCO ₃	-14.91 (9)	1 Fe ²⁺	1 H ₂ CO ₃		-2 H ⁺	
SO ₄ ²⁻	0.0	1 S ²⁻	-8 El		-4 H ⁺	4 OH ⁻
HS ⁻	286.33 (10)	1 S ²⁻	1 H ⁺			
H ₂ S	266.20 (10)	1 S ²⁻	2 H ⁺			
CaCO ₃ s	-26.00 (8)	1 Ca ²⁺	1 H ₂ CO ₃		-2 H ⁺	
FeCO ₃ s	-28.00 (25)	1 Fe ²⁺	1 H ₂ CO ₃		-2 H ⁺	
FeS s	280.00 (25)	1 Fe ²⁺	1 S ²⁻			
Cu ⁺	23.75 (11)	1 Cu ⁺				
CuHS	275.44 (10)	1 Cu ⁺	1 S ²⁻		1 H ⁺	
CuHS ²⁻	548.84 (10)	1 Cu ⁺	2 S ²⁻		2 H ⁺	
Cd ²⁺	0.0	1 Cd ²⁺				
CdHS ₂	531.01 (12)	1 Cd ²⁺	2 S ²⁻		2 H ⁺	
CdHSOH	233.17 (13)	1 Cd ²⁺	1 S ²⁻		1 H ⁺	1 OH ⁻
CdHCO ³⁺	36.65 (14)	1 Cd ²⁺	1 H ₂ CO ₃		-1 H ⁺	
CdCO ₃	-18.05 (14)	1 Cd ²⁺	1 H ₂ CO ₃		-2 H ⁺	
Zn ²⁺	0.0	1 Zn ²⁺				
ZnHS ₂	529.63 (12)	1 Zn ²⁺	2 S ²⁻		2 H ⁺	
ZnHSOH	239.15 (12)	1 Zn ²⁺	1 S ²⁻		1 H ⁺	1 OH ⁻
ZnHCO ³⁺	36.65 (14)	1 Zn ²⁺	1 H ₂ CO ₃		-1 H ⁺	
ZnCO ₃	-14.95 (14)	1 Zn ²⁺	1 H ₂ CO ₃		-2 H ⁺	
AsOH ₃	0.0	1 AsOH ₃				
CrOH ²⁺	-27.06 (15)	1 Cr ²⁺	1 OH ⁻			
CrOH ⁺	50.16 (15)	1 Cr ³⁺	2 OH ⁻			
CrOH ₃	-67.30 (15)	1 Cr ²⁺	3 OH ⁻			
CuS s	280.00 (25)	1 Cu ⁺	-1 El		1 S ²⁻	
CdS s	257.00 (25)	1 Cd ⁺	1 S ²⁻			
ZnS s	267.70 (25)	1 Zn ⁺	1 S ²⁻			
CrOH ₃ s	-91.00 (25)	1 Cr ³⁺	3 OH ⁻			
HCEC s	-9.73 (b)	1 CEC	1 CEC		1 H ⁺	
CaCEC s	0.0	1 CEC	1 H ⁺			
CuCEC s	-21.80 (22)	1 CEC	1 Cu ⁺		1 OH ⁻	
CdCEC s	-31.40 (21)	1 CEC	1 Cd ²⁺		1 OH ⁻	
ZnCEC s	-29.60 (23)	1 CEC	1 Zn ²⁺		1 OH ⁻	
CrCEC s	-57.00 (24)	1 CEC	1 Cr ²⁺		1 OH ⁻	
CH ₂ O s	0.0	1 CH ₂ O				
AsCH ₂ O s	-8.62 (25)	1 CH ₂ O	1 AsOH ₃			

^a s indicates a solid.

^b Calibrated with the following conditions: 99% CaCEC at pH = 7.0 and 99% HECEC at pH = 4.0

formulations. An example of the chemical system definition for heavy metals in a groundwater-soil system given in Table 3.

The soil-groundwater system can be schematised 3-dimensionally by means of layers or compartments. CHARON needs a groundwater flow field and dispersion coefficients to calculate the exchange of mass between the segments. The flow field can be supplied by a number of groundwater models for saturated and unsaturated systems, such as MODFLOW, EIGER, MAZURE and DEMGEN.

Several transport models with simplified chemistry such as ORPHEUS and STYXZ have been developed for large soil-groundwater systems with long time scales in order to minimize the computational burden and the amount of input data. These models are partially based on so called reprofuctions, which describe the adsorption and precipitation equilibria as simple functions of the pH, alkalinity and several other parameters. The reprofuctions were derived from CHARON calculations. ORPHEUS is a model for the evaluation of the dispersion of pollutants from dredging sludge depots on land or under water into surface water and into a reduced groundwater environment. Fig. 1 gives an overview of the compartments and aspects included in ORPHEUS. STYXZ can be used for the dispersion of pollutants into oxidized as well as reduced groundwater systems from a soil layer or from the water bottom. In addition to mass transport, STYXZ also includes the processes of adsorption and degradation.

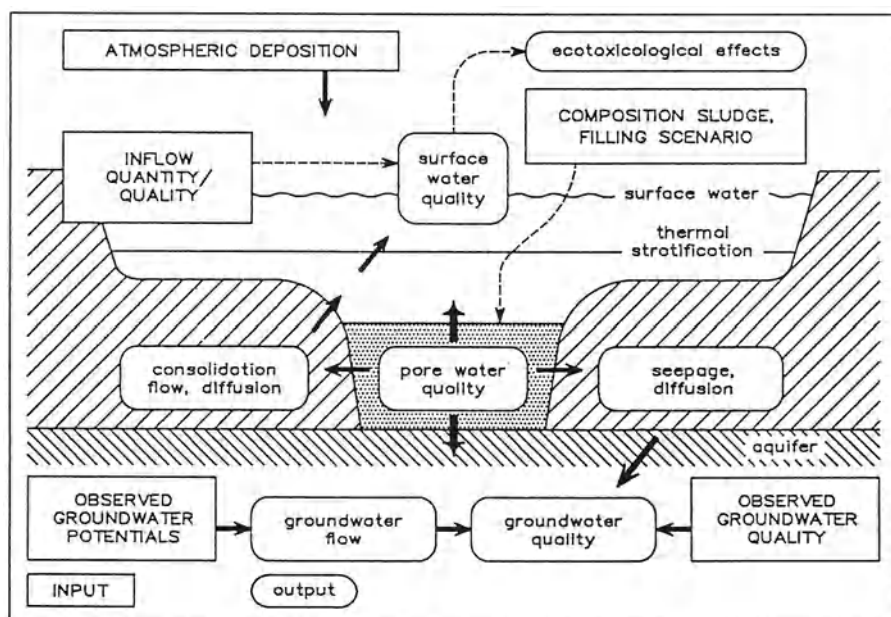


Fig. 1. Overview of compartments and aspects in ORPHEUS

5 Application of Models

The first application of CHARON on soil-groundwater systems in 1983-84 concerned the large depot for polluted dredging sludge from the Rotterdam harbours, known as 'Slufter'. The modeling was carried out within the framework of environmental impact assessment (Fig. 2). The model inputs were based on literature data for the Gibbs free energies of relevant substances. The chemical system definition was calibrated on data of diagenesis experiments with dredging sludge. These experiments also provided data on the short-term value and decrease of the degradation rate of organic matter in the sludge.

Some typical model results are shown in Figs. 3-5. The results show that the pH in the depot decreases substantially several decades after the depletion of oxidized

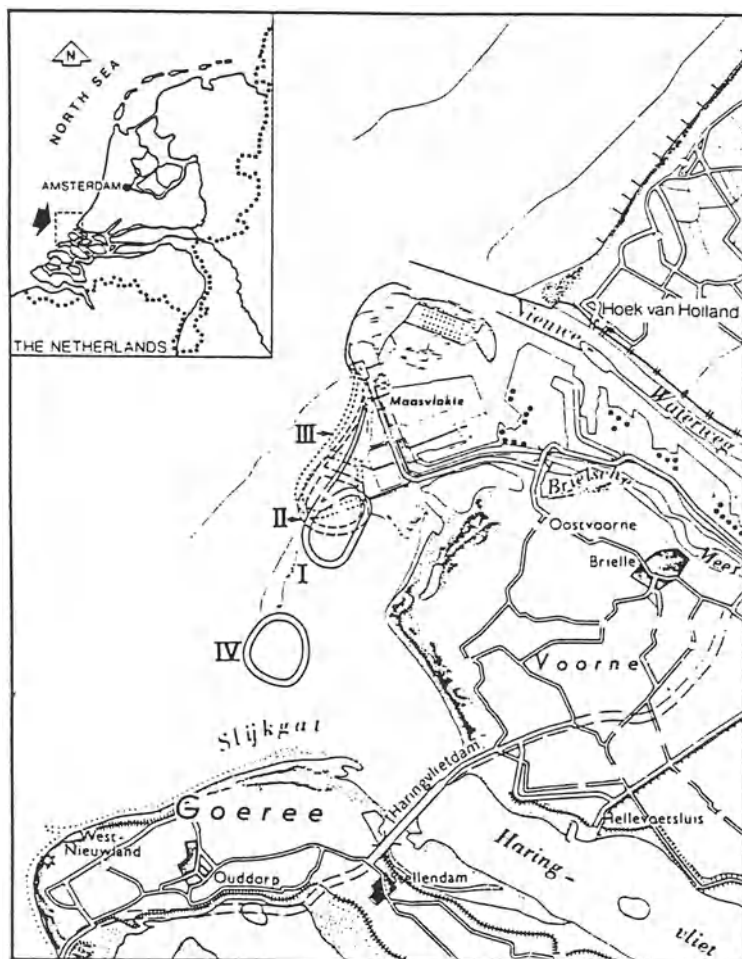


Fig. 2. Possible locations for the harbour sludge depot 'Slufter'

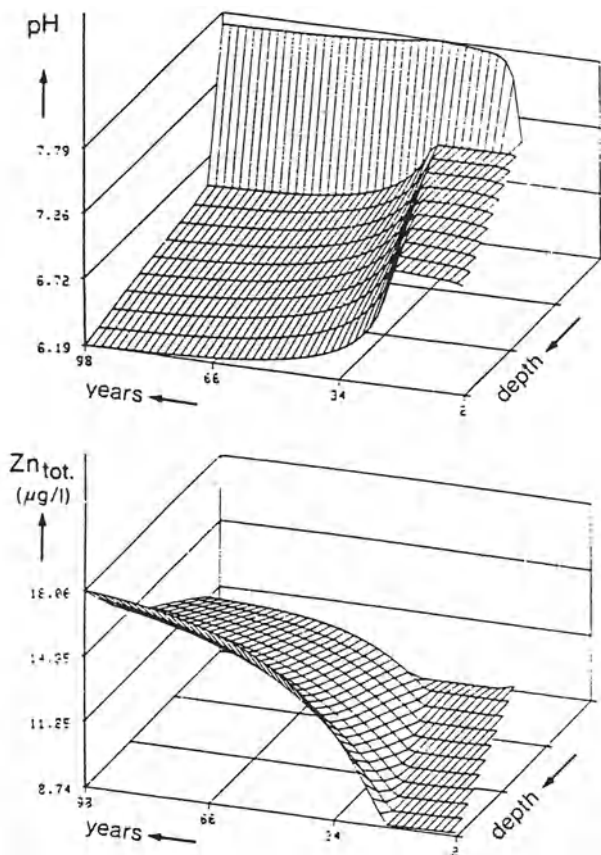


Fig. 3. The development of the pH and the dissolved concentration of zinc in the depot

iron, which is being reduced in connection with the degradation of organic matter (Fig. 3). Except for arsenic and chromium, the heavy metals are precipitated as poorly soluble sulfides under strongly reduced conditions. The sulfide is produced by sulfate reduction related with the degradation of organic matter. The pH-decrease causes the dissolution of heavy metals such as zinc as the metals get more strongly bound in sulfide complexes in the pore water. Even then, the dissolved concentrations remain very low.

Uncertainty existed concerning the value of the longterm degradation rate of organic matter, the quantity of reducible iron and the stability of some minerals. Sensitivity analysis for realistic ranges of parameter values showed that the conclusions are essentially not affected by the uncertainties. The main uncertainty in the simulations concerns the moment at which the pH decline occurs (Fig. 4).

An example of the spreading of heavy metals into the groundwater system at the depot is shown in Fig. 5 at a time of 1000 years after the construction of the

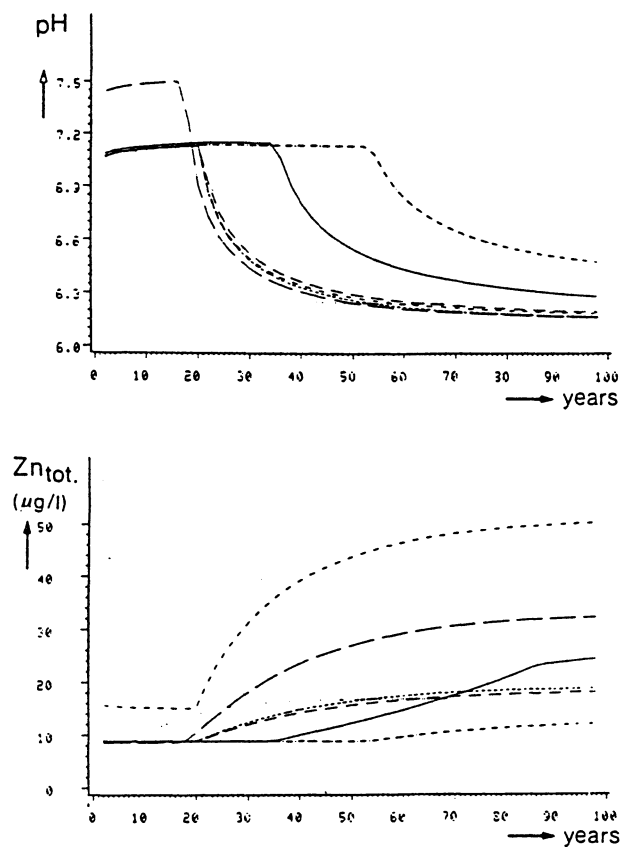


Fig. 4. The development of the pH and the dissolved concentration of zinc in the lower layer of the depot for various scenarios

depot. These results confirm the overall conclusion that the dispersion of heavy metals into the groundwater was very small due to the combination of:

- strongly and permanently reduced conditions in and under the depot, caused by the degradation of organic matter in the sludge;
- abundant availability of sulfate for the reduction into sulfide; and
- very low hydraulic conductivity in the 40 meters thick depot.

The conclusions contributed to the decision to build the sludge depot.

Later applications of CHARON to 4 meter thick dredging sludge depots on top of polders showed that heavy metals could be transported in low concentrations into the groundwater system due to seepage (example Capelle-west, Fig. 6). The simulations indicated in the case of Capelle-West that the pH in the aquifer would drop from 7.5 to 6.3. The heavy metals would be transported to an upwelling area where they may accumulate in the topsoil after several hundreds of years (Fig. 7). For location Schuddebeurs it was found that mainly due to dilution by upgradient groundwater hardly any change of the pH and the background metal concentrations

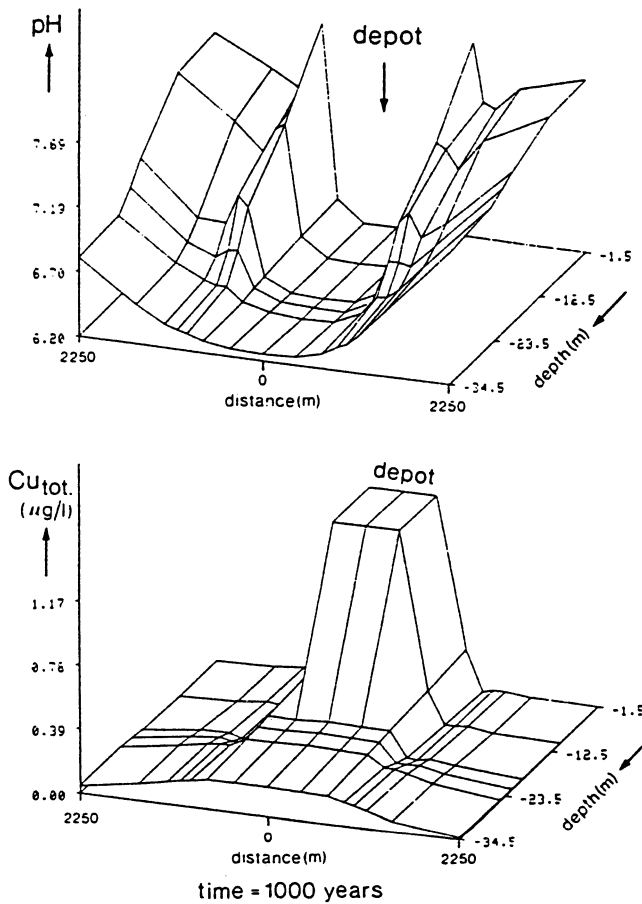


Fig. 5. The pH and the dissolved concentration of copper in the depot and the surrounding groundwater

would occur in the aquifer (Smits et al. 1985). Some of the sludge depots have not been established.

Recent studies with the STYXZ model have focussed on the transport of pollutants from the water bottom in the sedimentation basins of Dutch rivers into the underlying groundwater. Such sedimentation basins are located in the estuary of the rivers Rhine and Meuse near Rotterdam and at the mouth of the river IJssel, a branch of the river Rhine to the north (Fig. 8). These studies contribute to the assessment of the necessity to clean up the bottom sediments.

The study for Lake Ketel, which is fed by the river IJssel, revealed that the level of pollutants arising from the bottom sediments is determined by the permanently reduced conditions in the sediments. The fate of the pollutants is determined by seepage into the underlying reduced soil-groundwater system, by the south-westerly and north-westerly direction of groundwater flow in the upper aquifer and by the flow velocity in and the depth of this aquifer. The spreading of

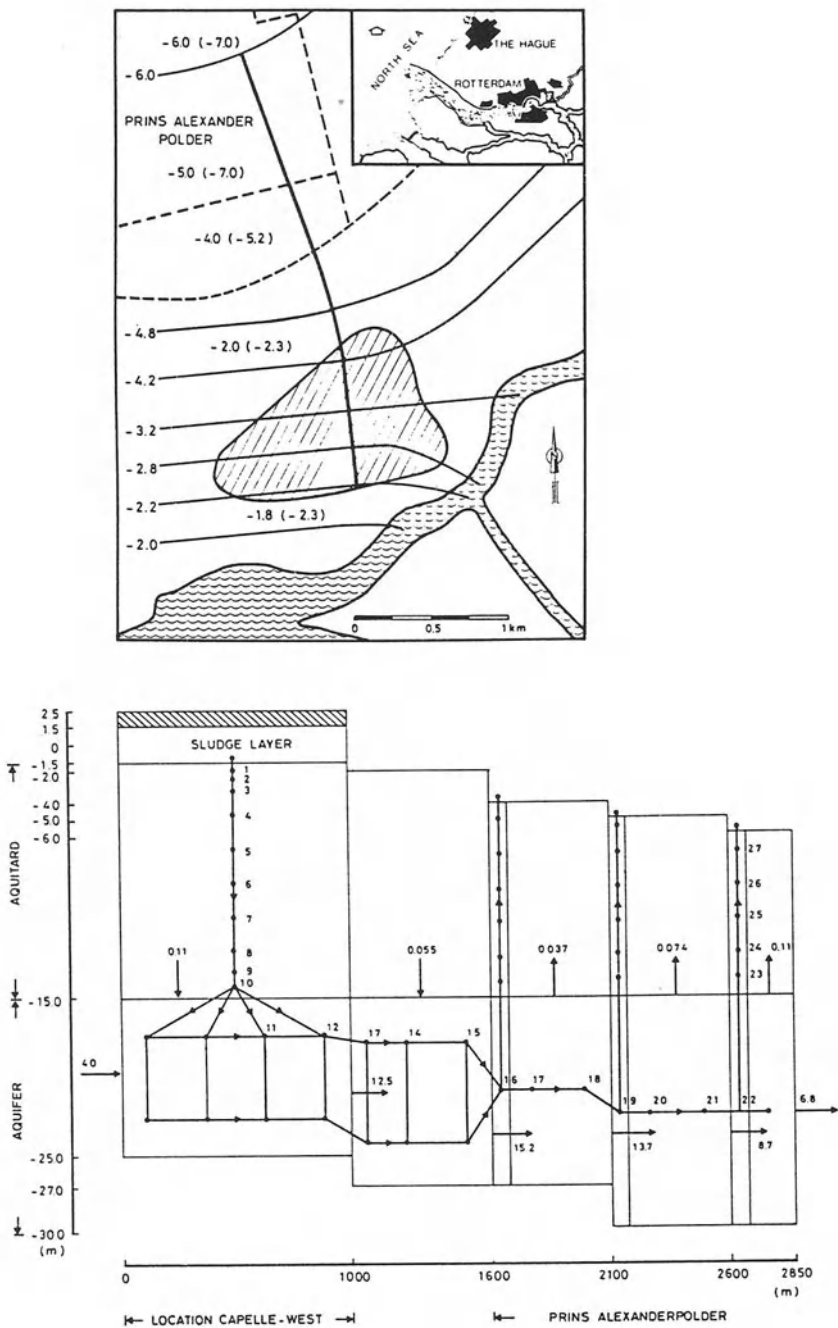


Fig. 6. Location Capelle-West; situation, isopotentials, modeled stretch, segmentation of the stretch and hydraulic flow velocities

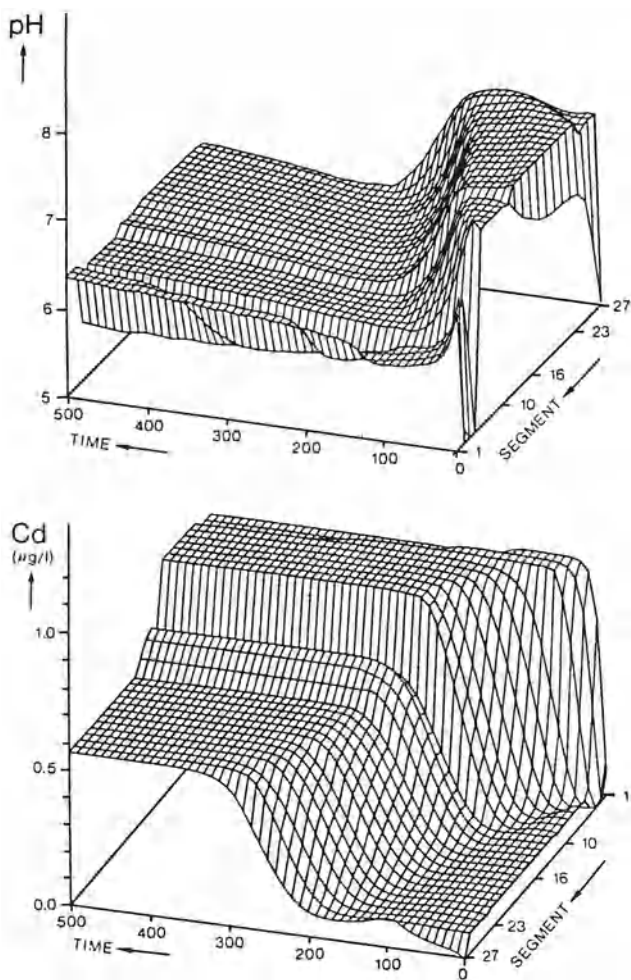


Fig. 7. The development of the pH and the dissolved cadmium concentration in the sludge-soil-groundwater system of location Capelle-West

heavy metals into the groundwater system was shown to be unimportant, and a violation of the Dutch groundwater quality standards is not to be expected. Therefore, the modeling focussed on the spreading of persistent organic micropollutants such as dichlorobenzene (DCB) to the surrounding upwelling regions via the underlying aquifer. Although longitudinal and transversal dispersion cause a substantial decrease of the concentration, a severe violation of the Dutch groundwater quality standard for DCB (0.01 mg/l) is predicted for the regions adjacent to the lake (Figs. 9, 10). The violation of the standard in the upper soil layer begins after a few hundred years in the central part of Lake Ketel and gradually shifts to the western part. The removal of polluted sediment seems

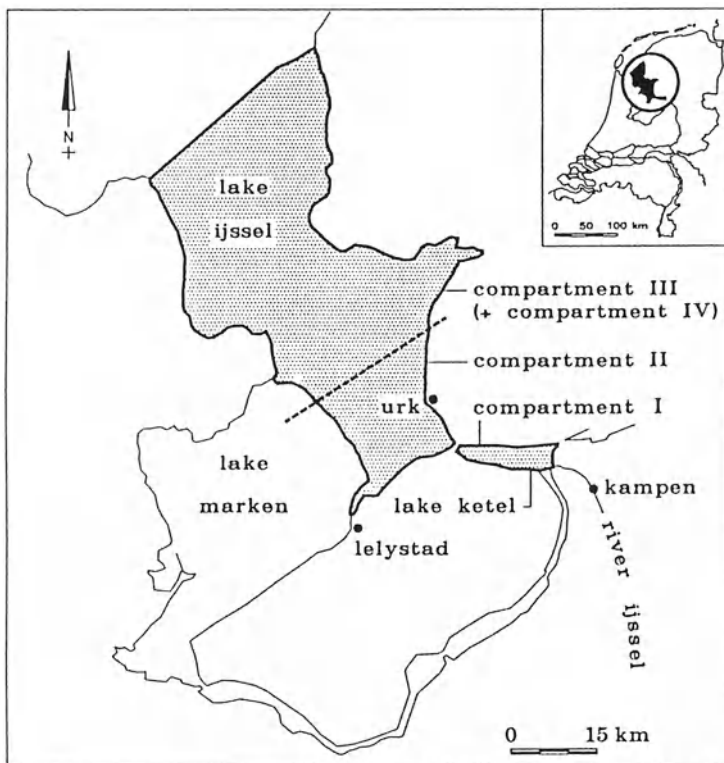


Fig. 8. The location of Lake Ketel

justified, provided that the load of pollutants from the River IJssel has been reduced to an acceptable level. It was decided that the bottom of Lake Ketel is to be cleaned up.

An ongoing research project concerns the (im)mobilization of heavy metals in mixtures of dredging sludge, drinking water sludge, water treatment sludge and polluted soil. CHARON is used to calculate the longterm development of dissolved heavy metal concentrations in mixtures containing at least 75% dredging sludge. The modeling is supported with experiments. The results point out that the addition to dredging sludge of drinking water sludge, which is rich in iron(III) hydroxide, causes an initial increase in the dissolved concentrations of cadmium, copper, lead, zinc, nickel, arsenic and chromium. In the long term no change or even a decrease occurs, except for copper. The addition to dredging sludge of water treatment sludge, which is rich in organic matter, decreases the dissolved concentrations of the heavy metals, except for chromium. The addition of polluted soil to dredging sludge does not substantially affect the dissolved concentrations of most metals. An increase was calculated for copper and a decrease for arsenic.

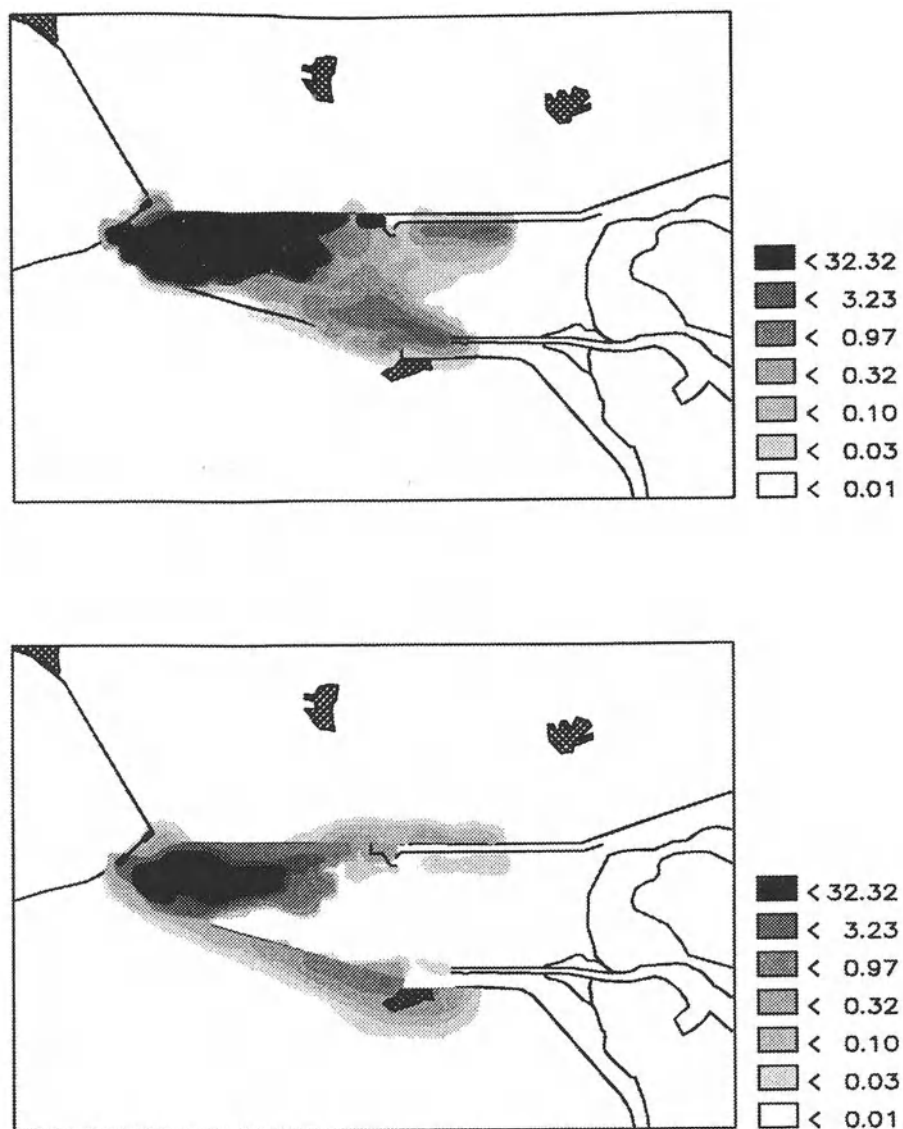


Fig. 9. The spreading of dichlorobenzene (mg/l) in the upper soil layer (< 1 m) in and around lake Ketel from year 200 (upper graph) to year 520 (lower graph)

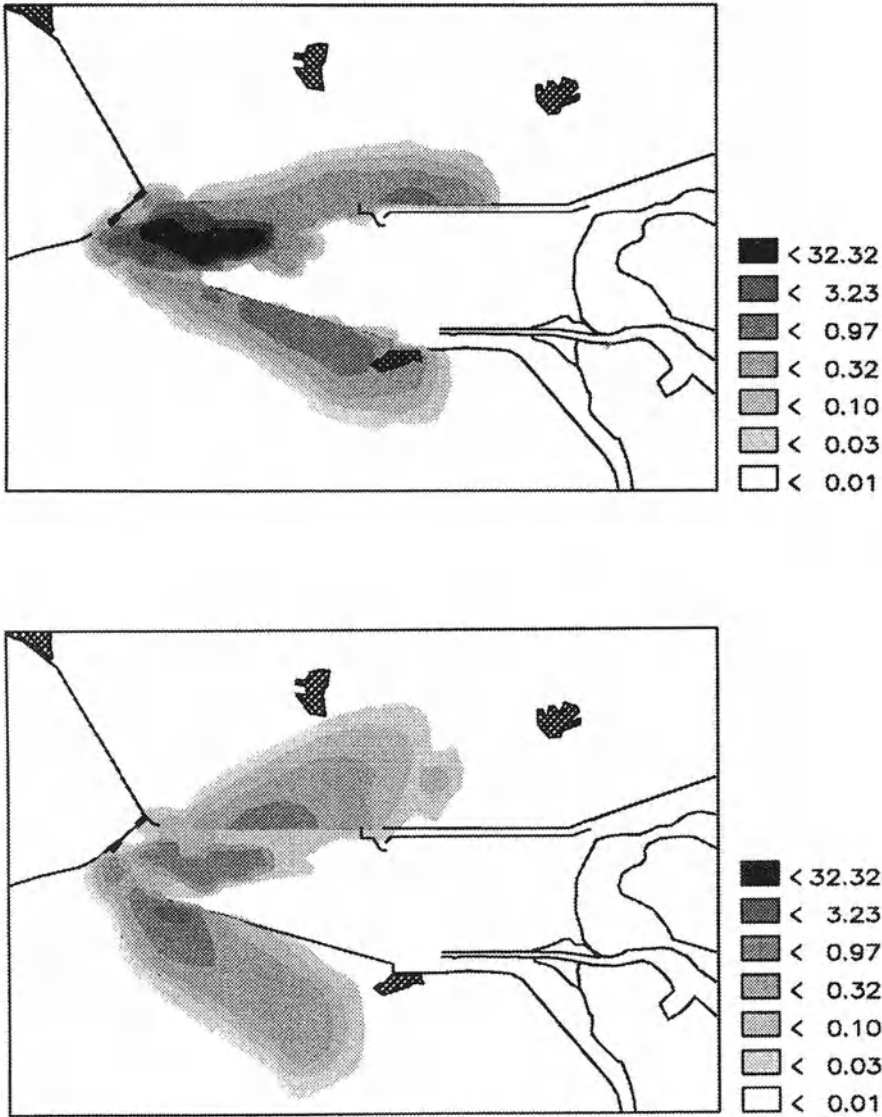


Fig. 10. The spreading of dichlorobenzene (mg/l) in the upper soil layer (<1 m) in and around lake Ketel from year 1000 (upper graph) to year 3000 (lower graph)

6 Conclusions

The applications of CHARON, STYXZ and ORPHEUS have shown that the prediction of longterm spreading of pollutants from sludge layers into soil-groundwater systems is useful for the assessment of:

- the concentrations of heavy metals and organic micropollutants in aquifers; and
- the path, travel time and eventual destination of these pollutants.

The model results may be used for analysis of the effects of groundwater pollution on drinking water supply, on surface water ecosystems and on terrestrial ecosystems.

The model results have contributed to the setting of priorities for the clean-up of polluted sites and to the assessment of alternatives for the storage of polluted sludge.

The main uncertainties in the chemical modeling concern the organic matter degradation rate and the stabilities of some of the metal complexes and precipitates. Dispersion in groundwater may also be an uncertain factor due to the inhomogeneity in composition and structure of the soil.

The model applications in the Netherlands have focussed on the behaviour of heavy metals and organic micropollutants in chemically reduced sludge-soil-groundwater systems. Only one application was made regarding oxidized polluted topsoil. The simulated reduced conditions are rather typical for soils in the Netherlands, which are composed of peat and clay containing layers on top of sandy aquifers. Application of the models to (oxidized) soils in Central and Eastern Europe may therefore necessitate adaptation of the chemical system definition in the model. Further adaptation will be required to include the behaviour of macrochemical substances in solid wastes other than (natural) sludge.

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II Engineering Approaches to Remediation

8 Impact of Mining Activities on the Terrestrial and Aquatic Environment with Emphasis on Mitigation and Remedial Measures

R. J. Allan

National Water Research Institute, Canada Centre for Inland Waters, Burlington,
Ontario L7R 4A6, Canada

Abstract

Mining activities have both local and regional impacts on terrestrial and aquatic ecosystems. Mines produce large quantities of waste-rock and tailings which must be disposed of on land or into aquatic ecosystems. The major results in terms of contamination by heavy metals are areas of wasteland and sources of acid and metal-rich runoff from land-sited tailings piles or waste-rock heaps and the subsequent pollution of soils, lakes, rivers, and coastal areas. After the fact remediation or control of leachates from tailings and waste-rock on land or remediation of waterways polluted by mine tailings are being found to be complicated and expensive. New mines often successfully incorporate mitigation measures that are economically sound in the long-term. This paper overviews these problems and concerns with examples from around the world.

1 Introduction

Mining has gone on for thousands of years and abandoned mines and mining operations are found throughout the world. Mines are local phenomena and their major impacts are largely local but not always and dispersion of heavy metals can be regional, and even global (Allan, 1988).

Today, the main metals mined other than iron and chromium, are copper, zinc, lead and nickel (Table 1). Tonnage produced of all the other metals mined is relatively insignificant in comparison to these six. For example, in 1985, some 1500 tonnes of Au were produced versus some 8,000,000 tonnes of Cu; and some 19,000 tonnes of Cd versus some 6,000,000 tonnes of Zn. The order of metal production in 1985 was Fe > Cr > Cu > Zn > Pb > Ni > Sn > Mo > Co > Cd > Ag > Hg > Au and this has been similar for several decades. In the last few decades, the major producers for the major metals, other than Fe and Cr, have been the U.S.A. for Cu; Canada for Zn and Ni; and the U.S.S.R. for Pb.

Table 1. Historical changes in global production of metals commonly associated with pollution from mining activities (x1000 tonnes). (Abstracted from Nriagu, 1979; Nriagu & Pacyna, 1987.)

Metal	Pre-1850	1850-1900	1900-1940	1950	1960	1970	1980
Copper	45,000	13,000	49,000	2650	4212	6026	7660
Zinc	50,000	15,000	40,000	1970	3286	5469	5220
Lead	55,000	25,000	51,000	1670	2378	3395	3096
Nickel	-	200	1,500	144	327	639	759
Cadmium	-	-	-	6.0	11	17	15
Silver	-	-	-	6.2	7.5	9.4	11
Mercury	-	-	-	4.9	8.3	9.8	7.1
Gold	-	-	-	1.0	1.4	1.5	1.2

Mining and metal beneficiation industries have developed into sophisticated operations, yet the basic causes of pollution remain unchanged. In a typical metal mine operation (Fig. 1), more water by weight is employed in production of the metal concentrate than the weight of ore grade material itself. Water losses and water gains at a typical metal mine show that the main direct release of metals to freshwaters is from tailings and polishing ponds and emissions later in the beneficiation stage (Fig. 2).

The objective of the following is to examine the sources of acid mine drainage and related or other heavy metal contamination of the terrestrial and aquatic environment by mining activities; and mitigation or remediation measures to reduce such contamination of terrestrial and particularly aquatic environments.

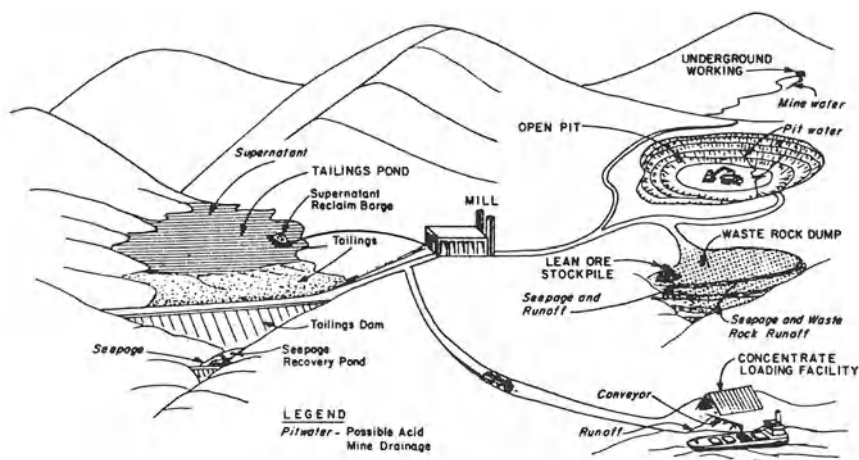


Fig. 1. A typical mining operation. (After Ferguson & Erickson, 1988)

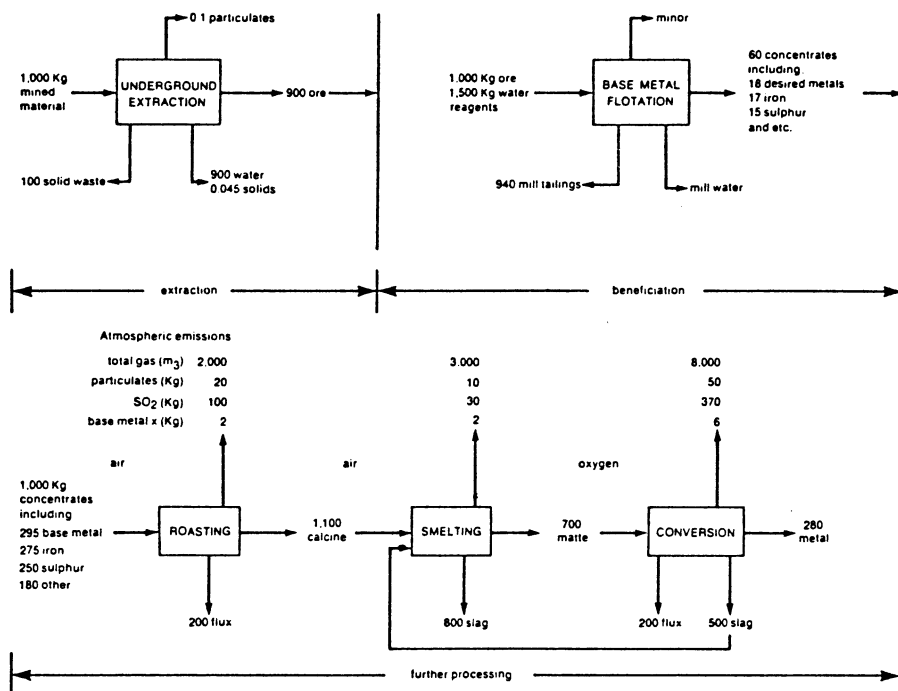


Fig. 2. Composite generalized materials flow diagram for the extractive, beneficiation, and further processing phases of a typical base-metal mining operation. (After Marshall, 1982)

2 Impacts of Terrestrial and Aquatic Disposal of Mine Tailings

2.1 Terrestrial Disposal of Mine Tailings

Acid mine drainage (AMD) is generated by chemical reactions and bacterial oxidation processes. Sulphide ores contain large quantities of pyrite which is discarded in the tailings and produces sulphuric acid (AMD) when exposed to water and oxygen. The ferrous iron produced is then oxidized to ferric ions which become the dominant oxidizing agent of the exposed sulphide minerals. The process thus becomes auto-catalytic in the production of AMD. In addition, the reduced sulphur and iron compounds in the deposits are excellent ecological niches for *Thiobacillus ferrooxidans* which oxidizes ferrous iron, thiosulphate, sulphur and metallic sulphides to obtain energy for growth while using oxygen as the final electron acceptor, using CO₂ as its sole source of carbon and requiring an environment with an acidic pH. Other species with related or similar needs and abilities are *Ferrobacillus ferrooxidans*, *Ferrobacillus sulphooxidans*, and *T. thiooxidans*.

The eventual pH of surface or groundwaters receiving AMD depends on their original alkalinity and the rate of AMD production. Natural alkalinity may keep

the receiving waters neutral for some time, but there may be a rapid shift to acidity, usually difficult to predict, depending on hydrological and geochemical factors. For example, the production of acidity and alkalinity differs greatly in relation to the frequency of drying out and flushing of land disposed mine waste. Laboratory tests to predict acid versus alkaline production and thus the potential AMD are used extensively and include the use of kinetic titration tests, *Thiobacillus ferrooxidans* in inoculated, incubated shake flasks; soxhlet extraction procedures; and lysimeters; amongst others.

2.2 Subaqueous Disposal of Mine Tailings

Subaqueous disposal of mine tailings is employed to avoid terrestrial AMD. While land disposal of mine wastes is ideal for *T. ferrooxidans*, under water disposal in lakes or coastal marine sites makes colonization by the bacteria difficult if not impossible. There is less oxygen available in aquatic systems and it is unlikely that pH could drop low enough to accelerate *T. ferrooxidans* activity. In addition, chlorine in marine systems is toxic to the bacteria. However, there are negative effects of subaqueous tailings disposal related to turbidity, sedimentation, toxicity and contamination. The tailings particles may effect filter feeding or respiratory structures, cause gill damage in fishes, or increased oxygen consumption rates, along with other problems. Rapid tailings deposition causes burial of organisms. At lesser rates of sedimentation, benthic organism food supply to is reduced, habitats are affected, or upstream movement of biota can be physically blocked. In addition, many components of mining wastes are lethally or chronically toxic to fish or cause sub-lethal effects. Phytoplankton, periphyton, macrophytes, zooplankton, zoobenthos, and fish to varying degrees are effected by one or another of metals such as As, Cd, Cr, Cu, Fe, Pb, Hg, Zn, Ni, Sn, mixtures thereof and cyanide as well as other materials in mine effluents. There area a vast number of references relate to these toxicity aspects of metals to freshwater biota (Rescan, 1989) and there is no value in listing them here. The basic point is that mine effluents and emissions have been documented to cause both lethal and chronic effects on a range of aquatic biota, depending on factors such as the composition of the effluents and the receiving waters. There is also a vast literature on the uptake by biota, bioaccumulation and biomagnification of many mining related metals including Zn, Pb, Ni, Cd, Cu and Hg.

Assessment of sediment (tailings) associated metal impact on biota requires a knowledge of the bioavailable fraction of the metals in sediments because the total metal content is not the biologically important concentration. Chemical fractionation of sediments can be used to assess this bioavailable fraction. A series of reagents can be used to sequentially extract correctly collected and stored sediments and determine this bioavailable fraction. The exchangeable or loosely-held fraction can be removed by extractants such as ammonium acetate, ammonium chloride and magnesium chloride. The carbonate faction can then be removed by extractants such as acetic acid and sodium acetate. The easily

reducible fraction which is mainly associated with new Mn oxides, can then be removed by extractants such as sodium acetate/hydroxylamine hydrochloride and nitric acid/hydroxylamine hydrochloride. The moderately reducible fraction, which is mainly associated with aged Mn and Fe oxides, can then be removed by extractants such as acetic acid/hydroxylamine and ammonium oxalate/oxalic acid. The organic and/or sulphide fraction can then be removed by extractants such as hydrogen peroxide/nitric acid and hydrogen peroxide/ammonium acetate. Finally, the residual fraction, mainly associated with the matrix, or lattice structures of sedimentary minerals, can be dissolved by reagents such as perchloric acid/hydrofluoric acid and nitric acid/hydrofluoric acid. These sequential metal extraction procedures for sediments can also be used to predict the remobilization of metals under changing environmental conditions.

In Canada, the Federal Metal Mining Liquid Effluent Regulations prohibit subaqueous disposal of mine tailings but exemptions are sought and given and subaqueous disposal of mine tailings occurs into both freshwater and marine environments. Whether underwater disposal of mine wastes is less of an environmental insult than terrestrial disposal is a subject of ongoing study and some debate. To resolve the questions raised will require extensive research at sites of former tailings disposal in lakes and at sites where this is still going on. The factors which play a major role on the fate of heavy metals in bottom sediments (and deposited tailings) are oxidation state; benthic organism type and density; sedimentation rate; type of sediments, e.g., oxyhydroxide phases; and organic matter accumulated. Lake sediments are chemically zoned with depth, and oxygen is depleted at some depth below the sediment-water interface. In mesotrophic and eutrophic lakes, the organic carbon content usually results in anoxic conditions at sediment depths of a few millimetres to 10 cm. The input of inorganic mine tailings to lakes dilutes the organic content of the natural sediments and buries this more rapidly. With rapid tailings impacts, the smaller quantities of oxygen buried are more rapidly used up, and anoxic conditions established at shallow sediment depths. However, bioturbation and physical processes in both marine and lacustrine situations compound the basic geochemistry by mixing oxygen to depth in the sediments, causing oxidation of sulphides and release of metals to the pore waters. Seasonal limnological processes, such as turnover, stratification and productivity also affect oxygen content of bottom waters and thus affect the oxic zone thickness and resulting transfers of bioavailable metals.

The amorphous iron and manganese oxides and hydroxides which can make up to 10% by weight of lake sediments, are important scavengers of heavy metals because of their high specific surface area; high negative surface charges; and high cation adsorption capacity over the pH range of most natural waters. Dissolved metals may diffuse upwards in sediments with thick oxic layers but diffuse into sediments where anoxic sediments are at shallow depths. Thus elevated bottom sediment surface concentrations of Cu, Ni, Zn, Cd, Pb and Mo may not always reflect anthropogenic inputs if the pH of the overlying water is low. At polluted sites, metals diffuse into the near surface anoxic sediments to be precipitated as sulphides whereas at unpolluted, oxygen-rich sites, metals in sediment porewaters

may be released to the overlying water. Under anoxic conditions in sediments, most heavy metals should be present as precipitated, insoluble sulphides, e.g., ZnS, HgS and FeS (thought to be a significant sink of heavy metals in anoxic sediments). These considerations of the general behaviour of metals in lakes should be used to assess the efficacy of sub-aqueous disposal of metal-rich tailings. When tailings are to be dispersed into water systems, be they lakes, rivers, reservoirs, or coastal areas, then a great deal of basic information on the site is needed. Many of the effects will depend on the depth and size of the water body, flow, flushing rates, natural geochemical conditions, currents and many other site specific variables. In lakes, stratification, mixing patterns and biotic transfer mechanisms will be very important and for large rivers, mixing patterns and side effects.

3 General Principles of Mitigation and Remediation

Remedial measures to reduce metal releases to terrestrial environments should first be applied near the source of their release. Solid wastes on land can be limed or encapsulated by use of impermeable base liners and surface covers to reduce AMD and related metal movements and resulting biological availability of the metals.

Achieving a neutral or slightly alkaline pH by application of lime, limestone, alkaline fly ash and similar materials favours adsorption or precipitation of metals.

Limestone liners for landfills may be an economical chemical barrier to precipitate solubilized metals in AMD. If the initial interstitial water in wastes is reduced, lower concentrations of metals are found in the leachate and an impermeable lining or an elaborate leachate treatment system may not be needed at the disposal sites.

In general, control of AMD is more difficult than prevention but mitigation of AMD can include: biologically enhancing AMD to remove sulphides, collecting the leachate and removing the metals; covering mine wastes with lime or limestone; diverting water inflow to the waste or from the waste; capping the wastes with clay or other material or flooding the surface to reduce oxygen ingress; using bactericides to kill bacteria that cause AMD; and applying phosphate to the surface to break the ferrous/ferric/pyrite cycle. Such procedures can be costly and only have varying degrees of success. For example, diverting water, then applying lime and sewage sludge followed by re-vegetation resulted in only a modest improvement in AMD from gold mine wastes after 10 years (Hinkle, 1984).

In aquatic systems, contaminated sediments can be isolated from overlying waters by physical barriers such as polymer films, or covered by sand and gravel. Waters can be limed. The best way to prevent problems with metal-rich wastes in aquatic systems is by isolating them in a permanently reducing environment. In general, the marine sulphidic environment is more favourable for metal-rich waste disposal than freshwater lakes due to the high stability of metal sulphides. Deposits above the marine floor can be capped or the waste placed in subaqueous depressions which are then covered by clean sediments.

Table 2. Authorized levels of substances in mine effluents

Parameter	Authorized Concentrations ^a	
	Maximum acceptable arithmetic monthly	Maximum acceptable in grab sample
Arsenic	0.5 mg/L	1.0 mg/L
Copper	0.3 mg/L	0.6 mg/L
Lead	0.2 mg/L	0.4 mg/L
Nickel	0.5 mg/L	1.0 mg/L
Zinc	0.5 mg/L	1.0 mg/L
Total Suspended Solids	25.0 mg/L	50.0 mg/L
Radium-226	0.37 Bq/L	1.11 Bq/L
pH	6.0 or greater	5.0 or greater

^a All concentrations are total values except for Ra-226 which is at the dissolved level after filtration of the sample through a 3-micrometre filter. The levels shown apply to undiluted effluent at the point of discharge to the environment.

In Canada, the Federal Metal Mining Liquid Effluent Regulations and Guidelines give the authorized acceptable levels for substances in mine effluents (Table 2). The federal regulations in Canada are for base metal, iron and uranium mines and only apply to new, re-opened or expanded mines after 1977. Provincial requirements apply where they are more stringent and site specific regulations may also be applied. However, regulations need to be enforced, not simply developed and ignored as is the case in many developing and even in some cases developed countries.

3.1 Mine Wastewater

Processing of ore grade metals introduces a variety of chemicals to the mine waste streams (Table 3) including nitrogen compounds from blasting operations, colloidal suspended solids, many other trace metals of non-ore grade (usually Al, As, Cd, Cu, Fe, Pb, Mn, Ni, Zn, Rd), and thiosalts ($S_2O_3^{2-}$; $S_3O_6^{2-}$, $S_4O_6^{2-}$) which on further oxidation cause acidification of rivers and lakes. Wastewater treatment most commonly uses neutralization and concurrent precipitation of the metals as hydroxides under alkaline conditions. The most frequently used reagent is hydrated lime ($Ca(OH)_2$), often produced on site by slaking of quicklime (CaO). Multistage precipitation is used for different metals and specific to the metal content of the ores. Solid/liquid separation occurs between treatment stages and difficulties can arise in separation of the amorphous sludges. Cyanide needs to be removed from the effluent of precious metal mines (Au and Ag). NaCN is used to complex the Au which is then replaced by Zn or extracted directly by sorbtion onto carbon granules. Both processes release highly alkaline effluents rich in CN ions

Table 3. Typical ore processing reagents

Reagents	Comments
Acids (H_2SO_4 , HCl , HNO_3)	-
Alkalis (CaO , $\text{Ca}(\text{OH})_2$, CaCO_3 , Na_2CO_3 , NaOH , NH_4OH , NH_3)	-
Frothers and Collectors	Surface active organics
Modifiers	Surface active organics and various inorganics such as NaCN , Na_2SO_3 , CuSO_4 , ZnSO_4 , Na_2S , AlCl_3 , $\text{Pb}(\text{NO}_3)_2$, silicates and chromates
Sodium Cyanide	Used for precious-metal cyanidation and as a depressant in flotation processes
Flocculants, Coagulants	Aluminum and iron salts, and organic polymers

and various cyanide containing complexes. Gold mines use many ways of removing CN including natural degradation; alkaline chlorination; various SO_2 processes; hydrogen peroxide oxidation; anion exchange; and biodegradation. Radium in mine wastewaters can be removed by precipitation with barium sulphates. Thiosalts are removed in effluents as sulphur, sulphides or as H_2S gas.

3.2 Contaminated Groundwater

Effects of mining on groundwater can be rapid or long-term (Loxham, 1988). Predicting effects requires a detailed knowledge of groundwater characteristics, flows and volumes as well as of the materials in the tailings and those onto or into which the tailings are introduced. Control options include preventing the infiltration of contaminants; stabilizing the contaminants chemically; or removal and treatment of the contaminated groundwater. One option is to attempt to cut off the movement of contaminants but most such options are not long-term. Cut-off walls can isolate a leachate so that it can be pumped out and treated but the walls must extend to an impermeable layer beneath the aquifer. If such layers are deep, cost can prove prohibitive, as they can be to seal the bottom. When wells are used to remove a leachate, a difficult choice has to be made on the number of wells and, based on the expected contaminant concentration, the cost of treatment of the water volume expected to be removed. However, given adequately constructed cut-off walls, and shallow depths to an impermeable barrier as well as removal and treatment of leachates, a long-term, relatively safe scenario can be developed.

3.3 Contaminated Sediments

Techniques to treat metal contaminated sediments should be based on the short and long-term leachability of the metals. Dredging, compaction (dewatering and

hydrocyclonage), and disposal are the normal procedures but in some cases additional decontamination steps can be used such as leaching, ion exchange, extraction or flotation techniques. Hydrocyclonage has a limit of separation of some 10 mm but is large capacity and costs are low. Flotation skims off air bubbles attached to particles because of their hydrophilicity. High gradient magnetic separation techniques can be used on particles larger than 1 mm and separate ferro and paramagnetic compounds; metals coprecipitated with ferric hydroxide; and non-magnetic particles bonded to a magnetic floc. These

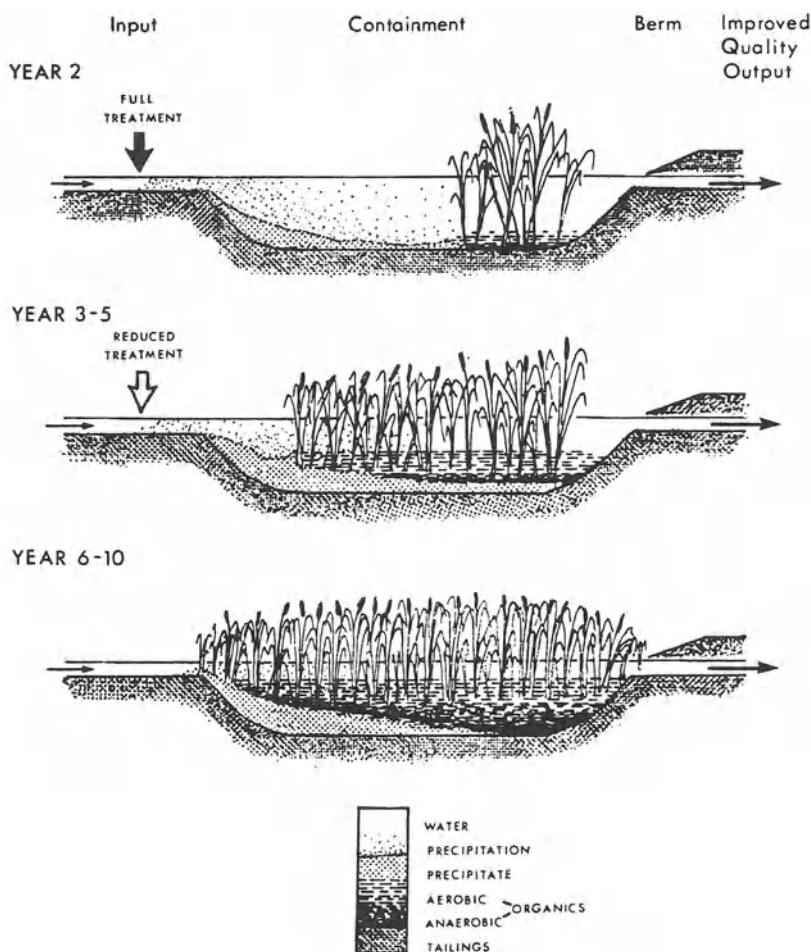


Fig. 3. Schematic development of wetlands on waste sites. The first 2 years might require some neutralization treatment to assist in the establishment of suitable indigenous species. As establishment of the wetland vegetation increases throughout years 3 to 5, the treatment can be reduced and is gradually withdrawn within years 6 to 10 when the system is self-sustaining. The anticipated sediment development is depicted in the enlarged insert providing an anaerobic, aerobic and finally precipitate layer underneath the treated water. (Kalin and van Everdingen, 1988)

techniques can be used on a large scale. Small scale techniques include removal by leaching, e.g., Hg with sodium hypochlorite when the Hg is present as a sulphide or an organic compound, e.g., in anoxic lake bottom sediments. Heavy metals can be dissolved by acid leaching at pHs of 0.5 to 1.0 with separation of the acid solution and precipitation of the metals with lime, or ion exchange can be used but requires long contact times. Sediments can be pretreated by formation of flocs by use of agents such as FeCl_3 , $\text{Ca}(\text{OH})_2$ and polyelectrolytes and then dewatering by sedimentation or filtering, or dewatered directly by electro-osmosis.

3.4 Passive Biological Techniques

Self maintained, passive biological systems can be employed to treat mine wastewater and waste leachates. These methods are attractive because of the low cost. Systems proposed include use of mosses which can reduce infiltration of precipitation into terrestrial mine wastes or remove metals such as Cu and Ni from leachates or wastewater, if flow rates are low. Wetlands (Fig. 3) are now being studied as to their value in reducing acidity and heavy metals but their use for biofiltration is not yet widespread. Cattails can be introduced to alkaline mine slimes by hand transplanting or by mechanical means. Seeding cattails show varying degrees of success and burial of the rhizomes under compacted material deeper than 10 cm inhibits expansion. Bacteria or fungi can concentrate and remove metals from mining effluents. Some macroscopic attached algae (*Charophytes*) have been tested in alkaline waters in polishing ponds at uranium and nickel mines and concentrated several metals and increased pH to neutral conditions.

4 Specific Examples of Mitigation, Remediation and Lack Thereof

Mitigation and remediation are not absolute concepts. There is now an extensive literature base describing metal contamination at sites around the world. At most, sites, some basic attempts at mitigation are employed. There is a complete spectrum from virtually zero mitigation to extremely well planned long-term mitigation-remediation programs. The following examples show this wide range of situations from local to regional; from well managed where regulations are strictly enforced, to where less controlled situations can lead to major impacts; and various remediation procedures as well as situations where clean-up is now virtually impossible.

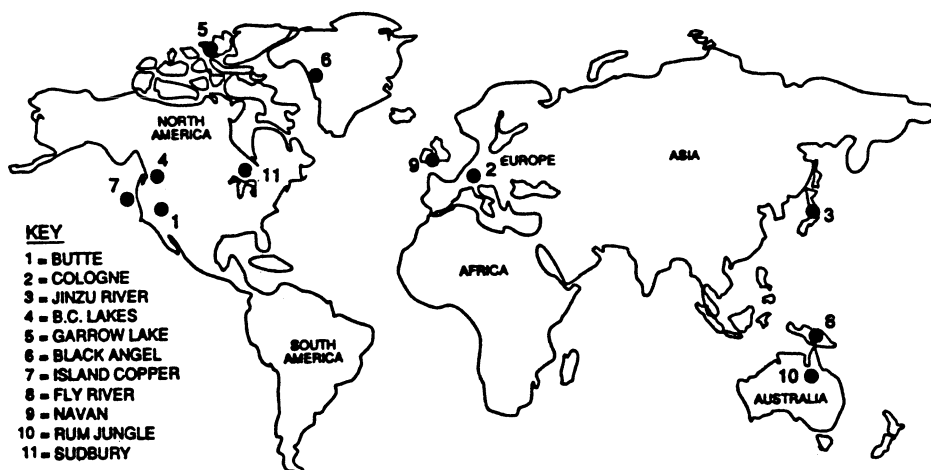


Fig. 4. Location of the main sites mentioned in the text

4.1 Flood Plain Contamination and Remediation

Flood plain contamination and long-term, long range effects are seen in the Clark Fork River system U.S.A. (Fig. 4). The headwaters area of the river include the Butte District Cu mining and smelting complex which opened in the late 1800s. Smelting ceased in 1980 after more than 1 billion tonnes of ore had been removed and primary wastes covered 35 km² with associated heavy metal contamination from smelting covering hundreds of km². Although metal concentrations in river bed sediments declined rapidly downstream from the mining area, the concentrations for some metals, some 380 km from the primary sources were still an order of magnitude higher than in (non-contaminated) tributaries (Luoma, 1989). This long range effect was partly related to the storage of metals in the flood plain soils which became a secondary source of metal input as new river channels were cut. Flood plain soils often had higher Cu and Zn concentrations than the adjacent river bed sediments. Concentrations trends of metals in various biota for up to at least 380 km downstream closely paralleled the river bed sediment concentrations. Such extensive contamination of the flood plain for hundreds of km, virtually precluded any remediation for technical reasons and cost.

A similar situation but one feasible to partial remediation occurred in the Jinzu River mining area of Japan (Fig. 4). Ore deposits of Zn, Pb, Au, Ag and Cd were found some 1,200 years ago and were rapidly developed from 1890 on. Over 4,000 tons of ore were mined daily at peak productivity and smelting occurred at the site. Downstream river paddy soils became contaminated by Cd and the area experienced Itai-Itai disease from 1971 to 1976. The remediation technique used was to cover the most polluted soils with 20 to 30 cm of unpolluted soil at a cost of some \$80,000 U.S./ha (1978). Rice grown in the clean soil cover had Cd concentrations below that in rice from unpolluted paddy fields. Measures were

also implemented to reduce effluents from the mines and smelters so that the problem did not repeat itself. Regional soil pollution from smelter emissions was also well documented but was so widespread that remedial action for such soils was not considered.

4.2 Subaqueous Disposal of Mine Tailings and Remediation

Benson Lake, in British Columbia (Fig. 4) received tailings from a copper mine between 1962 and 1973. Some 3.6 million tons of ore were mined and the tailings discharged to the lake under permit. Tailings were introduced to the lake at a depth of about 43 m. The central and deepest part of the lake was just over 50 m and the lake bottom became covered with tailings. By 1967, no benthic organisms were found except near the lake outflow. The main problem was seen as turbidity from colloids which did not settle out and which appeared at the surface once lake stratification broke down. The mitigation measure which proved generally unsuccessful, was the extension of the tailings pipe to some 48 m. Buttle Lake, also in British Columbia (Fig. 4) also received tailings from several mines with recoverable quantities of Cu, Zn, Pb, Au, Ag and Cd. Buttle Lake is 30 km long by 1.5 km wide with a maximum depth 87 m, in an area of high relief. Some 5.5 million tons of mill tailings were deposited in the lake between 1967 and 1984.

Prior to discharge into the lake, sand size particles were removed from the tailings and back filled into the mine workings. The discharge outfall was 30 m below the thermocline and a flocculent was used to promote settling to the bottom some 30 to 50 m deeper than the discharge point. The pH in the milling circuit was kept high by additions of lime. The permit levels for the dissolved metals were 0.3 ppm Cu, 0.1 ppm Pb, 5.0 ppm Zn and levels achieved with a chlorination plant were 0.09 ppm Cu, 0.08 ppm Pb and 0.43 ppm Zn. Analyses of sediment cores and their porewaters from natural sediment and tailings areas showed that remobilization of metals was minimal and concentrations for some metals were lower than the overlying bottom waters. Oxidation of the tailings did not appear to be taking place due to the rate of tailings discharge (rapid burial). There was no release of Zn and Cu and these metals were diffusing into the natural sediments and being precipitated as sulphides because anoxic conditions occurred at shallow sediment depths. When tailings discharge ended in 1984, natural sedimentation of some 0.2 cm per year bury the tailings to a depth of some 3 cm by 1999. This should prove sufficient to have anoxic conditions at the 3 cm sediment depth or less and thus seal the tailings. When high Zn and Cu levels were found in the lake water and it was proposed that these came from the deposited tailings, studies discovered the power to be a creek draining a waste rock site subject to AMD. Once this source of AMD was eliminated by leachate collection and treatment after 1983, the concentrations of Zn and Cu in the lake water began to drop and by 1990, they were near pre-mining concentrations of <5 ppb Zn and <1 ppb Cu. Today, the mine continues to operate, but the tailings are now stored in ponds near the mine, the dissolved metals in the discharge water removed by liming, and the water then

recycled to the mill. It is extremely rare that an ore body is conveniently discovered near a meromictic lake, but this was the case for the Polaris Pb-Zn mine in the Canadian High Arctic. Tailings are being deposited at depth into meromictic Garrow Lake (Fig. 4) and no deleterious impact on the surface waters or outflow have been recorded.

Turning to the marine-coastal situation, the Pb-Zn Black Angel Mine is located on a fjord system on the west coast of Greenland (Fig. 4). Since 1973 approximately 500,000 tons/year of metal rich tailings has been discharged in a salt water suspension into Agfardlikavsa Fjord at a depth of 30 to 42 m. The tailings are 50% marble/dolomite and 50% pyrite. The effects are Zn, Cd and Pb contamination of the water and suspended particulate matter in the fjords (Loring & Asmond, 1989). Dissolved Zn and Pb reached levels of 1 ppm at the bottom of the fjord and metal enrichment in biota occurred up to 50 km from the effluent input. Seaweeds and mussels in the fjord were contaminated by Zn. Seasonal stratification played an important role in the transfer of particulate and dissolved metals and during the winter mixed conditions, metal-rich particulates were transported over the fjord sill into an outer fjord where they were deposited in decreasing amounts seaward. Attempts to remediate such underwater tailings at marine disposal sites are virtually non-existent (Ellis & Taylor, 1988). Whereas coal mine open pits in areas of high land values, such as the brown coal mines pits near Cologne, Germany (Fig. 4), are often restored to a semi-original state, the same does not apply to subaqueous lacustrine or coastal disposal which is out of sight. However, reclamation procedures could involve construction of artificial habitats with concrete, car bodies, or tires, or other waste materials that are eventually colonized to create new ecosystems. One benefit is that these habitats can even be constructed from other wastes, for example blocks made from the waste from coal-fired power plants even processed mine tailings. Attempts at nearshore revegetation, for example, by shoreline algae, have varying degrees of success. Colonization of tailings by marine benthos has only been studied rarely. The ability of benthos to colonize subaqueous tailings deposits depends on the tailings toxicity and rate of burial by unpolluted sediments. At the Island Copper Mine in B.C. (Fig. 4), some 106 million tons of tailings were deposited in two fjords between 1960 and 1981. Some 50 km² are covered by tailings averaging 15 m in depth and a maximum of 35 m. Some polychaete worms and some clams have been able to grow on the tailings and form a new benthic population or rather to survive. Other organisms that appeared able to colonize on or near the tailings are oysters and crabs. Closer to natural conditions can be reached after about two years once the tailings have stabilized and turbidity is reduced. Fishing often occurs at sites of marine disposal of mine tailings including near Island Copper. Natural recovery occurs but could perhaps be accelerated by fertilization or capping of the submerged tailings.

4.3 Natural Controls and Modern Mitigation

At new mines, even at remote sites in developing countries, impact assessments and implementation of mitigation measures and ongoing remediation can be made part of the cost of metal mining. The OK Tedi Mine in Papua New Guinea (Fig. 4) has become one of the most studied sites of tailings discharge to a large tropical river system (Salomons & Eagle, 1990). By 1989, some 150,000 tons of Cu-rich ore was milled each day. Tailings and other waste materials are discharged to the OK Tedi, a tributary of the Fly River which is the largest river in Papua New Guinea and which discharges to the Coral Sea. Questions about potential pollution of the Coral Sea and impacts on the Great Barrier Reef resulted in analyses of the fate of the metals in the tailings. Most of the Cu-rich tailings have particle sizes $<100\text{ }\mu\text{m}$ and are thus transported down the entire river system, a distance of over 1,000 km before being largely deposited in quiet coastal zones. The natural carbonate-bicarbonate geochemistry of the river system buffers acidity. Because of the high dissolved organic carbon geochemistry of the river, Cu remains largely in the suspended sediments. Some dissolution of Cu occurs in the coastal marine environment. Since 1981, a progressively more complex monitoring program has been used to assess the impact of the tailings discharge. Hydrological, geochemical and biological measurements included cation exchange capacity (CEC) of the suspended sediments and the water complexing capacity for Cu. Copper-enriched tailings are diluted downstream by natural sediments with a higher CEC capacity. Modelling of dissolved Cu has taken into account alkalinity, pH and dissolved organic carbon and predictions closely match measured concentrations.

The Navan deposit in Ireland (Fig. 4) is 80 million tons of Zn-Pb located 50 km north-west of Dublin. Modern technology and mine practices are employed (Aldwell, 1990). All aspects of soil and water contamination by Zn, Pb and Cd are considered. Various European Community environmental directives came into effect during the opening of the mine in 1977. Dust with elevated Pb concentrations was considered a worse problem for local human health than waterborne contamination of the nearby rivers. The dust problem was found to be mainly related to drying out of the tailings in spring due to frost and strong winds, a situation probably unique to this site. The water quality standards to be met after any effluents were released were those recommended for salmonoid rivers. There was a specified sampling regime for effluents and the river, including fish analyses for metals and population surveys. The main sources of water pollution are as usual, mine drainage; surface drainage from the site; mineral processing effluent; and tailings discharge. Water is stored and recycled and the final discharge to the River Boyne is by a 31 m long distributor on the bed of the river and is altered depending on river flow. A three-stage tailings pond is some 5 km from the river. The tailings are kept saturated, drains intersect seepage, and areas of the dam floor that need it have a clay liner. Observation wells allow metal analysis of seepage. Rehabilitation of the tailings involves revegetation with Zn and Pb tolerant grasses and is expected to produce a permanent vegetation cover without the need for a

surface soil layer. Everything at this site is being done to reduce effects and to monitor all possible contamination in a manner that could result in immediate action to reverse it. Any complaints by the local population of the surrounding farming community are dealt with immediately.

4.4 Post Mining Leachate Remediation

The Rum Jungle mining area is in the tropical Northern Territory of Australia (Fig. 4). Uranium and copper were extracted from a number of ore bodies. After the mine closed in 1971, aquatic flora and fauna in the river below the mine site were adversely affected by trace metals. Waste rock dumps and the copper heap leach were found to be the dominant sources of Cu. Calculations of annual sulphate release and sulphur present showed that the waste dumps would continue to be a source of AMD and heavy metal pollution for hundreds of years. The rehabilitation strategy developed (Harries and Ritchie, 1988) consisted of covering the dumps with a seal to reduce water percolation; collecting the tailings and covering them with enough material to reduce radon release (because this was partly a uranium mine); removing the copper heap leach pile and disposing of the material above the water table in a location with minimal water ingress; treating the water in the open cuts to raise the pH and reducing the metal concentrations to a recreational standard where limited nose and ear contact with the pit water would be permissible; and cleaning up and revegetating the other areas.

4.5 Mine Tailings Revegetation

A major effort at revegetation has been underway for many years at Sudbury where the Inco Limited mining, milling, smelting complex is one of the world's largest (Fig. 4). Tailings were deposited in the valleys but as the tailings piles grew, dust control became a problem. A series of bituminous sprays, limestone chips, water and chemical sprays and snow fences were used to mitigate the problem. In the 1950's, a revegetation research program began using various local grasses and other plants (Peters, 1988). The tailings were pre-treated by mixing in limestone and fertilizer. Other additions tried with varying success were wastes from cement, paper, chemical and sewage plants. The mixing of wastes to achieve a benefit is a valuable concept but costs can be prohibitive due to transportation. Irrigation was used when needed.

Over the 30-year program, several key guidelines to revegetation were developed. These included adding limestone to raise pH to 4.5 to 5.0 before seeding; planting be at a time of adequate water supply; introducing seedlings closest to the prevailing winds to prevent their burial; creating rapid colonization; using combinations of plants to provide shade for grasses; using mulch to provide shade and to reduce moisture loss; reducing moisture loss on slopes by clay covers using

local species of plants; applying nitrogenous fertilizer frequently; and using nitrogen fixing plants if possible.

By the mid-1960's, local birch trees and some aspen and willow had invaded the grassed areas. In the early 1970's, several types of trees were subsequently tested. Jack pine proved the most successful. Cattails, bulrushes and mosses became established around ponds. Insects, smaller mammals and birds followed. Uptake of heavy metals by these animals was investigated and not considered a problem. Finally, Canada geese were introduced in 1985.

Revegetation mitigates effluent water quality because plants intercept precipitation, transpire it, and form an oxygen consuming barrier, reducing AMD and thus heavy metals in leachates. These general procedures and principles applied at the Sudbury area could be the basis for similar revegetation attempts elsewhere. Specific additions of limestone, fertilizer, or rock phosphate are required depending on local conditions, as well as the composition of the species mix. However, at any site, much is on a test, trial and error basis and must usually be long-term to guarantee a satisfactory outcome.

5 Regional Remediation

Regional pollution related to mining activities, other than by aquatic transport, is usually the result of airborne dispersion. Locally, dust from tailings or other waste sites can be a problem and this was mentioned above. Regional airborne dispersion occurs from the stacks of smelters and roasters. At such sites there are tailings or waste piles and local soil pollution and groundwater contamination. These local problems can be remediated by the procedures described earlier. The regional scale is outside the plant fence, perhaps several kilometres out from the plant. The outward extent of contamination can be tens to hundreds to even thousands of kilometres if the smelter has a super-stack. Other than cutting off all emissions, there is little that can be done to reduce long-range, low-level impacts of contaminants in smelter emissions. However, at the medium regional scale of tens of kilometres around the plant, some forms of pollution can be remediated.

The first step in regional remediation is to assess the extent of the contamination. Pollution from a smelter could involve acidification and heavy metal contamination of waterways, particularly lakes, and soils, and impacts on crops and vegetation, for example, forests. Pollutant transport models can be used to define the most polluted areas or actual analyses of soils, vegetation and water bodies to determine the extent of the most contaminated sites. Once the most severely acidified or heavy metal contaminated water bodies or soils are identified, remedial options similar to those described above for local problems can be considered. The impacts of the pollutants vary, of course, dependent on the natural geochemistry of the soils and water bodies, namely their buffering or metal sorption capacity. Clean-up will be a priority if urban areas or villages are within the highly polluted zones, especially if human health is directly affected. It may be

necessary to replace or treat garden soils used to grow food. If, on the other hand, the major impact is in a wilderness area, the priority may be lower for expensive *in situ* remediation.

The options that can be used regionally, range from doing nothing to closing the smelter. Intermediate remedial options are to define the most polluted sites in a socio-economic context and to clean these up. Remediation could include treatment of contaminated drinking water reservoirs to removing metals; setting fish consumption advisories for water bodies; liming of lakes or soils; covering of contaminated soils with new top soil; immobilizing metals in the soil by adding clay or manure to increase sorption capacity; *in situ* treatment of soils to remove heavy metals; removal and disposal of contaminated soils or sediment; deep ploughing of soils to lower surface metal contamination; leaching soils with irrigation techniques and perhaps collecting and treating the run-off.

The above options should only be pursued if accompanied by application of the best available or practical technology at the emission source. Application of best available technology can be a costly hard option. Soft options are to better educate the smelter operators; to inform the operators of the regional pollution consequences, even to their own families, of mistakes or carelessness; better discipline at the plant; good housekeeping; preventative maintenance; and quality management. All of these low cost, soft options can result in emission and regional pollution reductions. Some of the options to reduce emissions are cost effective. For example, SO_2 can be converted to sulphuric acid and sold and Cd can be removed and sold.

Various land use alternatives should be considered. For example, crops and animals for human consumption can be raised on the least contaminated zones; for some animal feed (not for human consumption) on the more contaminated sites; and the most contaminated sites used for crops to produce textiles or for non-agricultural uses. Some metal hyperaccumulator crops can be used on a regional scale to bioaccumulate metals from the soils and help to decontaminate them. If groundwater has been contaminated, then the remediation procedures described earlier can be considered. These involve hydraulic curtains; extraction and treatment; isolation of aquifers; and regulations on aquifer uses. If a considerable area is severely contaminated, a final drastic option is simply to abandon the area, move the people and let it return to nature as best it can.

6 Remediation to Pre-Mining Status

In Canada, the last twenty years has seen a great increase in the number of lake and stream sediments systematically sampled and analyzed for heavy metals for ore deposit exploration purposes. By using GIS systems to link these individual surveys, maps of extremely large areas can be produced. The sampling procedures for the Canadian Shield were such that the concentrations reflected background conditions and excluded anthropogenic influences such as mining or smelting.

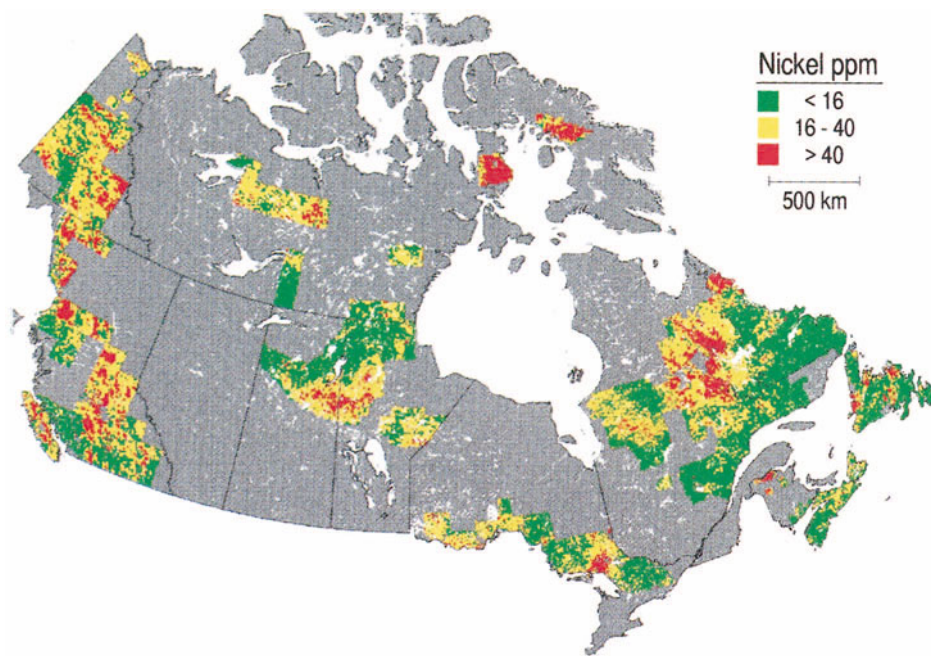


Fig. 5. Nickel distribution in aquatic sediments in Canada

The Ni anomaly associated with the Sudbury area is clearly seen north of Lake Huron (Fig. 5). Similar naturally elevated concentrations are found for other heavy metals in other parts of Canada.

When ore deposits are discovered, they often have surface outcrops which are already oxidized and leached and already have heavy metal rich, acidic runoff resulting in heavy metal anomalies in downstream rivers and lakes. Such weathering may have gone on for thousands (glaciated) to millions (tropics) of years and the vegetation and biota at these sites adapted to the conditions. In all cases, local and regional, consideration of the natural heavy metal concentrations in soils, sediment, water and effects on biota at mineralized sites should be considered as a baseline for remediation. Most metal-rich waste sites are hostile environments for most plants because of toxic metal concentrations; low plant nutrient levels; physical structure in the wastes; and variable oxygen access to the wastes. However, vegetation and biota that are metal tolerant often occurs at mine sites in spite of existing geochemical anomalies related to the ore deposits and such plants may be useful in mine waste remediation.

7 Conclusions

Terrestrial and aquatic ecosystem contamination by acid mine drainage and heavy metals is a global phenomenon. In some developing countries, there are often no environmental restrictions on mining activities or if they exist, are seldom enforced. The same now appears to have applied under the former regimes in eastern Europe and the Soviet Union and may still apply to remaining communist states. In the industrialized nations, the situation, although normally much better, is sometimes far from satisfactory. Many mines have operated for years, even centuries, with few restrictions. Regulations have been applied only recently and often only to new mines.

The basic problem with mining is the enormous volume of the wastes. Disposal on land has been the historic procedure but it is clear that in nearly all cases this results in acid mine drainage and heavy metal dispersal and contamination. Disposal of tailings or effluents into waterways injects the contamination directly. However, under specific conditions subaqueous disposal greatly reduces AMD but alternatively toxic metals are released or recycled or other impacts occur on biota.

Given the ongoing development of legislation on mine wastes and disposal practices, it is likely that subaqueous disposal may not always be sanctioned, even when it avoids some terrestrial contamination problems.

The main steps in remediation of mining site pollution are to: (1) assess the extent of the local site pollution and quantify the sources of AMD, heavy metals and other pollutants; (2) control the major sources (waste dumps, tailings, air pollution, etc.). [Control effluents/emissions, reduce leachates, bury, lime, remove treat (leach, extract etc.)]; (3) assess the regional pollution status and identify hot spots. [Remediate hot spots - dredge rivers, lime lakes, treat *in situ* (create anoxic conditions), flood, bury, cover, etc.]; (4) leave to natural recovery or accelerate. [Increase erosion/deposition of clean sediments in bays/rivers, divert alkaline streams (AMD), eutrophy, flush, create wetlands, etc.] The terrestrial techniques that can be employed include covering tailings to reduce infiltration (soils, vegetation, clays, tills, polymers or cement like materials); artificial creation of hard pans (limonite, goethite, iron hydroxide) to reduce infiltration; or blending in alkaline wastes. Polluted soils can be removed (treated, better disposed of) given new soil covers (buried) or limed. Aquatic sediments can be dredged (dewatered, leached, treated, disposed of in new, well designed waste sites), buried, or treated *in situ* (limed), or left to nature to restore. The aquatic techniques include subaqueous disposal in general or creation of water covers (anoxic conditions), or wetlands (to leach, filter contaminants and create anoxic conditions). High technology is not often the best long-term solution. Low technology, in particular the evolving biotechnology that would be especially practical in less wealthy nations, may be the best solution at many sites.

Remediation of mine sites is often beyond the financial ability of all but major corporations. Vast open pits, and polluted soils, river, floodplains, lakes and coastal zones such as fjords abound, even in the most advanced environmentally

conscious nations. Given the number of mines, historical and present, and their associated waste rocked tailings piles and dumps and zones of aquatic ecosystem contamination, remediation or at least mitigation are a monumental task. Hopefully, new mines - and this is far from true - will employ state-of-the-art mitigation procedures such that additions to the global mining pollution inventory are kept to a minimum. The general requirement is that the best remediation is prevention or at least economically feasible mitigation while the mine is in operation. A mine site is usually already mineralized and often a geochemical anomaly for heavy metals and a source of AMD. The geochemical characteristics of the site should be assessed in detail. Exploration - trenching, drilling - and construction can enhance these long before mining itself begins. Environmental controls need to be in place even during these pre-production stages and eventual environmental impacts should be carefully assessed. Future environmental problems should be mitigated or avoided in the design of the mine and its operation. Environmental controls should be built in as construction proceeds and mining gets underway. Retrofitting or eventual clean-up is likely to be far more costly, never mind the corporate image generated by a lack of environmental awareness. During all stages, but especially from the start of construction, all environmental impacts should be monitored.

During mining operations, impacts should be continually assessed against predictions, for example the changed geochemical characteristics of lakes or rivers, and adaptation made as required - perhaps less routine measurements and more process research becomes the key requirement. Remediation should be ongoing so that as much as possible is done while the mine is producing and generating income. For old sites at operating mines, retroactive procedures such as revegetation, leachate treatment and others should be tried. Where human health concerns occur, for example due to food toxicity from mining pollution or wildlife and aquatic resources are impacted, the will is often there to remediate. In other cases, the situation may well be left to nature to heal as best it can.

Open metal mine pits present distinct problems. When pits result from coal mining, there may be little of the deposit left. The pits can be filled, flooded, and subject to various remedial measures, although these may well be costly and fraught with questionable predictions as to future groundwater impacts. In some cases, where coal mining has involved vast open pits, for example in the brown coal area west of Cologne in Germany, the plans for remediation are carefully implemented in great detail. As the coal is mined, waste from other pits is used to fill them, the landscape and soils are restored, and even the villages mined around or moved and rebuilt. This enormous remedial effort is only possible with decades of forward planning and because of agricultural land scarcity and economics. However, metal mine open pits are different, in that the viability of the mine depends on fluctuating world metal values and supply and demand. When a metal mine open pit is abandoned, this usually does not mean that the metals are all removed, only those economically feasible to do so at that time. Metal mine pits are opened, closed, opened and may well be needed by future generations when techniques to extract lower grade ore are used or developed or when the

economics change. Remediation of such pits may only add or even prevent re-opening. There is a question then as to just what degree of remediation is desired for metal mine pits.

Innovative techniques for *in situ* treatment may need to be attempted. For example, once sources are controlled, a polluted water may be decontaminated by a series of well planned flushing stages, with construction of temporary dams to collect contaminated sediments, or the flushed sediments (to lakes, reservoirs) may then be subject to accelerated natural burial by increased upstream erosion or by *in situ* generated eutrophication. Such scenarios have not been attempted because of the faster than predicted rate of natural recovery and the fear of making the situation worse. The latter often also applies to dredging of hot spots. Nevertheless, if the situation is bad enough and the health consequences serious enough, costly engineering solutions may have to be considered.

If wise regulations, based on good ecosystem science, are set, monitored by adequate indicators of ecosystem health, and enforced, then pollution from future mines will be substantially mitigated. Meanwhile, and for the foreseeable future, the implementation of adequate mitigation globally remains an issue as well as the requirements for remediation of existing wastes. The need for innovative remediation techniques will escalate as well the need for the research to arrive at these techniques and predict their outcome. However, in many cases, remediation is beyond engineering and economical feasibility and assessment of impacts may be all that is possible while nature attempts to self-cleanse.

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9 Decontamination or Consolidation of Metal-Contaminated Soils by Biological Means

W. H. O. Ernst

Department of Ecology and Ecotoxicology, Faculty of Biology, Vrije Universiteit,
De Boelelaan 1087, 1081 HV Amsterdam, The Netherlands

1 Introduction

All industrialized and nonindustrialized countries have used and are deliberately using heavy metals for industrial, agricultural, and domestic purposes without any consideration in advance of the treatment of the remnant metals. As a consequence, heavy metals are being deposited widespread in the environment. The metal deposition chain starts with the remnants of mining activities in the form of mine tailings, spoil heaps, and dumps, in Southern, Central, and Western Europe, often dating back to Greek and Roman minings (Ernst 1974, 1990). Insufficient precautions for stored ore dust and for a strong reduction in metal emission during grinding, smelting, and processing of ores and metal products and refining has polluted and still pollutes the surroundings of smelters, blast furnaces, and other metal-processing industries either by dust and particulate matter or by metal-enriched effluents (Ernst and Joosse-van Damme 1983, 1989). Environmental pollution was and is independent of political regimes, and unfortunately, in many cases, even independent of the technological conditions of a country, as the metal pollution around metal smelters has demonstrated in former West Germany (Ernst 1972; MAGS 1977), former East Germany (Fiedler and Rösler 1987), Bulgaria (Tsuldschijan 1978), former Yugoslavia (Djuric et al. 1971), and Poland (Fabiszewski et al. 1983; Greszta 1988). Although mining and processing activities have often been finished for some time, tailings and dumps are still scarcely covered by vegetation (Ernst 1974; Banášová 1976) and are exposed to water and wind erosion, thus extending the pollution of the environments. By water erosion, heavy metals have enriched river sediments throughout Europe (Förstner and Wittmann 1981) and can affect ecosystem processes up to the estuaries (Otte 1991; Otte et al. 1990). Listing of polluted sites and analyses of the degree of pollution and of its impact on flora and fauna are the first necessities on the long way to problem solution. This chapter discusses the possibilities of decontamination and consolidation of metal-contaminated soils in Europe by biological means. The response of plants and vegetation to mine tailings and dredged materials have recently been reviewed (Ernst 1988) and will be updated here as necessary for the demonstration of adequate plant material.

2 Potential of Plants for the Evolution of Metal Resistance

The natural exposure of plants to a surplus of heavy metals, i.e., on outcropping ore bodies, has given rise to the evolution of metal-resistant plants all over the world, thus also in Europe (Ernst 1974, 1990). The specific impact of the various heavy metals on biological processes is the reason for a metal-specific resistance (Ernst 1994; Ernst et al. 1994) and at the same time the limitation of the evolution of resistance to a lot of metals within one genotype (Schat and ten Bookum 1992). The evolution of resistance to very high metal concentrations in the environment is restricted to a few plant species, from bacteria to higher plants, primarily detected in *Melandrium rubrum* on a copper mine in Piesky/CFR (Prat 1934). Despite a low species diversity already on ore outcrops and a further decrease of this diversity on anthropogenically polluted sites, even a heavily polluted soil can support a complete functional ecosystem, as is demonstrated by the surroundings of a zinc-cadmium smelter in The Netherlands (Vekleij and Ernst 1991) with Zn-Cd resistance in the bacteria *Alcaligenes eutrophus* (Diels and Mergeay 1990), in vesicular-arbuscular mycorrhizal fungi (Ietswaart et al. 1992), and in several grasses such as *Agrostis capillaris* and *Festuca rubra* (Dueck et al. 1984). At a certain distance to the smelter, several soil arthropods have also evolved some resistance to a surplus of zinc and cadmium, such as the woodanse *Porcellio scaber* (van Capelleveen 1985) and the springtail *Orchesella cincta* (Posthuma 1990). As a consequence of metal resistance, the productivity of biota and the turnover of nutrients via decomposition of metal-enriched litter is very low. This decrease of productivity is even stronger when a plant is able to hyperaccumulate a metal, i.e., to concentrate the metal to more than 1000 mg Me²⁺ per kg dry matter. Such hyperaccumulators, e.g., *Thlaspi coerulescens* for zinc, cadmium, and copper, and *Alyssum* species for nickel (Ernst 1994) not only grow slowly, but their leaves are arranged in a rosette, remaining near the soil surface, so that they are difficult to be removed by mowing.

There is sufficient evidence that some of the plant species with a high potential for the evolution of metal resistance occur in every country of Eastern and Central Europe, e.g., *Silene cucubalus* (Prat 1934; Ernst 1974; Banášová 1989; Ernst et al. 1990), *Agrostis capillaris* (Banášová 1976; Dobrzanska 1955), *Festuca ovina/rubra* (Banášová 1970; Petrunina 1974), *Cardaminopsis halleri* (Ernst 1974). A survey of experimentally proven metal resistance is presented in Table 1.

Table 1. Metal resistance of plant species in Europe as tested by well-designed experiments

Plant species	Metal resistance	Reference
<i>Agrostis capillaris</i> (= <i>A. tenuis</i>)	Zn	Dueck et al. (1984)
	Zn	Gartside and McNeilly (1974)
	Cu	Nichols and McNeilly (1982)
<i>Agrostis stolonifera</i>	Cd, Ni, Cu, Pb, Zn	Symenoides et al. (1985)
	Zn, Cu	Wu and Antonovics (1975)
<i>Anthoxanthum odoratum</i>	Zn	Cox and Thurman (1978)
<i>Deschampsia caespitosa</i>	Zn	Godbold et al. (1984)
<i>Festuca ovina</i>	Zn	Brown and Brinkman (1992)
	Zn	Simon and Lefebvre (1975)
	Pb	Urquhardt (1971)
<i>Festuca rubra</i>	Cu	Karataglis (1982)
<i>Melandrium rubrum</i> (<i>M. sylvestre</i>)	Cu	Prat (1934)
<i>Silene otites</i>	Cu	Ernst (1975)
<i>Silene vulgaris</i> (= <i>S. cucubalus</i>) (= <i>S. inflata</i>)	Zn	Bröker (1963)
	Cu	Schat and ten Bookum (1992)
	Cd	Verkleij and Prast (1989)

3 Decontamination of Metal-Polluted Soil by Plants

With the presence of metal hyperaccumulators, it is very tempting to believe that contaminated soils can easily have their metal surplus removed. Several molecular biologists/biotechnologists believe they have achieved this aim by transferring resistant genes from slow-growing metal-tolerant plants to highly productive agricultural crops. Up to now, our knowledge of the genetics (Schat and ten Bookum 1992) and the physiology of the various resistances to metals (cf. Ernst et al. 1994) is too incomplete to realize these ideas within the next two decades.

Therefore, the principal aspect of decontamination is the degree of pollution and metal speciation of the polluted soil; but in advance of the discussion of soil decontamination by biological means, a definite solution has to be found for the final destination of the metals received by the decontamination procedure. How do we handle the contaminated plant material? Or do we simply aim to decontaminate one site by dispersing the contaminated plant material to less contaminated sites as it was done after an in-situ Cd-decontamination of a soil in the Netherlands by transporting the Cd-enriched solutions to Belgium for uncontrolled disposal. In this way, a local problem is solved by increasing a regional problem.

A soil should never be decontaminated as long as there is no solution for the processing of the metals, extracted by chemical or biological means from that soil.

Slightly metal-contaminated soils can be decontaminated by growing very productive crops so that they can be brought to nationally accepted standards for clean soil. However, such a procedure will result in a lot of slightly contaminated

biomass, which should not be mixed with uncontaminated material for animal or human consumption. This contaminated biomass can be reduced in volume and mass by controlled decomposition. Care should be taken to trap volatile metals during the decomposition process.

Heavily contaminated soil can be decontaminated by growing metal-resistant plants on it, moving the standing biomass at the end of each growing season, and carefully extracting the metals from this biomass and recycling the metals for further industrial purposes. This procedure, however, is only effective over a long term (see Tables 2, 3), often lasting some hundreds or thousands of years. This process can be partially enhanced when other growth-limiting factors, often present in heavily metal contaminated soils, are improved. Soil acidity can be diminished by the application of chalkstone, but at the same time the availability of metals to plants is decreased, thus prolonging the period of decontamination. Shortage of soil water can be mediated by sprinklers, but care has to be taken to avoid metal transport to deeper soil layers or runoff into other ecosystems. Shortage of major or minor nutrients can be improved by fertilization, but an addition of phosphorus may diminish the availability of metals to the plants and thus lower

Table 2. Decontamination of a tailing of a zinc-cadmium smelter

Assumption	1. The uptake of the heavy metals remains constant over time (i.e., no change due to speciation) 2. The productivity of the vegetation being made up by a locally selected metal-resistant population of <i>Agrostis capillaris</i> is kept at the same level. Mowing does not influence productivity 3. The contaminated soil layer is only 30 cm thick; there is no loss of metal by runoff			
Data	500 g dry matter standing crop per m ² ; 5 t ha ⁻¹ 400 g dry matter can annually be removed by mowing: 4 t ha ⁻¹ Specific mass of the tailing material 1.2 g cm ⁻³ Contaminated area: 1 ha, 30 cm depth			
Metal concentration (g kg ⁻¹)	Zn	Cd	Cu	Pb
Tailing material	15.000	0.007	2.000	0.300
Dutch clean soil standard	0.200	0.001	0.050	0.050
Grass (shoot)	1.185	0.0012	0.042	0.097
Mass balance	Zn	Cd	Cu	Pb
In 3600 t tailing kg metal	54 000	25.2	7 200	3 240
In 3600 t clean soil kg metal	720	3.6	180	180
X: to be extracted from the tailing kg	53 280	21.6	7 020	3 060
Y: annual removal by mowing, (kg): (4 t hay)	4.74	0.0048	0.168	0.388
Period necessary for biological clean-up in years (X/Y)	11 241	4 500	41 786	7 887

Table 3. Decontamination of agricultural fields, formerly supplied with sewage sludge

Assumptions	1. The uptake of metals by plants remains constant 2. The productivity of the nonresistant plants (maize) is not affected by the bioavailable metal fractions: it is at 8 t ha⁻¹ yr⁻¹ 3. The contaminated soil layer is restricted to 50 cm soil depth (plowing depth) There is no percolation of metals to the groundwater			
Data	Productivity: 8 t aboveground biomass of maizes ha⁻¹ Specific mass of a sandy clay: 1.2 g cm⁻³ Contaminated area: 1 ha, 50 cm depth			
Metal concentration (g kg ⁻¹)	Zn	Cd	Cu	Pb
In the field soil	0.700	0.003	0.092	0.150
Dutch soil standard (A level)	0.200	0.001	0.050	0.050
In maize shoots	0.156	0.0025	0.003	0.0028
Mass balance	Zn	Cd	Cu	Pb
Metal in the plowing layer (6 000 t soil) kg	4 200	18	558	900
Clean soil (6 000 t)	1 200	6	300	300
X: to be removed from field soil (kg)	3 000	12	258	600
Y: annual removal by maize harvest of 8 t ha ⁻¹ (kg)	1.248	0.021	0.024	0.224
Period necessary for biological clean-up (X/Y) in years to achieve A-level	2 404	571	10 750	2 679

^a The choice of another plant species can enhance metal accumulation in the shoot.

the efficiency of the decontamination. The application of municipal sewage sludge (Gemmel 1977) can diminish nutrient deficiency, but due to the rapid breakdown of the organic matter and its enrichment by heavy metals (Ernst and Joosse-van Damme 1983), such a procedure will not help to solve the problem.

The influence of redox potential and plant species on uptake of heavy metals may modify the general uptake pattern (Brown et al. 1989). Generally, in the case of nickel, it has been demonstrated that the uptake rates by plants, with *Avena sativa* as model plant, was inversely related to the concentration of dissolved organic carbon in the soil solution (Dunemann et al. 1991). With regard to grasses, it is very important to recognize that grasses release specific iron-binding compounds, the siderophores (Römheld and Marschner 1990), which affect not only the uptake of iron, but may also influence that of other heavy metals.

Removal of the soil and cleaning it up with the aid of microorganisms, especially *Thiobacillus ferro-oxidans*, is a technique well known from the extraction of metals for mining purposes (Kelly and Tuovinen 1988). With regard to soil de-

contamination, an operational procedure has not yet been developed which also takes into account the treatment of the metal-enriched solvents.

Decontamination of soils by thermal treatment or chemical extraction of the metals are technical means, which can result in partially cleaned-up material. Recolonization of such decontaminated soils presents many biological problems. Using earthworms (*Eisenia foetida*), lettuce (*Lactuca sativa*), and radish (*Raphanus sativus* cv. Novired) as test organisms on cleaned-up soil, with and without addition of compost and incubation for some months, resulted in nonacceptable plant growth. Despite the extraction of metals, the metal bioavailability of the cleaned-up soil increased relative to its total concentration. As a final result, the cadmium concentration of lettuce and radish exceeded the acceptable reference concentration (Van Gestel et al. 1992). In conclusion, recolonization of decontaminated soils by vegetables is strongly hampered, often by not-yet-identified factors. In addition, nothing is known of the fate of the metals which have been extracted from the soil.

4 Consolidation of Metal-Contaminated Soils

Tailings, dumps, and spoil heaps of metal-processing industries contain such quantities of heavy metals that they can only be colonized by metal-resistant plants. By enhancing the revegetation, soil erosion by water and wind can be prevented, until a time when decontamination procedures are sufficiently sophisticated to solve the problems. After a thorough analysis of the bioavailable and total metal concentration of such soils, an appropriate selection of the specific metal-resistant genotypes of plants can be made (for species and genotypes, see Table 1). As long as commercial seed is not available, the manager of such an area has to breed the plants himself, an easy, but time-consuming task. A mixture of grasses and herbs will help to develop a functional, metal-resistant grassland ecosystem at metal-contaminated sites; but managers and planners have to be aware that this green is a dangerous green. It is not suitable for grazing cattle (cf. Ernst and Joosse-van Damme 1983, 1989) or for children to use as playgrounds, due to intoxication problems (MAGS 1975). Therefore these areas have to be forbidden for human activities.

One of the factors which hamper a rapid revegetation of these contaminated soils even by metal-resistant plant is a high imbalance of the major and minor nutrients (Ernst 1974, 1988), which can easily be restored by application of small amounts of fertilizers. During the vegetation succession, plant species with a symbiosis with nitrogen-fixing bacteria, especially the *Rhizobium*-legume symbiosis, may establish themselves or can be artificially implanted into this grassland. Another symbiosis, i.e., that of higher plants with vesicular-arbuscular fungi, will establish itself due to the rapid spore dispersal of VAM fungi (Gildon and Tinker 1981; Ietswaart et al. 1992). Only copper-contaminated soils will not allow the

establishment of VAM fungi because the well-known fungicidal function of copper is effective for mycorrhizal fungi (Griffioen and Ernst 1990).

Reforestation of heavily metal-polluted soils will remain unsuccessful, because some tree species (birch, poplar) can achieve only a very moderate metal-resistance (Brown and Wilkins 1985; Eltrop et al. 1991). Ectomycorrhizal fungi can even enhance the metal toxicity to coniferous trees, as demonstrated for the symbiosis of Scots pine with *Telephora terrestris* (Colpaert and van Assche 1992). Even if a tree seedling establishes itself on a heavily polluted soil, it will have a very stunted growth, and often die after a few years of growth due to the inevitable uptake of a surplus of heavy metals (Ernst 1985).

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10 Engineering Methods for Control of Polluted Sites and Solid Waste Disposal

C. C. D. F. van Ree

Delft Geotechnics, P.O. Box 69, 2600 AB DELFT, The Netherlands

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This article is largely based on existing publications from the author and his colleagues of Delft Geotechnics. It is intended to give an overview of strategies which are followed with respect to soil and groundwater pollution based on a number of case studies. The author greatly appreciates the contribution of materials to produce this article.

1 Introduction

Due to a wide range of activities (industrial, mining, agricultural etcetera), it is clear that at numerous locations soil- and groundwater quality have been and are affected in a way that makes measures necessary. However, the extent of the problem, the state of technology and available resources impose more or less severe constraints in finding adequate solutions. Nullifying this damage is not possible and it is clear that at a large number of sites the soil environment will remain at risk. It is noted here that the term risk is used to define potential damage as well as uncertainties in this prediction. That soil- and groundwater quality will be at risk for some time, also due to future activities, has to be evaluated and quantification of risk can clearly contribute to optimization of spending scarce resources and the resulting environmental efficiency.

This article deals with the methodology used to identify problem areas for which countermeasures are necessary. Quite often it is found that soil contamination is present over large industrialized areas making a more overall approach necessary. Therefore the clusterconcept is presented.

Since this paper also deals with engineering methods some important aspects of geohydrological containment, cement bentonite barriers and sand-bentonite and clay liners are dealt with.

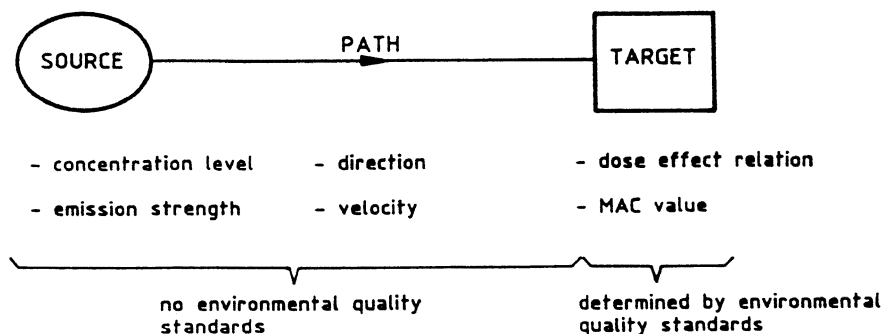


Fig. 1. "Source - path - target" model

2 Methodology

In order to be able to weigh the available options a framework has to be established.

Two elements can be identified:

- I The methodology
- II The standards set for soil, water and air quality

For example the A, B, and C-values of the Dutch Soil Clean-up interim act.

The conceptual approach is the "Source - Path - Target" model (see Fig. 1). In order to identify soil contamination as a problem which needs to be addressed, all three elements should be present. There has to be a source of contamination, a (clean) path, via which the pollutants can migrate and a target has to exist which is (potentially) threatened. Solving the problem can therefore consist of addressing at least one of the elements and reduce it to acceptable levels. Important in this respect are both the standards and the location where they are applied, for instance some distance along the path. Two approaches can be chosen for setting the standards. One is based on absolute concentrations derived from a general ecotoxicological evaluation. One could also consider standards differentiated to local conditions, however changes of land-use might in this case render a former remediation of a contaminated site inadequate.

3 The Cluster Concept [1]

Regional evaluation showed that some industrial activities will lead inevitably to significant emissions into the soil even without calamities occurring, meaning that the standards for a clean soil [2] can never be met under these conditions. This is mainly caused by the large toxicity ratio between the products produced and

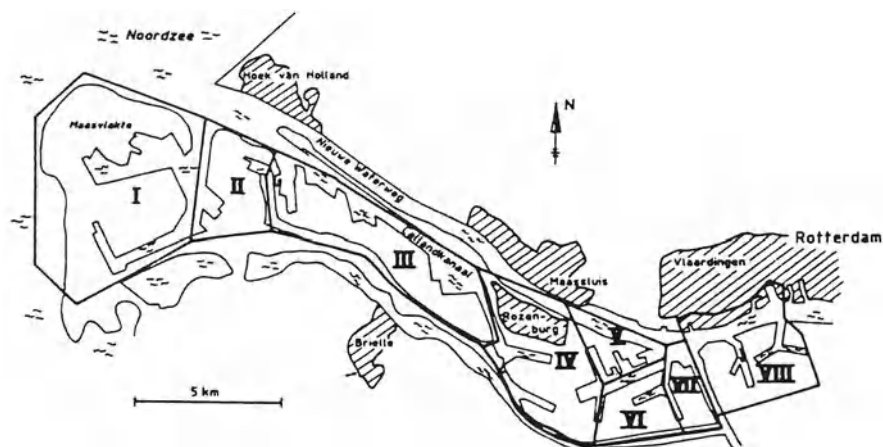


Fig. 2. Map of the 50 km² EBB-area and division into clusters

processed within the facilities and the maximum allowable concentrations in the soil and groundwater. Small quantities of product emitted to the groundwater have the potential to contaminate large quantities of groundwater.

West of the city of Rotterdam an extensive industrial area is situated which is called the "Europoort-Botlek" area. It comprises a total surface area of 50 km² completely taken up by petro-chemical complexes, bulk transshipment facilities, container terminals etc. (see Fig. 2). All these different industrial activities have had their own impact on the local soil and groundwater quality, during decades of operation. Moreover it became clear that in many cases a site contamination might easily migrate towards adjoining sites through the groundwater, resulting in counter-measures needing the cooperation of the companies involved.

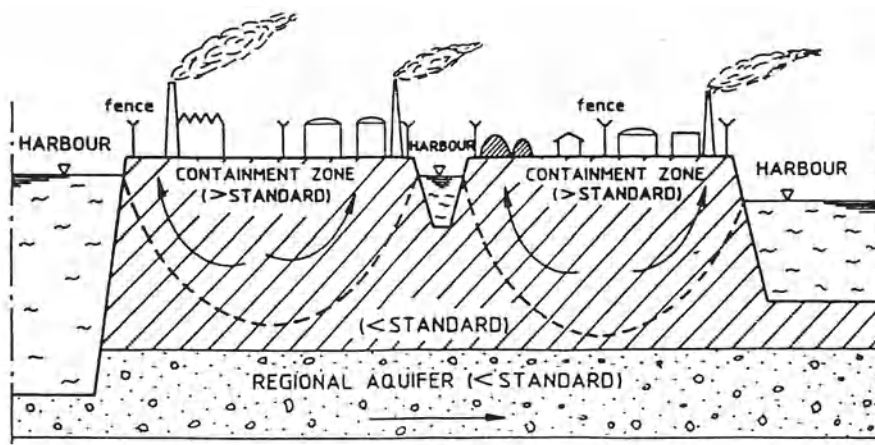


Fig. 3. Schematic representation of the cluster concept

In the EBB area there is much variety in industrial activities on relatively short distances. The diversity of products transhipped, processed or produced is enormous. In many cases soil remediation measures on individual company level will make no sense. Groundwater pollution plumes may pass site boundaries and are sure to influence groundwater quality below adjoining sites, certainly when (geohydrological) counter-measures are taken independently.

Delft Geotechnics set up a large-scale inventory and modelling study resulting in a completely new approach (the cluster approach) towards soil pollution control on industrial sites for the companies affiliated to the foundation "Europoort-Botlek Belangen" (EBB).

In this concept the area is divided into one or several management control units called the clusters. The cluster limits are defined by geohydrological boundaries according to Toth's definition of nested groundwater systems [3]. An essential element of the cluster concept is that fence lines are ignored when searching for common solutions. Within the cluster limits a certain contamination level may be accepted, but at the same time migration across the cluster limits should be avoided. In the cluster concept the emphasis is shifted from rigorous soil clean-up (by excavation) to pollution containment. The main principles of the cluster concept, as applied to the EBB area are shown schematically in Fig. 3.

Through short-term containment of contaminants and long term in-situ clean-up measures within the cluster limits, unacceptable risks for the surrounding area are avoided and soil quality standards applicable to sites for industrial use can be met in the long run [4].

The following principles were formulated to arrive at a plan of action:

- The quality of soil and groundwater may never be deteriorated to such an extent that serious risks for the environment or the public health are caused;
- In due course the quality of soil and groundwater shall comply with accepted standards for the industrial activities in the area;
- The occurrence of new cases of soil contamination will be avoided as much as possible by taking preventive measures. Should a new case of soil contamination occur then this will be cleaned up as soon as possible.

On the short term this policy will mainly result in the installation of containment and monitoring systems. In this way further spread of contamination and risks for the environment and public health will be avoided. On the longer term it is expected that better and cheaper technical means will become available for in-situ soil clean-up. Clean-up of the site will then be carried out in combination with major periodical renovation or construction works.

The cluster concept introduces the cluster as a basic unit for soil and groundwater pollution containment and remediation, as well as a management control unit. The concept creates a framework with which the main policy objectives can be realized.

In 1987 Delft Geotechnics started with a regional investigation into the possible consequences of industrial activities in the EBB area for the groundwater quality within the area and the risks of migration to the surrounding areas. Use was made

of an especially developed computer code REFCON (REFinary CONtamination model) [5,6] to simulate leakages and overflows and the consequences for local groundwater quality. Regional groundwater movement was calculated with the Delft Geotechnics' groundwater contaminant transport code VERA. It became clear that in some areas the shallow and intermediate groundwater systems would be significantly polluted and the regional groundwater quality could be seriously threatened.

The geohydrological investigation showed that the EBB area could be divided into 8 sub-regions, "clusters" (I-VIII, see Fig. 2), which would not influence each others groundwater quality or flow regime. The shallow and intermediate groundwater systems within the clusters are limited by the harbours and canals which divide the area (see Fig. 3). Within a cluster the individual firms are sure to influence each others groundwater quality so a joint approach is called for. This approach (the "cluster approach") gives a management framework and creates favorable conditions for a technical feasible containment concept.

4 Geohydrological Containment [7]

One of the option for containment is geohydrological containment. In principle this is a containment strategy were by means of a series of pumping wells contaminated groundwater is prevented from escaping from a site. In general this is a very flexible approach since the number of wells and the discharges can be varied even when the system is in operation. However there is a price to be paid in terms of clean groundwater drawn to the system and mixed with the contaminated water and the problems of water treatment. The main price however is that the system needs adequate monitoring and constant attention to check whether it fulfills its aims.

For an industrial site a containment has been developed addressing environmental, geohydrological, and geotechnical consequences. The development involved a program of extensive field investigations, the construction of computerized databases and the use of numerical models of the site. The field work and modelling activities have been performed as interrelated processes, which resulted in an optimization of both. In a series of steps involving data-acquisition, numerical modelling, and field-verification a geohydrological containment system has been developed. The attention given to geotechnical aspects results from the typical Dutch soft soils, where lowering of groundwater tables results in settlement which may lead to damage of construction and environmental and safety hazards.

Figure 4 shows the elements of which the approach is made up and which reflect separate studies performed. The major elements of the methodology for the design of a geohydrological containment system, consist of:

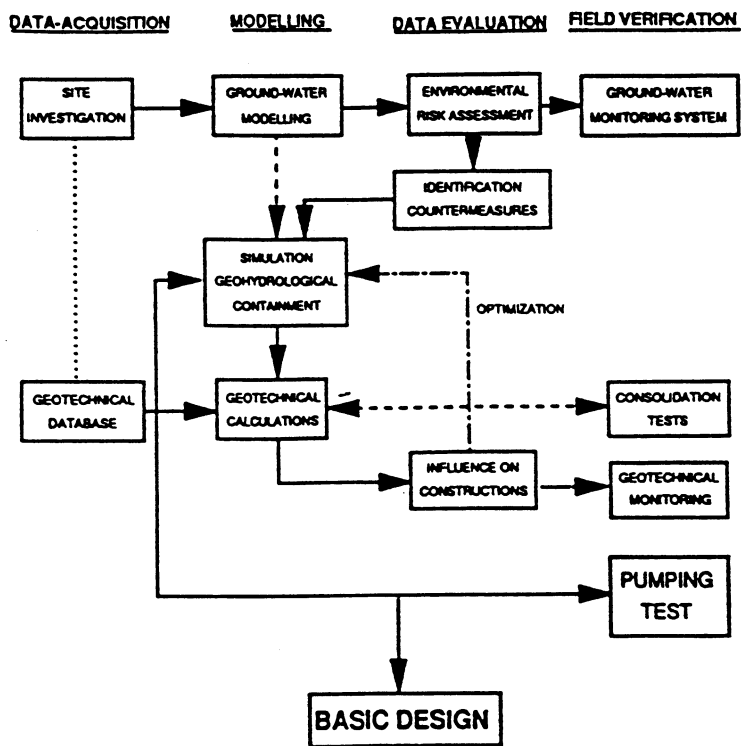


Fig. 4. Methodology used for the design of the geohydrological containment system

- "Source-path-target" analysis to determine the contaminant transport routes, coupled with a site investigation. Simulation of the three dimensional ground-water flow was used to quantify the distribution of water in the subsoil. Determination of transfer-functions for the quantification of emissions (contaminant transport fluxes),
- Comparison and weighing of environmental risks
- Identification of containment strategies and techniques
- Evaluation and selection based on technical, economical and social constraints

5 Case History of a Geohydrological Containment System for a Zinc-Smelting Works [8]

Industrial production of zinc from 1892 had caused contamination of groundwater in an area of a few hundred hectares.

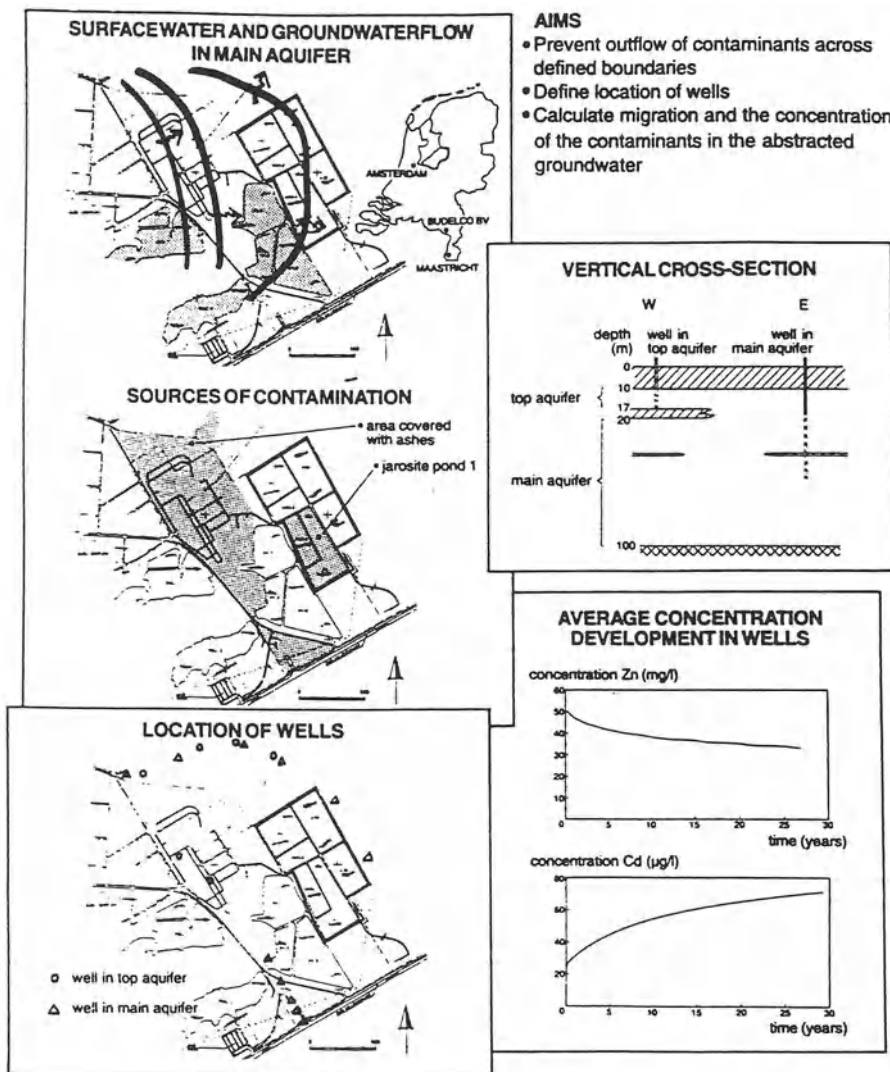


Fig. 5. Geohydrological containment system for a zinc-smelting works

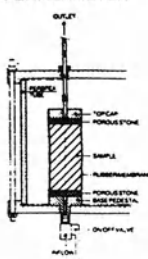
The sources of contamination are the area covered with the remaining ashes from the earliest production form of zinc and the leakage of pond 1, where jarosite, a remainder of the present electrolyses production proces was stored.

Investigations revealed contamination to a depth of 33 m (zinc) and 25 m (cadmium). Sulphate was present in higher than background values to a depth of 70 m.

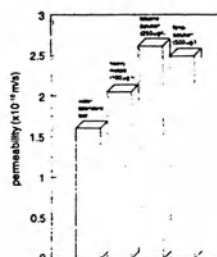
In a series of modelling exercises and site surveys a geohydrological containment system was developed.

- determination of the influence of dissolved contaminants on the hydraulic conductivity (k) of a cement/bentonite mixture

SCHEMATIC DRAWING OF PERMEAMETER

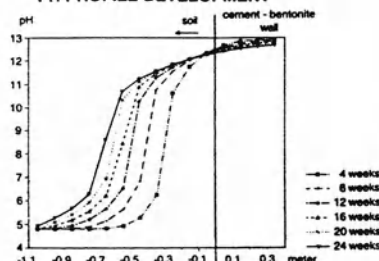


RESULTS



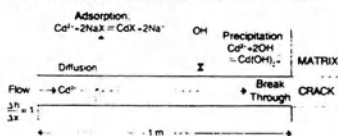
- diffusion of OH^- from the cement bentonite wall into the soil may result in an increase of soil pH and subsequent heavy metal precipitation

PH PROFILE DEVELOPMENT

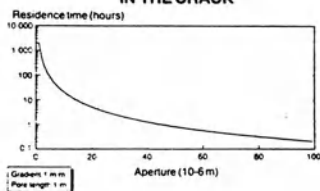


- transport of contaminants through cracks in cement bentonite

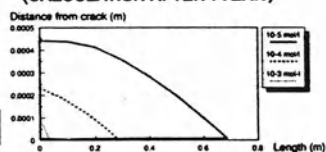
SCHEMATIC OVERVIEW OF PROCESS



MEAN RESIDENCE TIME IN THE CRACK



CADMIUM ADSORBED AND PRECIPITATED (CALCULATION AFTER 1 YEAR)



CALCULATED BREAKTHROUGH CURVES

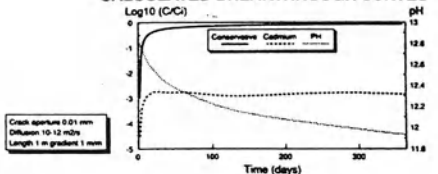


Fig. 6. The effects of contaminants on the properties of cement bentonite cut-off walls

6 Cement-Bentonite Barriers

In areas where geohydrological containment leads to unacceptable high discharges or prohibitive purification costs use of barriers might prove necessary. Use can be made of sheet piling, combi-curtain walls with synthetic liners, concrete walls and cement-bentonite walls.

The first intention is to introduce a low permeability zone resulting in higher resistances against groundwater flow. The closer the barrier is to the source, the higher the concentrations of the pollutants exposed to the material of the screen will be. This can cause mechanical and chemical stability problems to the barrier.

The hydraulic conductivity is the ruling parameter in terms of groundwater flow through the barrier. It is there important to identify the influence of dissolved contaminants on the permeability.

Experiments on the effects of contaminants on the properties of cement bentonite cut-off walls have been performed as part of a Dutch National Soil Research programme to gain insight on the long term stability of this type of barriers due to geochemical processes.

7 Design and Insection Procedure for Liners [9]

Nowadays, for waste dumps as well as industrial facilities like tank farms, use of liner systems to prevent emission of contaminants to the surrounding geosphere are common. These measures generally involve the application of a base and/or cover liner to reduce the infiltration in to and the leaching of contaminants out of the waste site or potentially polluted area. In practice, low permeability natural clays and sand/bentonite mixtures or synthetic materials are used, provided that some permeability specification is met. This paper restricts discussion to liners made from natural materials. Controlling such liners, both from a design point of view as well as testing the actual liner, is of great importance since processes involving groundwater flow and contaminant transport are relatively slow and the effectiveness cannot be measured immediately upon completion.

Inspection results have shown that a more rigid approach to the design process and quality control is necessary, in order to be able to compare actual performance of the liner based on test results with the original design criteria. A standard procedure has been developed and in this paper results for a number of liners are presented.

In order to attain adequate construction standards the following phased approach is applied. For a more extensive description reference is made to Delft Geotechnics (1991) [10].

- a. By means of preliminary investigations the relevant properties of the materials and mixtures used are determined, among these being the permeability values of laboratory-prepared sample-cores.

- b. In addition to the properties of the materials used, other factors such as the operation of mixing plants, construction methods, as well as field conditions to a large extent determine the quality of the liner construction. Field inspection and (laboratory) checks on procedures are an important element of the construction phase.
- c. The final step is the testing and quality control of the liner as built. For clay and sand/bentonite liners a procedure has been developed and tested using undisturbed samples subjected to laboratory tests, the most important being permeability testing. The results provide data which are used statistically to determine whether the overall performance of the actual liner meets the design specifications, taking into account the variability of the measurements.

It should be appreciated that the results of the laboratory permeability tests upon completion of a liner identify a situation which can, and probably will, change through time. Liners composed of Tertiary clay and sand/bentonite mixtures are physical and geochemical dynamic systems. Time-dependant behaviour, for example, is the consequence of consolidation processes as well as shrinking and cracking related to changes in moisture content. Furthermore, oxydation/reduction processes as well as acid/base reactions and precipitation/dissolution provide mechanisms which probably will influence the behaviour and effectiveness of a barrier system.

Results from simulations of contaminant transport, as well as compatibility testing, show that geochemical processes are important elements which should be taken into account during the design of liner systems. These processes can have both adverse and beneficial effects on the contaminant transport as a consequence of interaction with liner materials.

To demonstrate this simulation results on contaminant transport taking geochemical reactions into account as well as some results of leachate compatibility testing of a sand/bentonite liner are presented.

For sand/bentonite it has been shown that acid leachate can influence the permeability. Fig. 7 shows the results of a percolation test on a 5% sand/ bentonite mixture. During the first week the samples were percolated with tapwater. After this period (indicated as time-lag in Fig. 7) a sulphuric acid solution (pH 1.5) was used. During a period of more than 40 days the permeability of two samples was determined regularly. The results show that over the first 40 days a permeability between $8 \cdot 10^{-10}$ and $2 \cdot 10^{-10}$ m/s is found. Upon the exchange of tapwater by sulphuric acid a slight increase in permeability is found. After 42 days a sharp increase is found, which is related to a significant lowering of the pH as measured in the percolated fluid.

This test was performed to determine whether this type of liner could be used beneath a waste storage site producing an acid leachate. A NaCO_3 -activated European bentonite was used. Based on a titration curve, the mixture has a buffer capacity of 5.4 milli-equivalent per 10 gram of soil. A hydraulic gradient of about 30 was applied during the permeability test. After a period during which no more than 5% of the buffer capacity could have been used, sharp lowering of the pH as well as an increase in permeability occurs. Based on the displaced volume,

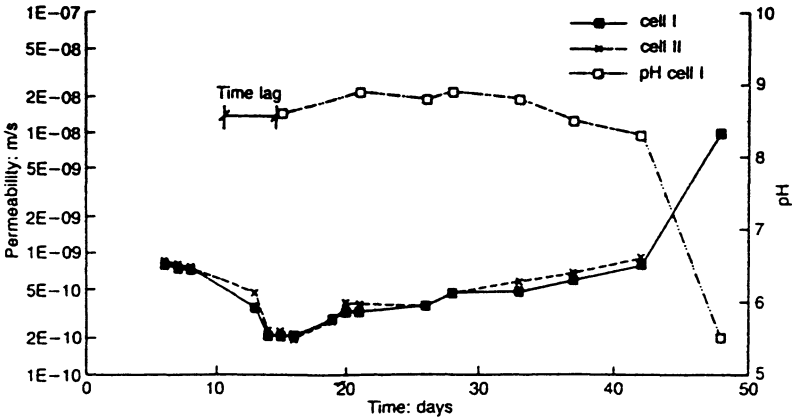


Fig. 7. Permeability behaviour of sand/bentonite under influence of a sulphuric acid solution (pH 1.5). Time-lag indicates the period after which tapwater was exchanged with the acid solution

this indicates preferential flow, with local velocities much higher than those derived from average flux values. Presuming analogous processes for the field situation the time scale can be adjusted according to the ratio between the flux found during the test and the actual flux expected from recharge values for the waste deposit site. Scaling of results in this case suggest that the duration of liner integrity is in the order of 10 years.

For a typical liner, a simulation of contaminant transport has been performed taking advection, dispersion, adsorption and geochemical equilibria into account, using the numerical finite difference computer code VERA. VERA is a coupled geochemical contaminant transport model of which the source of the transport

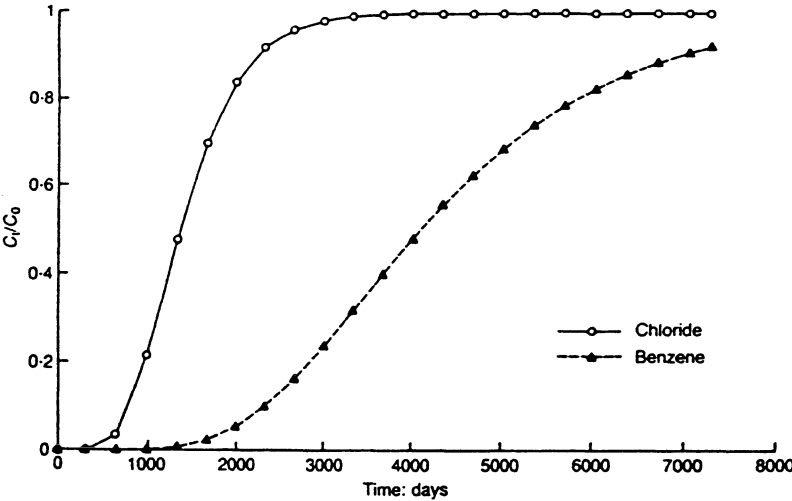


Fig. 8. Breakthrough curves of chloride and benzene for a sand/bentonite liner

Table 1. Leachate and sand/bentonite pore water composition. Concentrations in mol/l.

	Leachate	Sand/bentonite pore-water
pH	7.00	9.6
NH ⁺	5.00·10 ⁻²	- (1·10 ⁻²⁰)
Na ⁴⁺	8.70·10 ⁻²	2.33·10 ⁻¹
K ⁺	2.20·10 ⁻²	3.63·10 ⁻⁴
Ca ²⁺	7.00·10 ⁻³	5.83·10 ⁻⁶
Mg ²⁺	9.55·10 ⁻³	2.03·10 ⁻⁵
CO ₃ ²⁻	9.70·10 ⁻²	1.15·10 ⁻¹
Cl ⁻	9.32·10 ⁻²	6.20·10 ⁻²
pCO ₂	0.36	3.32
Cd ²⁺	1.00·10 ⁻⁶	- (1·10 ⁻²⁰)
Benzene	1.19·10 ⁻⁶	- (1·10 ⁻²⁰)

code has been developed by INTERA [11]. The chemical speciation code consists of the computer code MINEQL [12].

Chloride, benzene and cadmium breakthrough curves are simulated. A 0.5 m thick sand/bentonite liner with a permeability of 5·10⁻¹⁰ m/s was chosen, with a water flux of 1.5·10⁻⁹ m/s. The porosity was 35% and the dispersivity 0.05 m. An organic-matter content of 1% has been chosen.

Table 1 contains the relevant data on the leachate composition, which has been derived from a municipal waste deposit site, as well as the pore water composition for a 8% sand/bentonite mixture.

The results of the chloride and benzene breakthrough are presented in Fig. 8. Chloride in this case can be considered as a conservative (non-reacting) component. Breakthrough of benzene is retarded by a factor of 2.5 with respect to chloride.

Considering the breakthrough curve for cadmium (Fig. 9) (which is influenced by geochemical processes such as precipitation/dissolution due to the carbonate equilibrium) a number of interesting phenomena occur.

Initially cadmium concentrations rise at the base of the liner to a maximum, after which a slight decrease occurs, and then a steady rise sets in.

This particular pattern is determined by two precipitation/dissolution reactions and by adsorption of cadmium.



The leachate has high concentrations Ca²⁺ and Cd²⁺ whereas the sand/bentonite is very rich in CO₃²⁻ concentrations. As the leachate enters the liner system, cadmium

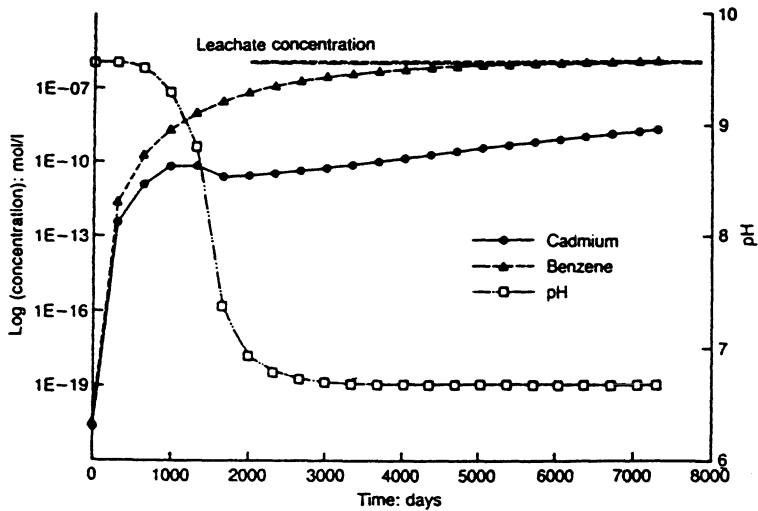


Fig. 9. Breakthrough curves of benzene and cadmium taking geochemical processes into account for a sand/bentonite liner

carbonate is supersaturated and precipitates. However, after some time, Ca^{2+} concentrations in the liner system have risen so that calcium carbonate will precipitate instead of cadmium carbonate. This results in a dissolution of cadmium carbonate and a subsequently rise in cadmium concentrations above the leachate concentrations. In other words, precipitation of cadmium carbonate in the liner system has resulted in the built-up of a cadmium reservoir which empties upon precipitation of calcium carbonate. When the cadmium carbonate buffer has been emptied, ultimate breakthrough of cadmium will only be influenced by sorption mechanisms.

Results from simulations of contaminant transport, as well as compatibility testing, show that geochemical processes are important elements which should be taken into account during the design of liner systems. These processes can have both adverse and beneficiary effects on the contaminant transport as a consequence of interaction with liner materials.

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11 Methods for Cleaning Contaminated Soils and Sediments

W. H. Rulkens¹, J. T. C. Grotenhuis¹, and R. Tichý²

¹ Wageningen Agricultural University, Department of Environmental Technology, Bomenweg 2, P.O. Box 8129, 6700 EV Wageningen, The Netherlands

² Institute of Landscape Ecology, Na Sádkách 7, 370 05 České Budejovice, Czech Republic

1 Introduction

Decontamination of soil polluted with different xenobiotic compounds is a world-wide problem. Apart from certain differences in technology-development among East and West, soil sanitation is required both in highly industrialized Western countries, as well as in Central and Eastern Europe. The extent of this problem has only recently become clear. A great effort has to be made to remediate the strongly polluted sites which have been identified till now. In The Netherlands, for example, more than 100,000 sites need remedial action [Soczó and Versluijs 1990]. A structural approach is necessary to solve this problem. One of the possibilities for remedial action is a *clean-up* of the soil, i.e. a remediation method aimed at *removal* of the contaminants.

Clean-up methods make use of the specific differences between the properties of contaminants or contaminated particles, and the properties of the soil particles. Properties at which a clean-up may be achieved are, for example, volatility of the contaminants, solubility in water or in another liquid, adsorption and desorption characteristics, size, density, shape of the polluted particles (or particle pollutants), biodegradability and chemical instability. Therefore, the following factors are important for the application of a clean-up technique:

- The soil type (granular structure, properties of the soil particles, humic substances in the soil).
- The type and the concentration of the contaminants.
- The physical state of the contaminants.
- The way the site has been polluted in the past with the contaminants and the time interval between the pollution process and the clean-up. Especially when considering in-situ treatment, it is important to know if the contaminated site is disturbed by mechanical processes or not.

The possibilities for clean-up depend on the *type and concentrations of pollutants* which can vary strongly in the soil. Main pollutants are:

- Non-volatile aliphatic and aromatic hydrocarbons.
- Volatile aliphatic and aromatic hydrocarbons.

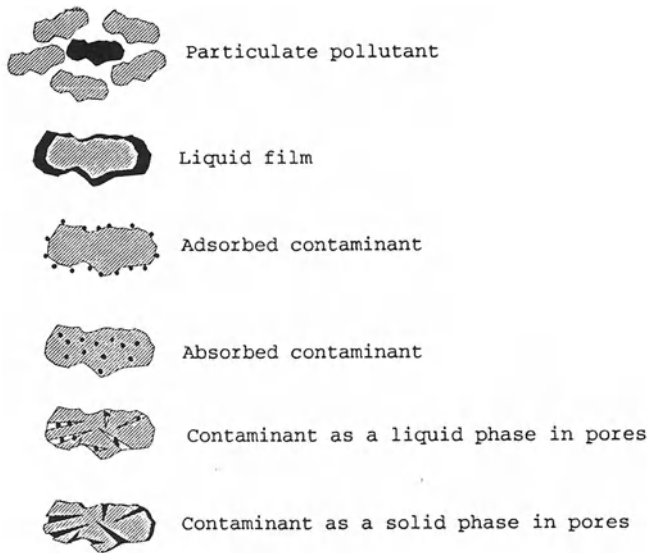


Fig. 1. Physical state of contaminants in soil

- Polycyclic aromatic hydrocarbons.
- Organic pesticides, PCB's.
- Heavy metals and heavy metal compounds.
- Free cyanides.
- Complex cyanides.

The soils contaminated with heavy metals or heavy metal compounds are in general most persistent to clean-up. The reason for this is that the metals and metal compounds can not be destructed and that, with exception of mercury an arsenic, the volatilization of these pollutants requires extremely high temperatures. Moreover, heavy metals are usually found in soils accompanied by other types of contamination, especially organic compounds. The occurrence of these organic pollutants can make the removal of metals from the soil substantially more complicated.

The *physical state of the pollutants* is also an important, but sometimes underestimated, factor in the clean-up possibilities of the soil. Figure 1 gives an overview of the ways the pollutants may be present in the soil. The following possibilities can be distinguished:

- Particulate pollutants (with particle size equal to, or smaller, or larger than the size of non polluted soil particles).
- Liquid films around soil particles.
- Adsorbed at the surface of soil particles.
- Absorbed in (organic) soil particles.
- Dissolved in the aqueous phase in the pores of the soil particles.
- Present as a solid or liquid phase in the pores of the soil particles.

Five main principles are applied for the clean-up of contaminated soil:

- Removal of contaminants by *molecular separation*. Examples are treatment by extraction and treatment by desorption.
- Removal of particulate contaminants by *phase separation*. Examples are classification with hydrocyclones, froth flotation and jig techniques.
- Removal of contaminants by *chemical/thermal destruction*.
- Removal of contaminants by *biodegradation*. Examples of these techniques are landfarming and biological slurry reactors.
- Removal of contaminants by biological absorption or biological mobilisation.

A large number of clean-up techniques have been developed on the basis of these principles. However, only a few are applied successfully in practice at present. Furthermore, it appears that with the techniques now available only a minor part of the contaminated sites can be treated with reasonable efficiency, i.e. within a relatively short treatment time and with the result that the treated soil can be considered as clean.

Contaminated sediments have been recently recognized also as a very serious environmental problem threatening the aquatic life and water resources in general. Besides, very often these contaminated sediments have to be dredged for nautical and water management reasons. Huge amounts of these materials present serious problems, since the concentrations of contaminants reach levels of hazardous wastes. Before dumping them into the sea or in a controlled disposal site the polluted sediments require remedial action, and clean-up provides one alternative. Techniques for clean-up of dredged sediments are for a large part similar to techniques used for cleaning of contaminated soil. However, four major differences between contaminated soil and contaminated sediments have to be taken in account in the application of these techniques:

- Sediments contain water in large quantities.
- Sediments have a lower mean granular diameter than polluted soils.
- The contaminants present in sediments vary less strongly and are limited to only a few.
- Contaminants soluble in water are not present in sediments.

The aim of this article is to give an overview of the possibilities of *clean-up techniques or principles* for contaminated soil and sediments that are polluted with *heavy metals* or *heavy metal compounds*. For each technique the treatment principle, several configurations, applicability, also for removal of organic pollutants, the development stage and the practical experience are briefly described.

2 Clean-Up of Contaminated Soil

2.1 Thermal Treatment of Excavated Soil

Principle. Thermal decontamination of soil consists of two treatment steps. The first step is aimed at evaporation of the contaminants from the soil particles at temperatures between 200 °C and 700 °C. At the same time, chemical transformation of pollutants may also occur, depending on the temperature. All types of organic contaminants can be transferred into a gas phase provided the temperature is high enough and the treatment time is sufficiently long. Organic soil substances like humic acids are also destructed and volatilized. Organic pollutants in the gas are completely oxidized at temperatures between 900 and 1100 °C in a separate incineration step. The cleaned soil leaving the installation is cooled with water [van de Leur 1990, Reijntjes and Schuler 1990].

Treatment Systems. A schematic representation of a complete thermal treatment installation is shown in Fig. 2.

The soil is sieved to remove particles larger than 40 to 50 mm. Subsequently, the soil is transported into a rotary kiln provided with an oil-fed burner. Soil particles get in intensive contact with the hot gases of the burner due to the rotation of the kiln. The gases leaving the kiln pass to an afterburner which is supplied with air and fuel in order to obtain a high incineration temperature which is required for a complete oxidation of all organic volatiles. The gases from the afterburner are cooled by means of a heat exchanger and are passed subsequently through a pollution control equipment. This equipment consists of a particle separation system, for example a cyclone, and a gas scrubber. Some other thermal treatment techniques can be mentioned:

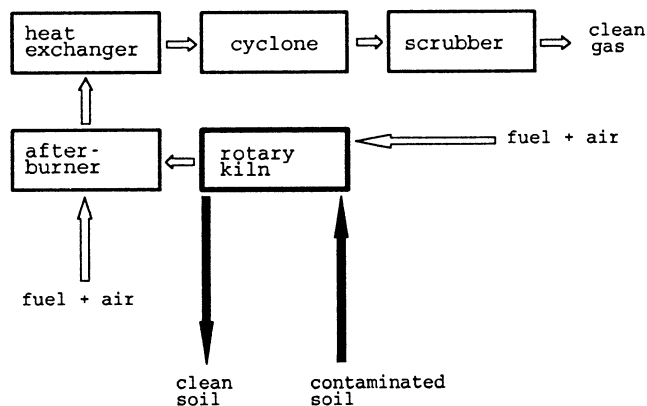


Fig. 2. Thermal treatment installation

- Rotary kiln provided with an internal or external heat exchanger.
- Fluidized bed thermal treatment system.
- Infrared thermal treatment system.

Applicability. Thermal treatment is suitable for the removal of all types of organic pollutants and for all types of soil. The temperature necessary for removal of the contaminants strongly depends on the type of contaminants. Petrol and diesel oil can be removed at temperatures of approximately 300 °C, polycyclic aromatics need temperatures of between 450 and 500 °C, complex iron cyanides can be destructed at temperatures of about 450 °C. It is also possible to remove halogenated organic compounds from the soil. However, to prevent emissions of dioxines, temperatures higher than 1000-1100 °C in the afterburner are required.

With respect to the removal of heavy metals, the following can be noticed:

- Mercury and mercury containing compounds can be removed by evaporation from the soil. However, for this removal sometimes high temperatures are necessary. Removal of evaporated mercury and its compounds from the gas phase leaving the kiln requires a special pollution control system, strongly different from the normal ones used in thermal treatment of soils contaminated with organic pollutants.
- Some species of heavy metals heavy metal compounds (Hg, As, Cd) may volatilize at temperatures above 800 °C. Part of these metals end up in the gas phase, sometimes adsorbed at the particulate matter in this gas phase. However, most of these metals end up in a solid phase, immobilized in the slag by physical or chemical mechanisms.

Practical Experience. Thermal treatment is applied at a large scale for soil clean-up. However, practical experience with this method is mainly limited to soils contaminated with non-halogenated organic pollutants. The costs of thermal treatment strongly depend on the type of soil, the water content of the soil and the type of contaminants, and are estimated between 100 and 150 US \$ per ton of soil.

2.2 Treatment of Excavated Soil by Extraction and/or Classification

Principle. Extraction/classification of contaminated soil is a treatment method in which the pollutants are removed from the soil using a liquid extracting agent. The extraction process comprises three major treatment steps: intensive mixing of contaminated soil and extracting agent, separation of extracting agent and soil particles, and a treatment of the extracting agent [US-EPA 1991a]. The intensive mixing step is aimed at a transfer of contaminants from the soil to an aqueous extracting agent. In principle, two removal mechanisms may be distinguished. The first mechanism is aimed at dissolving pollutants into the aqueous extracting agent. This process may be enhanced by the addition of chemicals such as acids, detergents, complexing agents or sodium hydroxide. The second mechanism is a

dispersion of polluted particles into the extracting agent. Chemicals that can be used to promote this process are sodium hydroxide and several types of detergents. The use of organic solvents has been recently proposed as an extractant. However, the use of organic extracting agent is much more complicated than the use of an aqueous extracting agent. This is the reason why until now almost always aqueous extracting agents are used in practice. Several techniques are available for the separation of the extracting agent containing dissolved and suspended pollutants from the clean soil particles. With respect to the selective removal of polluted particles from the non-polluted soil particles the separations are based on differences in particle size, settling velocity, magnetic properties and surface properties [Hinsenveld et al. 1990].

A large number of physical/chemical treatment techniques is available for the clean-up of the spent extracting agent. Some of them are listed further in the text.

Treatment Systems. A general process scheme of the extraction/classification process is given in Fig. 3. First, the soil to be cleaned is sieved to remove large objects such as pieces of wood, plant residues, concrete, stones, etc. The pre-treated soil is mixed intensively with an extracting agent. As already mentioned, the primary purpose of this step is to transfer the contaminants into the extracting phase. After the mixing step, clean soil particles and extracting agent containing dissolved and particle pollutants are separated. Several treatment techniques are available for this purpose. Subsequently, the separated soil undergoes a washing with clean water. The extracting phase obtained in the separation step contains still small amounts of relatively large clean soil particles, which are removed in a second separation step, if possible. Finally, the contaminated extracting agent is cleaned in a waste water treatment installation, whereupon a part of it is reused.

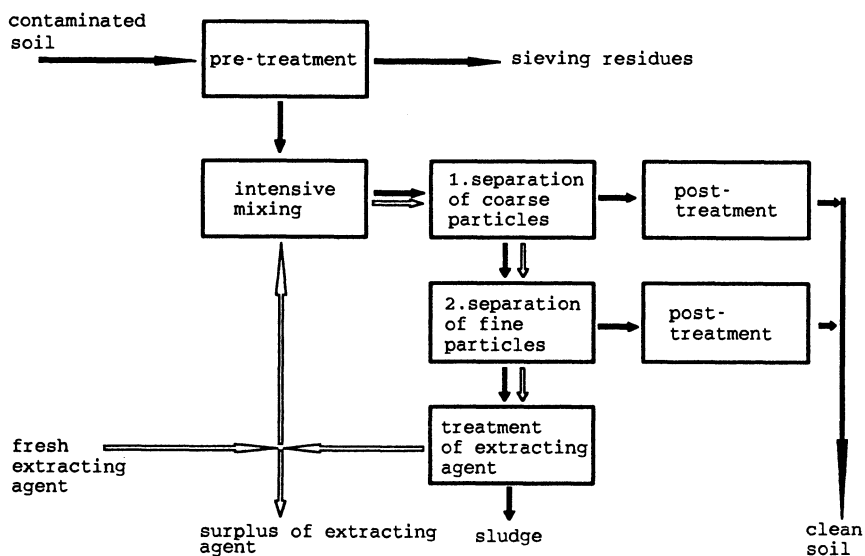


Fig. 3. Extraction/classification of excavated soil

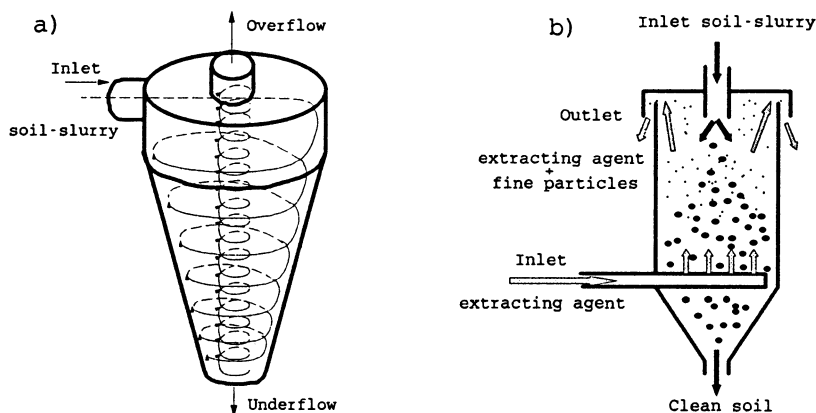


Fig. 4. Examples of extraction/classification installations: Hydrocyclone (4a), and fluidized-bed separator (4b)

Based on the general process scheme given in Fig. 3, several modifications of the extraction/classification process exist, allowing to distinguish between two groups of techniques, based on either particles classification or on leaching. Most of the installations in practise use a combination of these two methods.

The first group of techniques uses *particles classification* processes for cleaning the soil. The classification (size-selective separation) is aimed at removal of large, relatively clean soil particles from small polluted particles, such as soil particles to which pollutants are adsorbed or small particulate pollutants. Important particles classification techniques are:

- *Hydrocyclones* (see Fig. 4a). Particles separation in a hydrocyclone is based on centrifugal force. The slurry of soil particles and contaminated particles is separated into an underflow, containing the larger soil particles, and into an overflow containing the smaller particles. For an efficient operation of the system a number of hydrocyclones are placed in series. Selective separation is possible for particles with diameter larger than 10-20 μm .
- *Fluidized Bed Separation Systems* (see Fig. 4b). This separation system is based on the difference in gravimetric settling velocity of polluted small particles and clean soil particles. The slurry of clean soil particles and polluted particles is fed in countercurrent flow through a vertical column. The superficial velocity of the extracting agent in the column is selected in order to allow for settling of the large soil particles and their removal from the bottom of a column. The extracting agent with the contaminated particles is removed at the top of the column. With system, a selective separation for particles with a size larger than about 50 μm is possible.
- Gravimetric separation systems from mining industry. Several particle separation techniques are used in the mining industry for the recovery and upgrading of ores. Some of these techniques are suitable for the application in

a soil clean-up. Without going into a detailed description, here can be mentioned:

- Jig techniques.
 - Shaking tables.
 - Humphrey spiral separation techniques.
 - Tilting frame separation techniques.
- *Flotation*. In many cases the contaminants are adsorbed at the surface of the small soil particles, for example the clay particles, or are present as particulate contaminant. By addition of special chemicals it is possible to create a hydrophobic surface at the contaminated particles. Aeration of the slurry results in an attachment of small air bubbles to the hydrophobic particles, resulting in a selective flotation of these particles. Opposite to the other gravimetric separation techniques, flotation offers the possibility to separate polluted particles and non-polluted particles of equal size and density but different surface properties.

The second group of extraction/classification processes is based on *leaching* of the pollutants out of the soil particles, or in a complete dissolving of polluted particles. Leaching is especially focused on the removal of heavy metals and heavy metals containing compounds from the soil. The leaching process of the heavy metals can be executed with several types of leaching agents. Here can be mentioned:

- Inorganic acids such as hydrochloric acid and sulphuric acids ($\text{pH} < 2$).
- Organic acids such as acetic, lactic, and citric acids (pH not lower than 4).
- Complexing agents (EDTA, NTA).
- Combination of organic acids, complexing agents and inorganic acids [Tuin and Tels 1991, US-EPA 1991a].

For the leaching with acids, low pH values have to be applied for the efficient leaching of most of heavy metals. This requires special materials in order to prevent corrosion of equipment. The slow release of aluminium from the soil matrix should be considered as an undesired process. It has to be noticed that the leaching process can also be applied as a heap leaching, making longer treatment times at mild conditions possible without a strong increase in costs.

The extraction with complexing agents do not necessarily require very low pH. However, a substantial enhancement of extraction of lead with EDTA at lower pH was reported [Brown and Elliott 1992]. The disadvantage of the use of complexing agents is their price. Therefore, regeneration and re-use of these extracting agents should be accomplished.

With respect to the cleaning of the extraction agent, a large number of physical and chemical treatment systems is available. Among others, neutralization, precipitation, coagulation, flocculation, flotation, activated carbon adsorption, ion exchange and stripping can be mentioned. Which purification process is most suitable in a particular case depends on many factors such as the percentage of

clay particles and organic compounds in the soil, the nature and concentration of the contaminants and the composition of the extracting agent.

The sludge resulting from the treatment of the extracting agent can be dewatered with a centrifuge, filter press or sieve belt press. The produced amount of sludge in a treatment process on basis of extraction and classification is a substantial factor. This sludge mainly consists of soil substances. The fraction of polluted compounds is relatively small, however, overall concentrations of pollutants are high and the sludge has to be considered as a hazardous waste. Therefore, further treatment of the sludge using thermal methods or disposal on a controlled disposal site is necessary.

Applicability. Standard extraction/classification of excavated soil is a clean-up process that is primarily suitable for treating pure sandy soils or sandy soils with a clay and organics content less than 10-20%. Since the small clay particles and the humic substances are for a large part concentrated in the produced sludge, a higher content of these substances is not acceptable. Some modifications applicable for clay like soils are available, however, these modifications are still in a development stage at present.

With respect to the removal of contaminants it is possible to remove both organic pollutants and heavy metals. The physical state of the contaminant, i.e. being adsorbed or absorbed to soil particles, or present as a separate particulate pollutant is not a real limitation. However, the modification of the process and the process conditions which have to be applied strongly depend on the type of contaminated soil. In fact for each type of contaminated soil a tailor made process has to be applied [Hinsenveld et al. 1990].

Practical Experience. Extraction/classification of excavated contaminated soil is applied on a large scale in practice. Extensive experience is available with several modifications applied for the removal of all types of contaminants. However, as already mentioned, this experience is limited to sandy soils and soils containing small amounts of clay and humic substances. Costs of extraction/classification depend strongly on the type of contaminated soil and can vary between 50 US \$ (for pure sandy soil) and 150 US \$.

2.3 In Situ Extractive Treatment of Contaminated Soil

Principle. A schematic representation of an in-situ extraction process is shown in Fig. 5. The treatment process consists of infiltration of an aqueous extracting agent into the contaminated site. This infiltration can be achieved by means of surface trenches, horizontal drains or vertical deep wells, or by combinations of these three possibilities.

The infiltrated extracting agent percolates through the soil and soluble compounds present in the soil will dissolve in the percolate. The percolate is pumped into a water treatment system in order to remove pollutants (pump-and-treat

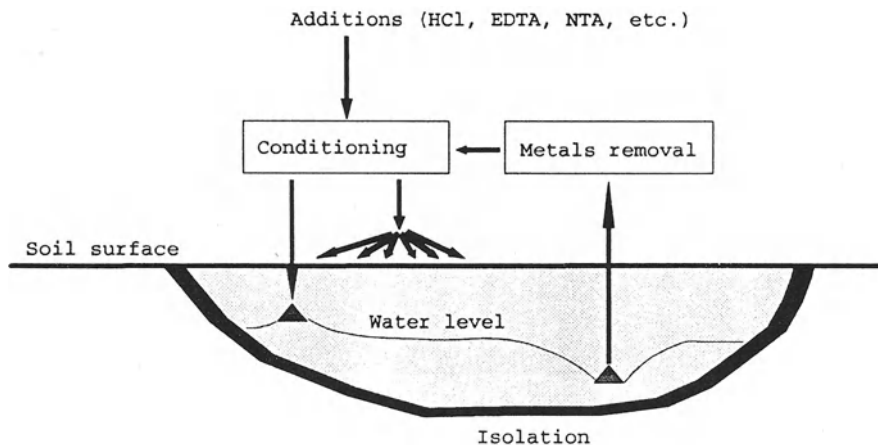


Fig. 5. In-situ extractive treatment

principle). Water is reused as extracting agent after reconditioning. The process is continued until the residual concentrations satisfy given limits [Staps 1990].

Process Parameters. Concerning the possibilities of in-situ extraction for practical application, the following aspects require attention:

- The hydraulic properties of the contaminated site.
- The mechanical disturbance of the soil in the contaminated site.
- The origin of the pollution.
- The solubility properties of the contaminants.
- The treatment of the withdrawn extracting agent.
- The conditioning of the extracting agent.

With respect to the hydraulic properties of the contaminated site, a high permeability of the soil profile is necessary. This means that only sandy soils are suitable for in-situ treatment. The presence of impermeable clay layers is not a principal bottleneck but requires special measures to achieve an appropriate infiltration and percolation of the extracting agent. It is important to ensure the percolation of extracting agent through the whole area where the contaminants may be present.

A contamination of the site can be removed most properly when the extracting agent follows the same pathways as the pollutant did. Mechanical disturbance of the surface layer of the contaminated site may have spread the contaminants to areas in the site that can not easily be percolated, for example due to clogging.

The origin of pollution strongly governs the possibilities for remediation. The chances for successful in-situ extraction are high if the pollutants were dissolved in a water phase. However, if the pollutants originally consisted of stable, metal containing particulate compounds and the polluted site is strongly disturbed by mechanical mixing, than the applicability of an in-situ extraction is doubtful.

In-situ extraction is only possible if the solubility of the contaminant in the extracting agent is high enough. In case of soil pollution caused by a waste water stream containing heavy metals, a strong binding of metals to the soil particles may be expected. The equilibrium concentration of heavy metals in a water phase between the soil particles is then very low. Increasing the concentration of heavy metals in the water phase is possible by the addition of chemicals. This conditioning can be mediated using the following agents:

- Inorganic acids (hydrochloric, sulphuric, nitric acids).
- Organic acids (although a very low pH cannot be obtained).
- Sodium hydroxide (suitable for amphoteric compounds, however organic soil substances can also be dissolved).
- Complexing agents such as citric acid, nitrilotriacetate (NTA), and inorganic chlorides at high concentrations.
- Combinations of acids and complexing agents.
- Oxidizing or reducing agents.

The percolate pumped from the site has to be treated. The first step is the removal of the heavy metals. A large number of techniques applicable for the removal of heavy metals is available. Here can be mentioned:

- Precipitation by increasing the pH with sodium hydroxide or by the use of sodium sulphide.
- Coagulation/flocculation followed by sedimentation.
- Ultrafiltration/microfiltration.
- Reverse osmosis.
- Electrolysis and electrodialysis.
- Ion exchange.
- Biological treatment [Patterson 1985].

Sometimes a combination of techniques is necessary, such as precipitation followed by coagulation/flocculation and a mechanical dewatering process. Secondly, the extractant is regenerated to allow for its re-use, i.e. appropriate chemicals are added to the desired concentration or pH.

Practical Experience. In-situ treatment is already applied at large scales, however mainly for the removal of organic pollutants. In situ extraction for removal of heavy metals has been successfully applied in the Netherlands for the clean-up of a sandy site (30,000 m³), contaminated with cadmium. In this case hydrochloric acid was used as the conditioner for the aqueous extracting agent. The pH of the extracting agent was about 3.5. Although the average concentration of Cd in the contaminated soil was approximately 10 mg Cd per kg soil, the removal was almost complete. Approximately 90% of soil samples gave Cd-concentration equal or less than 1 mg Cd/kg soil after a treatment time of about 1 year. The treatment costs amounted to approximately 100 US \$ per ton of soil and are estimated somewhat lower than the treatment costs in case of excavation the soil and treatment in an extraction/classification installation [Urlings 1990].

2.4 Treatment of Soil by Electroreclamation

Principle. Electroreclamation is a clean-up method based on electrokinetical processes occurring when an electric current is generated between a cathode and anode placed in the soil. Transport of moisture and groundwater in the soil together with a transport of ions and electrically charged small particles is achieved. Three transport phenomena are involved:

- Electro-osmosis: the transport of the pore liquid, containing the contaminant species, between the electrodes.
- Electrophoresis: the transport of electrically charged particles present in the pore liquid such as colloids, small clay particles and droplets.
- Electrolysis: the transport of ions and ionic complexes present in the pore liquid.

It has to be noticed that the transport of the charged particles and ions is not necessarily in the same direction as the bulk electro-osmotic flow [Lageman et al. 1990].

Treatment System. The electrokinetical installation is schematically shown in Fig. 6. It consists of a series of vertically or horizontally placed anodes and cathodes. Each electrode is provided with a housing system in which a purging solution is present. The aim of this solution is to capture the contaminants and to prevent undesired precipitation and conversion processes at the electrodes. All the housings of electrodes of the same charge are interconnected to make a recirculation and a central treatment possible. Electroreclamation can be applied either in-situ or after excavation at a special disposal site. Treatment times vary from several weeks to several months.

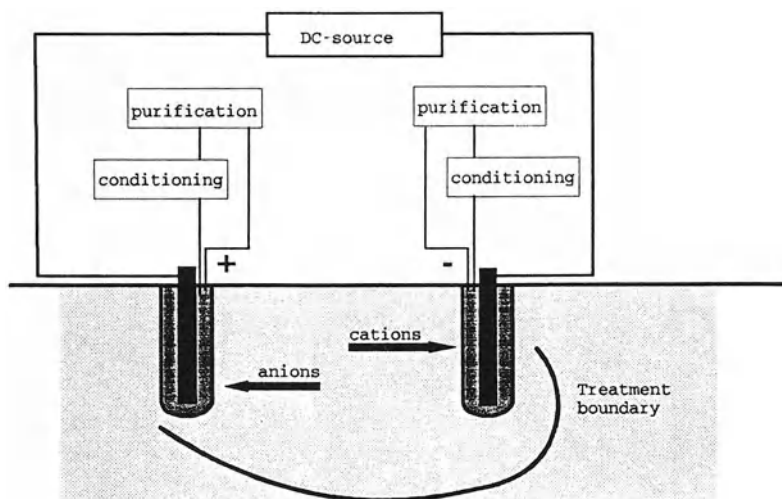


Fig. 6. Electroreclamation of soil

Applicability. Electroreclamation can be applied for removal of ionic contaminants or electrically charged small particles from the soil. The method is especially suitable for the removal of heavy metals from the soil. It should be noted that the technique does not remove only metals present in soluble, ionic species. Owing to the withdrawal of the metals, the concentration of ions in the pores decreases. Subsequently, the metals adsorbed to soil particles or bound as oxides, hydroxides, or carbonates get into the solution, and are also removed from the soil. Non-ionic contaminants dissolved in the pore liquids are also removed and transported by the electro-osmotic transport of the soil solution. A bottleneck in the treatment process are large metal objects that may be present in the contaminated soil. These objects may disturb the electrical current in the site.

With respect to the type of soil, electroreclamation is in fact the only method that can be used for in-situ removal of heavy metals from clay-like soil.

Practical Experience and Costs. Electroreclamation has been demonstrated successfully for the removal of heavy metals from clay soils in practice. However, the experience is limited at this moment and an estimation of treatment costs is difficult. Recent estimations of the costs of electroreclamation indicate substantially lower prices than standard ex-situ methods, theoretically in a range 10-50 US \$ per ton of contaminated soil [Alshawabkeh and Acar 1992].

2.5 In Situ Soil Vapour Extraction

Principle. Soil vapour extraction is a treatment method that makes use of the volatility of a contaminant. The gas phase between soil particles in a contaminated site is in a phase equilibrium with the pollutants adsorbed at or absorbed into the soil particles. The amount of contaminant in the gas phase between soil particles is substantial for contaminants with a high relative volatility. Flushing the contaminated site, using a combination of vacuum extraction of the gas phase, and

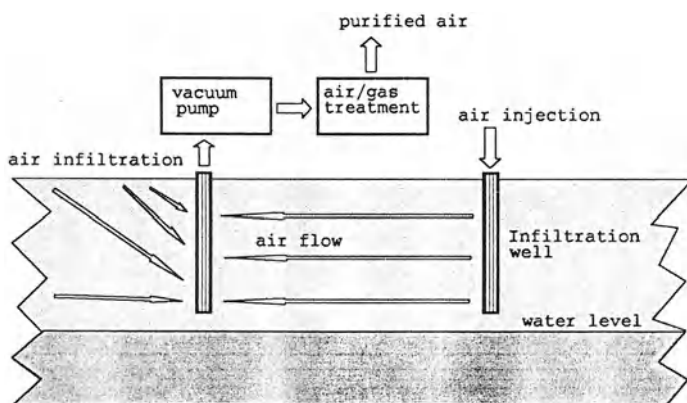


Fig. 7. In-situ soil vapour extraction

air infiltration, enables complete removal of the volatile pollutants from the contaminated site [US-EPA 1991b].

Treatment Installation. A schematic representation of a soil vapour extraction and air infiltration system is shown in Fig. 7. The contaminated site is provided with vertically installed soil vapour extraction and air infiltration wells. The vapour extraction wells are connected with a vapour treatment system in which the contaminants are removed. This can be done for example by adsorption at activated carbon or by catalytic incineration. Air infiltration into the soil is obtained by the negative pressure gradients in the unsaturated soil. Forced injection of air into the saturated zone can increase the stripping process of the contaminants from the soil layer as well [Spuy et al. 1990].

Vapour extraction is developed especially for in-situ treatment of soil contaminated with volatile pollutants. There are several modifications of this treatment system. The choice for an optimal modification strongly depends on the type of soil, soil structure and the type and concentration of the pollutants. The spatial variability of these parameters is another important factor.

A somewhat special modification is steam stripping. This clean-up process is basically similar to the air vapour extraction, except that the hot steam is injected into the soil instead of air. Due to the higher temperatures, the removal rate of contaminants is higher than with air stripping. Besides, the removal of contaminants with a low relative volatility at ambient temperatures is possible.

Applicability. Vapour extraction is applicable for in-situ treatment of soil contaminated with volatile compounds such as trichloroethylene, perchloroethylene, toluene, benzene and a large number of other organic solvents. It may be applicable to remove also (organic) volatile mercury compounds and arsenic. However, this possibility has not been thoroughly investigated so far. The technique is suitable only for the soils with high permeability. The permeability of clay like soils is in general too low for getting an efficient stripping process of the contaminants.

Practical Experience and Costs. In situ soil vapour extraction is applied in practice on a large scale. Practical experience exists with the removal of, among others, trichloroethylene, perchloroethylene, benzene and petrol. Soil vapour extraction is in some cases combined with two other in-situ treatment systems: in-situ extraction with a water phase and in-situ bioremediation. The injection of air results in an efficient oxygen transfer enhancing the biodegradation rate. The use of an aqueous extracting agents makes also the removal of non-volatile, non-biodegradable compounds possible.

The costs of in-situ vapour extraction are lower than the costs of thermal treatment or extractive treatment after excavation. However, detailed estimations are not available.

2.6 Treatment of Soil by Biodegradation of the Contaminants

Principle. Biodegradation of contaminated soil is aimed at the use of microorganisms for conversion of contaminants into non-polluting compounds such as water and carbon dioxide. Natural biodegradation of pollutants occurs in most soil environments, however, the conditions for biodegradation are in general not favourable for achieving an efficient clean-up. Bioremediation techniques are mostly aimed at improving the conditions for microbiological degradation. Among the conditions which have to be optimized are temperature, moisture content of the soil, pH, redox potential, concentration of the pollutant, type of electron-acceptor, presence of desired microorganisms, and the bioavailability of the pollutant to microorganisms. Biodegradation can occur both at aerobic and at anaerobic conditions. In general, aerobic conditions are mostly used, however, biodegradation of chlorinated hydrocarbons requires a combination of aerobic and anaerobic treatment steps for complete conversion of the pollutant. Several recalcitrant compounds were reported to be biodegradable in anaerobic environments [Holliger et al. 1988, Soczó and Visscher 1991].

Pretreatment Systems and Applicability. With respect to biological treatment of soils contaminated with organic pollutants, three major types of biological methods are available at present: landfarming, bioreactor techniques and in-situ bioremediation.

In *landfarming*, the polluted soil is spread out in a thin layer on top of a specially constructed impermeable sublayer provided with a drainage system. The thickness of the soil layer can vary between 0.5 and 1.5 m. Aerobic microbiological degradation of pollutants in this layer is stimulated by regularly cultivating the layer in order to enhance oxygen transfer and by the addition of water, nutrients and trace elements if necessary. Polluted drainage water is recirculated over the layer. Further acceleration and improvement of the process can be obtained by the use of greenhouse techniques, forced aeration, and increasing the temperature of the layer. Basically, landfarming is a relatively simple method and makes treatment times of 1 to 3 years acceptable [Harmsen 1991].

Bioreactor techniques (see Fig. 8) involve the treatment of a slurry of contaminated soil and water in a closed reactor system to which oxygen and nutrients, eventually a co-substrate, are supplied. The slurry is intensively mixed to promote maximal contact among microorganisms, pollutants, oxygen and nutrients. Due to this intensive contact and better possibilities for controlling the process, substantially higher biodegradation rates can be achieved than in landfarming. However, the process is more complicated than landfarming and requires a rather complex and expensive treatment installation. The size of the installation is strongly governed by the treatment capacity and the necessary treatment times. From a financial point of view it is assumed that the residence time of the soil in a bioreactor installation has to be less than a few days, preferably less than few hours [Kleijntjes et al. 1990].

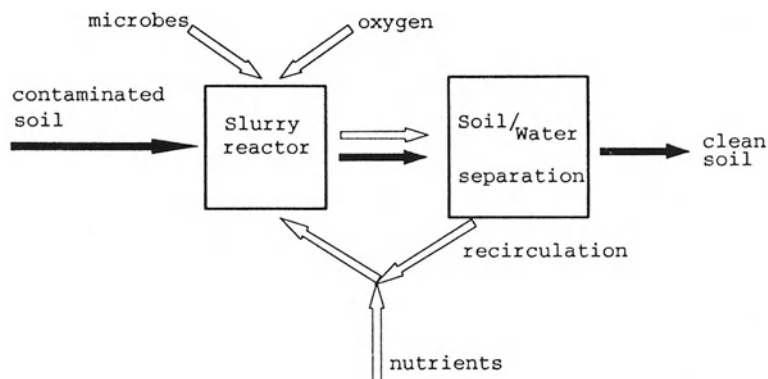


Fig. 8. Bioreactor for treatment of excavated soil

In-situ biological treatment (see Fig. 9) is focused on the improvement of process conditions for microbiological degradation in polluted sites by the addition of oxygen (or another electron acceptors), nutrients, and, if necessary, also microorganisms, co-substrate and surfactants. These additions are achieved by infiltration of a water phase via drains, trenches or wells. The infiltrated water is pumped up, treated to remove dissolved pollutants, conditioned and re-fed to the soil [Morgan and Watkinson 1989]. The process avoids excavation of the soil and is substantially cheaper than ex-situ processes. However, the treatment times are usually substantially longer, ranging from several weeks to several months, eventually few years.

Oxygen supply can also be achieved by soil venting. In-situ treatment of contaminated soil is only feasible if the permeability of the soil is high enough, thus only sandy soils are suitable for in-situ treatment at present. If a contaminated site is suitable for in-situ treatment, than the treatment is rather simple and cheap. Eventually, nitrate can be used as an electron-acceptor instead of oxygen. Moreover, oxidation can be enhanced using H_2O_2 [Hinchee et al. 1991].

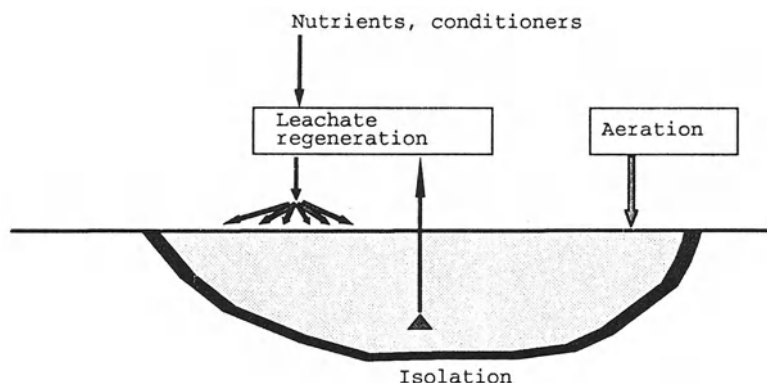


Fig. 9. In-situ biological treatment (bioremediation)

With respect to the practical application of bioremediation techniques, a large number of pollutants that are encountered in contaminated soils are biodegradable. However, notwithstanding intensive research, the practical application of bioremediation techniques is at present limited to the removal of easily biodegradable compounds such as gasoline and low molecular aromatic hydrocarbons, using landfarming and in-situ treatment. The biodegradability of a large number of other pollutants, among which halogenated organic compounds, has clearly been shown at laboratory and pilot plant scales. However, implementation of the results obtained from this research to successful practical clean-up application encounters several bottlenecks:

- The rate of biodegradation, also of easily biodegradable compounds, is low and the desired residual concentration is not always achieved.
- Till present only a limited number of pollutants exhibited a biodegradability that is high enough for practical application.
- Some pollutants are not expected to be biodegradable, even in the future.
- The presence of several types of organic pollutants, eventually in combination with heavy metals, makes bioremediation less attractive and practically impossible.
- The physical state of the pollutants, for example their presence as particles with a size larger or comparable with soil particles can result in low biodegradation rates and high residual concentrations of pollutant.

Most of the above mentioned bottlenecks can be characterised using the term "bioavailability" of the contaminants. A low bioavailability means that the biodegradation rate is too low for practical application, even at a relatively high total concentration of pollutants. A low bioavailability can also mean that the residual concentration of the contaminants in the soil remains above the target level to be achieved by the treatment.

There are several prospects for improving bioremediation techniques. One prospect is the development of improved microorganisms that can be tailored to degrade specific pollutants. Some other approaches are mentioned below:

- Separation of the soil into a fraction that is easily biodegradable and a poorly biodegradable residues.
- Application of physical methods to reduce mass transfer limitations.
- Use of chemicals that have positive effects on the solubility of the pollutants in a water phase.
- Use of detoxification techniques to convert non or slightly biodegradable pollutants into easily biodegradable pollutants.

It is expected that the introduction of physical-chemical treatment steps in the bioremediation process may increase the bioavailability of the pollutants. This means that for improvement of the bioremediation techniques an appropriate combination of biological and physical/chemical treatment steps is necessary.

Experience and Costs. Practical experience with microbiological treatment techniques is mainly available for landfarming and in-situ treatment. Contaminants that have been removed are in general easily biodegradable non-halogenated hydrocarbons. The costs of biological treatment are estimated to be by 30-40% lower than the costs of thermal treatment of excavated soil or treatment of excavated soil by extraction and classification.

2.7 Extensive Biological Treatment for Control of Diffused-Sources Pollution

Principles. Certain clean-up principles may provide possibilities to develop low-cost techniques. Since these processes use relatively moderate conditions, they need usually longer treatment times than most of the above-mentioned techniques. This group of processes is called *extensive techniques*. In-situ treatment systems, as well as the use of biological processes are the most promising tools to develop such techniques. However, possibilities are rather limited for the clean-up of soils contaminated with heavy metals. Here, two options are discussed, i.e. the use of bioleaching, connected with the use of the microbial sulphur cycle, and the vegetative in-situ extraction of metals.

Possible Use of Bioleaching. Certain acidophilic (acid-loving) bacteria can utilise reduced sulphur compounds as electron donors providing energy for their growth. Most of these bacteria belong to the genus *Thiobacillus*. These bacteria live in aerobic conditions, autotrophically, having the optimal pH for growth 1-4. Optimal temperatures vary with species and strain from 15 to 55 °C [Pronk 1991].

Microbiological leaching of heavy metals can be performed in direct and indirect ways, as described by the following equations:



Indirect leaching of heavy metals consists of rapid acidification by microbial oxidation of reduced sulphur compounds, Eq. (1). Subsequently, protons released into the liquor can substitute metals adsorbed on the soil particles, Eq. (2). In direct leaching, reduced compounds of heavy metals (sulphide) are directly oxidized by the bacterial enzymatic system, transferring electrons to oxygen and leading to the solubilization of heavy metals, Eq. (3).

Performance of the bioleaching process depends strongly on the oxidation state of heavy metals in the soil to be cleaned. Heavy metals in anoxic sediments are supposed to occur predominantly in sulphidic and other reduced forms. Thus, by the application of bioleaching, sulphides will be attacked directly, and other reduced metal-containing compounds will be quickly oxidized and thus usually

solubilized. If the pH is low enough, released metals will not significantly adsorb on the sediment matrix and their extractability will be high.

The situation is different in materials exposed to aerobic conditions. Since heavy metals are present in oxidized compounds, they are more readily available for further chemical transformation, adsorption and other effects resulting in a stronger binding of metals in the soil. Therefore, lower pH or longer extraction time are needed to achieve sufficient extraction efficiency.

The process can be run in three different ways: soil-slurry reactors, in on-site or heap-leaching mode, or in-situ. For a *soil-slurry* reactor (see Fig. 8), appropriate mixing and aeration is needed. The process control should involve the addition of substrate (preferably sulphur compound) as well as the control of pH in the reactor. This option is more feasible for anoxic sediments since *thiobacilli* can significantly increase the solubilization of reduced metallic compounds without dramatic decrease of pH below 2. Since the only role of *thiobacilli* is to produce sulphuric acid when a soil from aerobic conditions is treated, the applicability of the process is then doubtful.

However, *thiobacilli* might be employed for the *on-site operation* or *heap-leaching*. In heap-leaching (see Fig. 10) a sulphur compound and appropriate microorganisms are introduced before heaping of the soil or the sediment or are sprayed with the liquor on the surface. Spent liquor can be recycled in order to maintain the appropriate water content. The addition of elemental sulphur as a substrate seems to be most feasible.

Practical use of *thiobacilli* is at this moment almost exclusively limited to biohydrometallurgical production of Cu, Zn, U, Ag, and biotechnological desulphurization of coal. Economically feasible configurations for bioleaching of heavy metals from ores are heap leaching of low-grade ores and solubilization and deep shafts mining [Karavaiko et al. 1988].

Scaling-up of bioleaching process for the removal of heavy metals from waste sludge has been reported recently. Since heavy metals present in a sludge from anaerobic waste-water treatment are encountered in reduced, mostly sulphidic forms, they are susceptible to the direct bacterial solubilization, Eq. (3). This process uses ferrous iron as an additional substrate. Air-lift reactors and systems

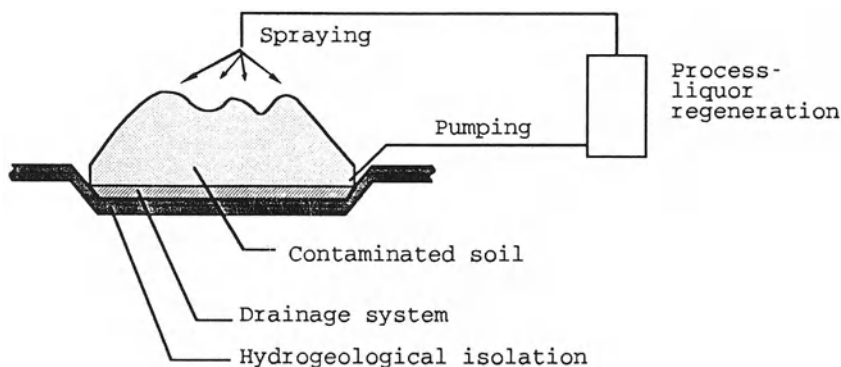


Fig. 10. Heap-leaching system for the removal of contaminants from the soil

using biomass immobilised on polyurethane support particles were found as best reactor configurations. Sufficient extraction efficiency was reported, enabling the use of treated waste in agriculture [Blais et al. 1992].

No practical application of bioleaching processes for the treatment of contaminated soils has been reported yet. However, several feasibility studies indicate its possible use in practise [Tichý et al. 1992, van der Steen et al. 1992].

The Use of Microbial Sulphur Cycle. The application of *thiobacilli*, or the use of sulphuric acid requires the treatment of spent extractant. The acidic liquor containing sulphates of heavy metals can be treated in an anaerobic reactor, resulting in a *sulphate reduction*. Sulphate is used by certain anaerobic microorganisms as an electron acceptor. This reaction leads to a formation of highly reactive sulphide, which immediately reacts with heavy metals in the suspension. Since the solubility of resulting metal sulphides is very low in water, metals can be easily separated by precipitation [Dvorak et al. 1992]. Withdrawn metallic sludge can be further treated. If the sulphur is returned to the system (sulphates can be re-fed to the sulphate reduction step), the concentration of sulphide in the system may overtake the stoichiometry of metals-sulphide formation [Scheeren et al. 1991]. In this way, extent sulphide can be treated subsequently using partial oxidation step. This process is governed by a special group of non-acidophilic *thiobacilli*, which can form elemental sulphur in an aqueous medium. This sulphur (biological sulphur) is less hydrophobic, and can be easily handled in a suspension [Buisman et al. 1990]. Consequently, this sulphur is faster oxidized by acidophilic *thiobacilli*. Above described process leads to a closed loop of sulphur (microbial sulphur cycle). Schematic representation of a possible configuration of this sulphur cycle is given in Fig. 11.

Vegetative In-Situ Extraction of Heavy Metals. Heavy metals are no major constituents of green plants and only very limited amounts of some of them are required for growth. However, certain plant species have proved to be able to accumulate high concentrations of heavy metals like cadmium, zinc, lead, copper, nickel in their biomass. Several highly heavy metal-accumulating plant species growing in a moderate European climate have been reported, like *Polygonum sachalinense*, *Thlaspi*, *Alyssum*, *Urtica*, or *Chenopodium* [Haase 1988, Baker et al. 1991].

For the removal of metals from contaminated soil the plants are cultivated at the contaminated site under optimal conditions required for maximal uptake by shoots or other harvestable parts. Biomass is subsequently harvested and several techniques can be applied for removal of the metals from the biomass. However, the opinions on this technique are rather controversial. Ernst [1988] calculated the treatment times using this method for several centuries. However, Baker et al. [1991] reported a theoretical possibility to shorten this period for several cropping periods. It should be mentioned that the estimations of Ernst are based on the theoretical removal of metals from mine tailings, i.e. the substrate with relatively high concentrations. The extensive approach is more directed towards the

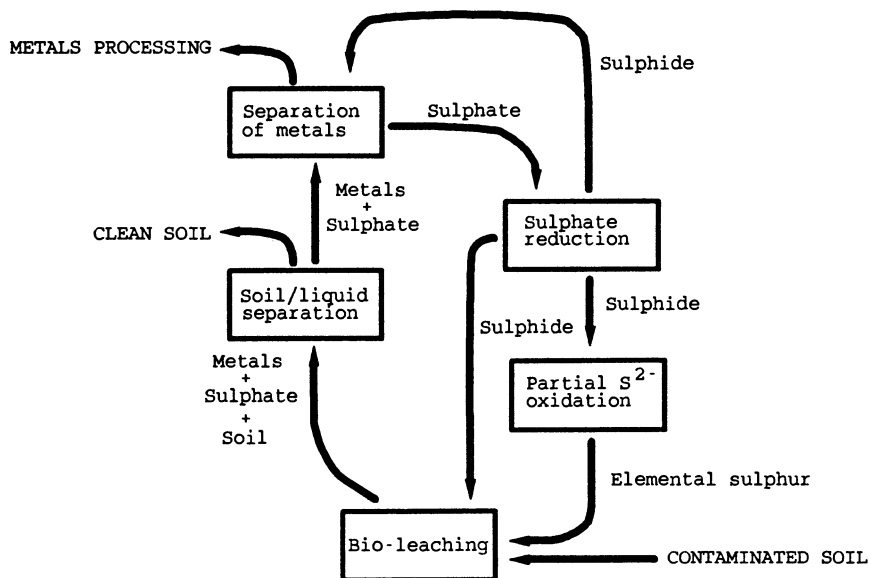


Fig. 11. Possible use of sulfur cycle for the removal of heavy metals from soils or sediments

treatment of moderately contaminated soils, which were used by Baker and coll. for their calculations. However, the estimations of Baker and coll. are based on assumed constant amounts of accumulated metal by plants over the treatment period, independent on changing metal concentration and availability in the soil. This assumption is not always relevant.

Yet the possibility to use the green plants for the treatment of contaminated soils should be considered. The accumulation of heavy metals should still be considered as an extensive, *indirect treatment method*. Possible combination of this soil clean-up technique with biomass production for special industrial purposes (fibres, oil, chlorophyll production, etc.) can be considered. The intensity of such clean-up processes is by several orders of magnitude lower than any intensive, ex-situ process. However, it is likely that these techniques will belong to the alternatives available for the clean-up of soils polluted with heavy metals originating from diffused sources.

When vegetative uptake is considered, following aspects need special attention:

- Selection of appropriate (hyperaccumulating) species with respect to the climatic conditions, soil type, and contamination, and with respect to the desired way of biomass treatment.
- Evaluation of the metal-pollution in the soil, especially as concerns the physical and chemical state of contaminant in the soil. Special attention should be paid to *bioavailability*, determining the part of metal which can be accumulated by plants.

- Appropriate measures to reduce risks connected with the spreading of contaminated biomass into the environment and thus endangering wildlife or agriculture production.
- Treatment techniques for the removal of heavy metals from the contaminated biomass.

Due to elevated levels of toxic metals in plant bodies, the use of biomass for agricultural purposes is excluded. However, several techniques can be used for its treatment, as given below:

- Thermal or physical-chemical methods such as drying, incineration, gasification, pyrolysis, extraction by mineral acids
- Biological methods, like anaerobic digestion of the residue, used as a pre-treatment
- Removal of heavy metals in technological processing of biomass to obtain useful products, like chlorophyll, oil, fibres, etc. [Bolenz et al. 1990].
- Disposal. It should be clear that contaminated biomass is easier to handle than contaminated soil. This is why, under certain circumstances, the disposal of biomass may provide to some extent a solution. This applies for example to highly toxic compounds, like radioactive metals, if the accumulation factors are high enough.

3 Clean-up of Contaminated Sediments

3.1 Extent of the Problem

Contaminated sediments show a strong similarity with contaminated soils. It should be therefore possible to use soil clean-up techniques for cleaning sediments. However, as already mentioned, there are also some characteristic differences which have to be taken into account when using soil clean-up methods for clean-up of sediments. These differences are:

- The main size of the sediment particles is smaller than the size of soil particles.
- Due to their long stay in a water phase, the sediments mostly contain no pollutants that are easily soluble in a water phase.
- Generally, contaminated sediments contain a smaller number of different pollutants than contaminated soils.
- Contaminated sediments contain large amounts of water.

Since the problem of contaminated sediments is more recent than the problem of contaminated soil, the development and application of special treatment systems for contaminated sediments has just been started. This chapter gives an overview of several treatment processes applicable for dredged sediments. As most of these treatment processes have already been described in Chapter 2, only a brief summary is given here.

3.2 Treatment Processes

The most important treatment processes that may be applied for clean-up of contaminated sediments are mentioned below.

Hydrocyclone-Separation as a Pretreatment Step. Hydrocyclones are aimed at separation of small and large sediment particles. The separation is useful if the contamination is selectively localized in one of these fractions. As already mentioned for soil treatment, hydrocyclones can be applied in several modifications. What type of modification is most useful depends on the type of the polluted sediment.

Dewatering. Dewatering of the dredged sediments or of the fraction leaving a hydrocyclone treatment can be necessary for several reasons. If the contaminated fraction has to be stored in a controlled disposal site, a reduction in volume is highly required. If the contaminated dredged sediment, or a contaminated fraction, is treated by means of a thermal treatment method or by landfarming, a reduction of the water content is a prerequisite for an appropriate performance. There are several possibilities for dewatering, mostly based on the use of flocculants and coagulants. The major dewatering processes are

- Natural dewatering in large lagoons.
- Mechanical dewatering using sieve belt presses or decanter centrifuges.
- Dewatering in large lagoons supported by the use of coagulants and flocculants.

Biological Decontamination Techniques. Depending on the type of pollution, biological decontamination of dredged sediments or fractions of dredged sediments are aimed at either the biodegradation of organic pollutants or the mobilization of heavy metals and heavy metals containing compounds. Major biodegradation techniques for removal of organic pollutants are:

- Aerobic bioreactor systems.
- Landfarming (coarse fraction).
- Aerated lagoon techniques (fine fraction).

With respect to techniques for biological mobilization of heavy metal there can be mentioned:

- Bioreactors using *thiobacilli*.
- Heap leaching techniques using *lactobacilli* (moderate extraction, pH=4), and/or *thiobacilli* (highly acidic extraction, pH<2).

Decontamination by Extraction and Classification. Similar techniques can be used as for soil treatment. Acids, complexing agents and detergents are used as chemicals to be added to the extracting agent in order to improve dissolving or dispersing of the contaminants. With respect to separation techniques for selective

removal of contaminated particles, hydrocyclones, flotation and conventional sedimentation techniques can be mentioned. Also the application of gravimetric separation techniques used in mining processes may be useful in certain cases.

3.3 Practical Experience and Costs

Compared with soil treatment the practical experience with clean-up techniques for contaminated sediments is rather scarce. Several treatment steps are still in the developing stage and are not applied in practice yet. Treatment processes that are applied in practice are given below:

- Hydrocyclone treatment for separation of polluted and non-polluting particles.
- Dewatering techniques for dredged sediments or dredged sediment fractions (natural or mechanical dewatering).
- Landfarming techniques for the biodegradation of organic pollutants.

The same bottlenecks of landfarming and acid leaching are observed as already mentioned for contaminated soils.

Owing to the lack on practical experience it is difficult to make a costs estimation. The costs of treatment techniques such as hydrocyclone treatment and dewatering are estimated at about 10 US \$ per ton of treated sediment. Costs of landfarming are estimated at the same order of magnitude as the treatment costs of contaminated soils.

4 Summary: Current and Future Applications

The most important clean-up techniques for contaminated soil are at present:

Ex-situ techniques:

- Extraction/classification of sandy soil.
- Thermal treatment of soil polluted with organic pollutants.
- Landfarming of soil polluted with easily biodegradable organic compounds.

In-situ techniques:

- Biorestitution of sandy soils polluted with easily biodegradable pollutants.
- Soil venting of sandy soils polluted with volatile pollutants.
- Extraction of sandy soils polluted with water-soluble contaminants.
- Electroreclamation of soil polluted with heavy metals (at this moment only limited practical experience).

From these clean-up techniques, only extraction/classification, in-situ extraction, and electroreclamation are suitable for the removal of heavy metals.

Costs of these techniques vary between 10 US \$ and 250 US \$ per ton of soil. Further development of clean-up methods in the future can be expected. This development is focused on:

- Improvement of existing methods by optimizing process conditions.
- Improvement and further development of existing methods by combination of physical, chemical, and microbiological clean-up principles.
- The development of innovative techniques. Here can be mentioned:
 - Bioleaching using *thiobacilli*.
 - The use of microbial sulphur cycle.
 - The use of green plants to accumulate heavy metals.
 - The use of extensive techniques for the treatment of soil at disposal sites, or
 - at large areas contaminated with metals originating from diffused sources. Moderate treatment conditions, removal and/or modification of the top layer, and coupling of clean-up processes with other activities can be mentioned.

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12 Improving Environmental Performance of a Primary Lead and Zinc Smelter

F. Elgersma^{*)}, J. N. Schinkel and M. P. C. Weijnen

Delft University of Technology, Delft University Clean Technology Institute,
Rotterdamseweg 145, 2628 AL Delft, the Netherlands

^{*)} now with Akzo Chemicals, P.O. Box 25, 7550 GC Hengelo, the Netherlands

also based on contributions by:

N.T. de Oude, Procter & Gamble, European Technical Center S.A., Strombeek, Belgium

E. Reichrtová, Slovak Academy of Sciences, Institute of Ecobiology, Bratislava, Czechoslovakia

L. Shllaku, Dardania, Pristina (former Yugoslavia)

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Abstract

Non-ferrous smelters have a bad reputation for their negative impact on the environment, particularly as a result of heavy metal emissions. In this paper a case study is made of a combined lead/zinc smelter, describing the most important sources of heavy metal emissions in the smelter plant. The suggested solutions include technical as well as non-technical measures, the latter category being concerned with management procedures, organization, planning etc. This type of measures, aimed at commitment to pollution prevention in all levels of the organization, is an essential element of any cleaner production programme. As the concept of cleaner production is largely based on more efficient use of raw materials and energy, significant economic benefits may be gained according to the principle *Pollution Prevention Pays*. Cleaner production requires a systematic approach, tracing the sources of wastes and emissions and defining realistic and measurable goals for structural waste and emission reduction. Monitoring programmes are needed to check the effectiveness of measures taken. Protective health care programmes are strongly recommended with a view to the occupational and public health risks posed by heavy metal emissions.

1 Introduction

Heavy metals are known for their (eco)toxicity. Some heavy metal ions, such as lead, cadmium and mercury, are particularly toxic with respect to human health and the environment. Even if present in extremely low concentrations, the effects of

heavy metal ions may be detrimental e.g., as a result of steady accumulation in the food chain. Like other persistent environmental pollutants, heavy metals can be transported over long distances throughout the environment, thus potentially causing adverse environmental and public health effects even after long periods of time, far from the original source of pollution. On the basis of our growing insight in the risks involved in environmental pollution with heavy metals, it is now obvious that prevention of pollution at the source is the safest option.

Environmental pollution with heavy metals is a common phenomenon with most mineral processing industries. Particularly the refining of metals in primary smelters is a well known source of heavy metal emissions. Under strict environmental regulations, smelter industries in Western Europe have been forced to implement cleaner technologies and better operational procedures. Primary smelters in Central and Eastern Europe, however, are still known to cause significant emissions of heavy metals. Because of growing evidence of detrimental effects to occupational and public health in and in the vicinity of smelters, respectively, Central and Eastern European countries are now investigating which strategies to follow to reduce these heavy metal emissions, without endangering economic competitiveness.

2 The Concept of Cleaner Production

Already in the early 1970's the OECD defined the *Polluter Pays Principle* which was implemented in many Western nations' environmental regulations. In response to this, in the mid 1980's industrial corporations started reporting how *Pollution Prevention Pays*. Pollution prevention often yields direct savings on raw materials and energy, as these are more efficiently processed into the desired product. In addition to an enhanced production efficiency, the costs of waste treatment, transportation and disposal can largely be avoided.

Pollution prevention in industrial practice is not only effected by technological changes, but also by a variety of non-technological measures concerning operational and administrative procedures, organization, logistics etc. The combination of managerial and procedural measures is known as *good housekeeping*. The technological measures involved in cleaner production are aimed at pollution prevention at the source. It is this source oriented approach which is characteristic for *clean technology*.

In addition to direct and indirect economic benefits, companies practicing cleaner production also gain from the effects of an improved public image. Through environmentally responsible production, industrial companies improve their negotiating position with federal and local authorities, as anticipating on environmental regulations gives a far better impression than complying afterwards. This also applies to their relationship with environmental pressure groups, consumer organizations and with the public in the direct vicinity of the production sites. These public affairs related aspects are of growing importance, in particular

for industries processing potentially hazardous substances. As a representative from the lead refining industry put it in 1990: *'We depend on the public consent to operate'*. The relevance of environmentally compatible production technology for avoiding future liabilities has already made the environmental theme a major issue in the granting of capital investment credits by major banks and in negotiating insurance contracts.

3 Aim

This paper will focuss on options for cleaner production in primary smelter operations. A combined lead and zinc smelter has been selected as a case study. This combined smelter operation is characteristic for the Trepca smelting plant (former Yugoslavia). The production technology and production capacity of the case study plant resemble the Trepca situation. Although this particular combination of smelters is uncommon, the proposed measures for cleaner production also apply to single lead and zinc smelters. The aim of this study is to provide some elements for an effective strategy towards structural reduction of heavy metal emissions, including technological as well as non-technological measures.

4 Description of the Smelter and its Raw Materials

4.1 Raw Materials

The imaginary lead and zinc smelter has a capacity of 100 ktpa of refined zinc and 100 ktpa of refined lead. It utilizes a mixed feed of galena (PbS) and sphalerite (ZnS). Table 1 provides the composition of these raw materials.

4.2 Process Description: Lead Smelter

The lead smelter consists of a series of unit operations which are described in the sequence from raw material to metal. Figure 1 provides a flowsheet of the combined lead and zinc plant. The lead concentrate produced by flotation at the mining site is crushed and milled at the smelter plant site. For efficient operation of the fluid bed roaster, over 95 wt% of the particulates should be smaller than 200 μm . After milling and crushing, the concentrate is stored in a warehouse, giving rise to dust formation both during the comminution operations and during storage.

In the roaster the metal sulfides are converted into metal oxides and sulfur dioxide by air, at ambient pressure and temperatures of approximately 900 °C. The roasting process yields a gas phase which contains about 7 wt% SO₂. At this SO₂ concentration the roast off-gas is suitable as a feedstock for H₂SO₄ production. For

The sulfuric acid plant is of the single-contact type with a typical conversion efficiency of 98%. Residual SO_2 in the sulfuric acid plant off-gas is emitted by a 150 m high stack, yielding an SO_2 emission of about 6 ktpa. Any mercury present in the concentrate is volatilized during roasting, thus either ending up in the sulfuric acid product or being emitted with the roast off gases.

After roasting, the resulting metal oxides are sintered to increase the particle size. This sintering operation causes severe dusting. In the blast furnace, coke is added to reduce the more noble metal oxides e.g., lead and silver, to metals. Since the coke production is not carried out on site and since the heavy metal content of the coke is negligible compared to that of the heavy metal concentrates, the environmental aspects of coke production are not discussed here. The blast furnace off gas contains minor amounts of lead (dust) which easily converts to lead oxide, and a substantial amount of carbon monoxide. Currently, the blast furnace off gas is sent to the stack which also discharges the roaster off gas.

The blast furnace process yields a so called lead bullion, composed of elementary lead, silver, nickel, gold and other noble metals, in addition to an iron oxides matte, containing most of the zinc originally present in the concentrate. The lead bullion is sent to a thermal refinery in order to separate lead from the more noble metals. Due to the high temperatures in this unit operation some heavy metal vapour losses are unavoidable.

Any gold present in the concentrate is dissolved in the lead product. Due to the small quantity of gold involved, separate recovery cannot be justified. Silver, however, is recovered commercially. Refined lead is finally processed in a melting and casting shop in order to meet consumer demands with respect to purity and alloy composition. The matte which consists of iron, zinc, cadmium and other less noble metal oxides is further processed in a Waelz kiln, this operation being shared with the zinc smelter.

4.3 Process Description: Zinc Smelter

Feed preparation for the zinc smelter proceeds in a similar way as described for the lead smelter. The sphalerite concentrate is crushed and milled to meet the particle size distribution requirements of the zinc plant roaster. After comminution the concentrate is stored in a warehouse. In a fluidized bed roaster the concentrate is processed at atmospheric pressure and temperatures of appr. 900 °C. As in the lead smelter roaster, the metal sulfides are exothermically converted into metal oxides and sulfur dioxide, except for mercury which reports to the gas phase. During roasting, iron forms a spinel compound with zinc which is called zinc ferrite.

The roasted product is fed to an alkaline solution (pH 3 to 5) in what is known as the 'neutral leach' step. Here, the oxides of zinc, cadmium, copper, magnesium and some other metals which are present as impurities in the concentrate will dissolve. The lead, the iron and some other trace elements remain in the solid phase. Also ferrite is not dissolved in the neutral leach. Since a substantial amount

of zinc (about 10 wt% of the zinc present in the concentrate) is trapped in the ferrite, the zinc ferrite is subsequently processed in a Waelz kiln to recover zinc.

The zinc, cadmium and other oxides which are dissolved in the neutral leach process are sent to the purification section, where cadmium, cobalt, copper, nickel and residual traces of arsenic and antimony are removed, a.o. by cementation with zinc dust. The resulting mixed cadmium-cobalt-etc. cement is then processed to recover most of the cadmium, copper and cobalt. The metal contaminated solid waste residues formed in these operations are stored with the slags from the Waelz kiln.

The purified neutral leach solution is processed in the electrolysis section, where metallic zinc is electrolytically precipitated on aluminum cathodes. The cathodes are periodically stripped. The zinc plates obtained are melted in electromagnetic furnaces and casted into commercial shapes. Spent electrolyte is recycled

Table 2. Emission sources in a primary lead/zinc smelter

process	substance(s)	hazardous comp.	phase
LEAD SMELTER			
concentrate storage and handling	dust ¹⁾	Pb,Cd,Zn,As	solid
gas purification section	waste water	Pb,Cd,Zn,As Hg	water gas
acid plant	sulphur dioxide		gas
sintering	dust ¹⁾ sulphur dioxide	Pb,Zn,Cd,As	solid gas
blast furnace	dust CO matte (to Waelz kiln)	Pb,Zn,Cd (oxides)	solid gas solid
refinery	metal vapour	Pb	gas
ZINC SMELTER			
concentrate storage and handling	dust ^a	Pb,Cd,Zn,As	solid
acid plant (see lead)			
electrolysis	gypsum waste	Zn, Cd (sulphates)	solid
WAE LZ KILN			
	slags off gases	heavy metals Pb,As,Cd (oxides)	solid solid

^a dust composition comparable to raw material composition

to the neutral leach for dissolving zinc oxide. In order to prevent accumulation of magnesium and manganese a bleed stream of the spent electrolyte is required. This strongly acidic solution is neutralized with lime, yielding a gypsum contaminated with zinc, magnesium and manganese which is stored with the Waelz kiln slags. Table 2 presents an overview of all emissions of hazardous substances, related to the individual process steps.

The neutral leach residue containing the insoluble compounds is sent to the Waelz kiln. The Waelz kiln converts the zinc ferrite from the zinc smelter as well as the matte from the lead smelter to readily soluble zinc oxides. These oxides report to a flyash which also contains arsenic, cadmium and lead and which can be returned to the neutral leach process in order to recover valuable metals. The slag residue formed in the Waelz kiln is primarily composed of iron oxides (magnetite, hematite), but also contains traces of more hazardous metals such as cadmium, zinc, lead etc. The slag is transported in open railroad cars to a waste dump site in the vicinity of the smelter plant.

Part of the lead, zinc, arsenic and cadmium fed to the Waelz kiln is emitted with the off gas, as a result of the fact that fly ash is not fully recovered from the kiln off gas. This unintended 'bleed' facilitates operation of the electrolysis circuit as it reduces the risk of accumulation of trace elements in the electrolyte solution.

5 Strategy for Cleaner Production - Vital Elements

5.1 Environmental Policy Statement

In order to both improve the plant's performance and to reduce heavy metal emissions, the management of this imaginary lead and zinc smelter should include some vital elements in its management strategy and procedures. Any environmental management programme starts with a clear environmental policy statement by the company's senior management, demonstrating their commitment to environmentally sound production practices. The execution of this policy must subsequently be integrated in the organization and personnel management of the company and be supported with technical improvements as well as monitoring programmes. All three elements will be discussed in the subsequent sections.

5.2 Environmental Management Procedures

Environmental management is by definition integrated in all other management structures and procedures and is aimed at reducing the emission of hazardous substances and their immission by the plant personnel to a minimum. Environmental management is closely related to health and safety management. Some companies have therefore selected to combine the health and safety functions with the environmental management function. This is a valid option, provided the safety

organization is not perceived as the group that will 'fix' the problem. If the safety group is considered responsible, commitment from the shop floor will be lacking and the results achieved less than what they could have been. It is worth considering to keep the safety engineers and medical staff separate from the environmental management group, particularly to make the difference clear to middle management.

Environmental management needs a small staff organization to instruct and motivate all levels in the line organization and all functions. It is of utmost importance that environmental management responsibilities are distributed over all levels of the line organization to encourage compliance as well as initiative from employees at all levels. Environmental management requires all groups to set objectives, goals, strategies and measures (OGSM's). The *objective* is a general statement, usually in terms of 'we want to be the best in this area'. The *goals* must be highly specific and measurable: e.g., 15% annual reduction in emissions of particulate matter over the next five years. The *strategy* defines how this reduction will be achieved and the *measures* describe how the changes will be monitored. The OGSM's must then get management commitment. That may require adding investment and/or operating cost data to the OGSM proposals. In the first phase of environmental management implementation, it is generally possible to report savings rather than expenses.

The environmental management staff is further responsible for effective internal communication on environmental matters and for consistency of the OGSM's within the company. The environmental staff should also ensure that experts are heard. External communication or supporting external communication with environmental reports is another responsibility: good environmental management builds company reputation.

Environmental audits are an important environmental management tool, aimed at identifying emissions and wastes and tracing their sources in the process and operating procedures. Administration and accountancy of raw materials, products and wastes is necessary as an additional tool for quantification of material losses with emissions and wastes, and to trace diffuse pollution sources in the processing plant. Audits should be performed both by external teams and, on a more regular basis, by internal audit teams. In the Netherlands and other Western European countries, industry is setting up so called internal environmental control systems. These systems are aimed at integrating environmental management in all management procedures and stimulating active involvement of all employees.

5.3 Technical Measures

The technical measures described in this section are only a to be considered as a general overview of the most important measures. Which measure is the best solution in a particular case depends on several plant specific details. Detailed studies, comparing several alternatives, are necessary before the most effective approach can be chosen.

5.3.1 Air Pollution - Dust Control

The emission of dust during storage of raw material should be minimized. Dust emission (and therefore emission of heavy metals) can be reduced by indoor storage and handling. If the transportation system cannot be closed, transport distances should be kept to a minimum. By proper planning and logistics the amount of material to be stored can be kept to a minimum. Further reduction of dust emissions can be achieved by spraying the material with water, although this may create an aqueous pollution problem when water treatment facilities are not available. The dust emission (and noise) problems of the comminution process are largely solved by indoor placement of the mills. Proper design and operation of the milling circuit can help to obtain the desired particle size distribution without production of too much fines.

The sintering circuit in the lead smelter is a major source of dust emissions (and sulfur dioxide). To control dust emission the off-gas should be filtered. Fabric bag filters are more efficient in removal of small particles than electrostatic precipitators. Ideally, a gas cleaning plant is installed to remove dust and sulfur dioxide, reflecting the state of the art at large integrated steel plants.

Because of the relatively high lead (and possibly cadmium) content the blast furnace off gas in the lead smelter must also be treated in suitable dust collectors, enabling separation of lead after condensation. It might be possible to use the gas (which contains a considerable amount of CO) as a fuel gas e.g., for direct heating of the Waelz kiln. Detailed studies are needed to check this possibility.

The processing of lead bullion in the thermal refinery is not a major source of heavy metal pollution. However, any process in which lead is raised to temperatures above 500 °C is a potential source of fume.

In the zinc smelter, the most important sources of heavy metal emissions to the atmosphere are the dust emissions resulting from comminution and handling of ore concentrate and the roasting section. These dust problems are similar to those of the lead smelter. Similar solutions can thus be applied to reduce dust emission, including mercury emission with the roaster off gas.

5.3.2 Air Pollution - Sulfur Dioxide

In order to reduce the emission of sulfur dioxide from the sulfuric acid plant two options are available. The single contact plant can be converted to a so called double contact plant with a much higher efficiency (up to 99.8% versus 98% in the single contact plant). This option is most effective but requires considerable capital investment. Operating costs are also higher than for a single contact plant. As an alternative, the single contact plant may be equipped with an ammonia scrubber. Up to 90% of the sulfur dioxide is thus converted to ammonium sulfate which can be used in the fertilizer industry. Conversion efficiency can also be improved by using modern catalysts, active at lower temperatures.

Another possibility is passing the off gasses through a bed of ZnO, readily available at the zinc production site as calcine. The calcine is partially converted

to ZnSO_4 and sent to the neutral leach step of the zinc plant. This solution is not proven technology yet but certainly worth further examination.

5.3.3 Solid Wastes

The solid cadmium/cobalt/copper cement formed in the electrolyte purification section may be upgraded to yield pure cadmium metal, cobalt cake and copper cement. The recovery of these metals may add significantly to the plants economy and will simultaneously reduce the solid waste problem. The technology required is available on a turn-key basis. In addition, technology is being developed for separate recovery of germanium and other valuable trace elements. The economic viability of trace element recovery is dependent on market conditions. It is not possible to predict what these market conditions will be on the long term, so recovery of trace elements is not regarded as a first priority.

Gypsum is precipitated as an outlet for manganese and magnesium, to prevent accumulation of these impurities in the electrolysis circuit. It is technically possible to extract zinc selectively from the spent electrolyte bleed stream as basic zinc sulfate before the actual gypsum precipitation takes place. Implementation of this extraction technology enables the zinc from this bleed stream to be recycled to the neutral leach. Though not yet proven on an industrial scale, solvent extraction may be applied to recover both zinc and sulfuric acid from the bleed. In this case less acid has to be neutralized and the amount of gypsum waste is proportionally reduced. The remaining gypsum, however, must anyhow be dumped in a controlled disposal site because of its residual metal content.

After filtration and washing of gypsum, a polluted waste water remains to be dealt with. Biotechnology is available to extract sulfate and (heavy) metals using sulfate reducing bacteria. After filtration and drying, the resulting sulfide sludge is recycled to the roasting section of the zinc smelter.

The slag produced by the Waelz kiln is another solid waste. A Waelz kiln process should be operated at a temperature as high as reasonably possible to reduce the heavy metal content in the remaining slag, thus improving its applicability as a construction material in civil engineering works. A slag fumer can be installed to further reduce the slag's metal content and to improve its properties as a construction material. Due to the high energy demand of slag fuming, this is a costly operation, which also necessitates adequate measures be taken to prevent emission of hazardous heavy metal vapours and dusts to the environment.

5.3.4 Water Pollution

Aqueous emissions of (heavy) metal oxides are related to the wet scrubber in the gas cleaning section. An option to be considered is to use this slightly polluted water phase to spray the milled ore concentrate, thus reducing dust formation during storage and handling of the concentrate.

Table 3. Equipment improvements for reducing heavy metal emissions in a lead/zinc smelter and related economic benefits

emission	improvement	economic benefit
dust in comminution and storage sections	water spraying minimization feedstock	reduced feedstock lower interest payments
SO ₂ from sulfuric acid plant	double contact acid plant ammonia scrubber high activity catalyst	higher value of acid byproduct byproduct amm.sulfate higher acid production
Hg in off gases	Hg removal plant	higher value of acid byproduct
dust from sinter plant	closed conveyers bag house	none
CO/dust blast furnace	use as direct fuel for Waelz kiln (speculative)	unknown
heavy metal vapours from thermal refinery	collection and solidification	insignificant
heavy metals in aqueous phase leaving wet scrubbers	use in spraying feedstock	insignificant
waste Cd/Co/Cu cement	optimized recovery	higher output and higher value of Cd/Co/Cu
zinc in waste gypsum	recovery of Zn	enhanced sales of zinc
heavy metals in waste water	biosulfidization	improved feedstock utilization
Waelz kiln slag waste	higher temperature	commercial application as construction material

To prevent soil and groundwater contamination solid waste disposal sites must be geographically isolated and be equipped with drainage and percolation water treatment facilities.

The suggested equipment improvements are summarized in Table 3.

It should be noted that this list is not exhaustive. The described technical measures are more or less generally applicable in smelter operations. Other suggestions require detailed study on site.

6 Monitoring

Waste and emission monitoring is essential to measure the effect of environmental management and technical measures. A monitoring programme must therefore be included in the OGSM proposals. In general, plants with significant emissions are enforced by environmental regulations to monitor emissions at the point of discharge (e.g., the stack) and/or outside the plant site. The frequency of sampling and the measurements to be performed are usually specified in a permit or regulation and will not be discussed here.

Where hazardous pollutants such as heavy metals are involved, an *occupational health monitoring* program should be included. The most important parameters influencing occupational health in a lead/zinc smelter are probably fume, dust and noise level. In designing an occupational health monitoring program, input of health and safety experts is essential: is it concentration, total dose or peak exposure that should be monitored? The selection of sampling and analytical equipment must be made by experts, including an analytical expert. The central part of the health monitoring programme is concerned with regular examination of the plant employees.

Since fume and dust emissions by smelter plants have a severe impact on the environment, *public health* in the vicinity of the smelter should also be monitored. Immune status is known to be a very sensitive marker in measuring the adverse health effects of environmental toxicants, as these evoke inappropriate immune system reactions. Through standardized laboratory measurements of *immune biomarkers* in blood serum, for a selected group of the exposed population, the risks for adverse health effects in the exposed population can be assessed. The actual health effect is largely determined by the interindividual susceptibility for the environmental pollutants involved. Susceptibility is generally highest for children and elder people. Adverse health effects may include: irritative and hypersensitivity reactions, immunodeficiencies, allergies and unregulated immune proliferation (e.g., leading to leukemia and lymphoma). Ecoimmunological studies in the vicinity of a nickel smelter have shown statistically significant effects on the immune system in children living in the downwind areas. The incidence of hospitalized pneumonia in children living in the vicinity of the smelter, as well as the incidence of upper respiratory tract diseases in occupationally exposed plant personnel were found to be 4 times higher than in a non-polluted reference area.

In heavily contaminated areas, as is the case with many smelter operations in Central and Easter Europe, *preventive health care programmes* are needed to protect plant personnel and the public in the vicinity against the adverse health effects of heavy metal contaminated fumes and dust. Such programmes involve relatively simple measures, such as increasing vitamin C supply to support resistance and to protect against mutagenic effects of metals. Susceptible persons suffering from an impairment of their immune system should be treated accordingly (not with antibiotics). Susceptible children should preferably be moved out

of the polluted area. These measures help to improve and protect health condition against low costs.

Monitoring the condition of the environment in the vicinity of the plant is not only needed to determine the actual state of conditions, but can also provide early warnings enabling the management to take corrective action before a major issue develops. Hence, *environmental monitoring programmes* can help to avoid more expensive liabilities and remediative actions. Environmental monitoring reports are vital to external communications, with a view to the public's 'right-to-know'.

As will be evident such programmes stretch beyond the responsibility of individual plants and, particularly where public health is concerned, should be carried out by independent authorities under governmental supervision.

6.1 Strategy for the Future

Management practices provide a framework for structural reduction of wastes and emissions to the environment. A systematic approach is helpful. In the following a few guiding principles are summarized:

6.1.1 Commit the Organisation

Commitment by the senior management to ongoing reduction of wastes and emissions should be demonstrated through policy, communication and educational programmes. Success demands that all employees develop a positive attitude to waste and emission prevention, that they feel responsible and that their active contribution is rewarded.

6.1.2 Inventory Wastes and Emissions

All sources of wastes and emissions should be traced and quantified as far as possible. These data are essential to identifying and understanding what reduction opportunities exist.

6.1.3 Evaluate Potential Impact

Evaluation by environmental monitoring and environmental impact assessment is necessary to assist in establishing reduction priorities. Open communication with employees and public is part of this step.

6.1.4 Establish a Reduction Plan, Goal and Priorities

In establishing of priorities, goals and plans for waste and emission reduction, both community concerns and the potential health, safety and environmental impacts as determined in the previous stages should be taken into account.

When setting their reduction priorities, companies also should consider criteria of technical and economic feasibility in order to stay competitive.

6.1.5 Implement the Reduction Plan

In ongoing reduction of wastes and emissions, first preference should be given to source reduction, second to recycling and third to end-of-pipe measures.

End-of-pipe measures may be needed as a short term solution for hazardous emissions, whereas source reduction may be more expensive and technically complicated. On the longer term, however, source oriented measures may be very cost effective, as a result of e.g., improved process efficiency and added product value.

6.1.6 Measure Progress

Tracking and measuring progress are essential to check if the reduction plan and goals are met. Also the quantitative inventory of wastes and emissions must be updated on a regular base. Ongoing dialogue should be maintained with employees and the public to show progress in achieving reductions and to explain or discuss future plans.

6.1.7 Periodic Evaluation

This element of the strategy requires companies to implement systematic evaluation procedures. Evaluations should not only be carried out by in-company teams, but also regularly involve independent external teams. Improvement should respond to community with respect to health safety and environmental impacts.

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Suggestions for Further Reading

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13 Reduction of Metal Emissions by Cleaner Mineral Processing Technology

M. P. C. Weijnen, J. N. Schinkel and F. Elgersma*,
Delft University of Technology, Delft University Clean Technology Institute,
Rotterdamseweg 145, 2628 AL Delft, the Netherlands

* now with: Akzo Chemicals, Research Centre Hengelo, P.O.Box 25,
7550 GC Hengelo, the Netherlands

Abstract

A review is given of the technology applied in four mineral processing industries aimed at reducing metal emissions to the environment. The processes selected are zinc and aluminum refining, phosphoric acid manufacturing and titanium dioxide production. Following a brief description of the state of the art, recent achievements and current R&D efforts towards cleaner production are summarized for each process. The four processes are subsequently compared to identify fundamental differences and similarities. It is concluded that a number of generic technological problems can be discerned in mineral processing. In spite of the entirely different nature of the processes and products described, general guidelines can be derived for reduction of metal emissions and improvement of the recovery of valuable ore components. Notwithstanding the poor environmental performance of the classical thermal and pyrometallurgical processes, pyrometallurgy holds some promises for waste and emission prevention in the future mineral processing industries.

1 Introduction

Unlike most organic substances, inorganics such as heavy metals are not degradable. On the one side, the occurrence of metal ions in the environment, including heavy metal ions, is a perfectly natural phenomenon as many metals are essential to life as micronutrients. On the other side, however, some heavy metals may be harmful to ecosystems, even if present in extremely low concentrations, as a result of their steady accumulation in the food chain. A major source of environmental pollution with heavy metals is the processing of mineral ores to produce e.g., basic metals, fertilizers, pigments and inorganic acids. In addition, some product applications of metals are intrinsically dissipative, such as the use of zinc as a sacrificial anode for corrosion prevention. In such product applications the metal product as well as the product impurities such as heavy metals are slowly released to the environment.

Over the past decades the specifications imposed on chemical products and refined metals have become considerably stricter with regard to the maximum impurity concentrations allowed. This was partly caused by the introduction of environmental regulations and legislation, partly by the development of new product applications requiring purer products. The growing market demand for higher product quality was pushed by the steady improvement of mineral processing technology itself. Due to the gradual depletion of richer ore deposits, the mineral ore processing industry was forced to apply more advanced separation technologies to increase the extraction efficiency of valuable components.

In the process of separating valuable components from a mineral ore, side components and impurities can either be recovered as byproducts or must be disposed of as a waste. General factors determining the value of a particular element in an ore body are its ease of recovery, the energy required for its recovery, its market price and its relative concentration in the ore compared to its abundance or scarcity on earth. In most types of mineral ores a variety of heavy metals is encountered in low concentrations. As their selective extraction as byproducts is mostly not economically feasible, these heavy metals were often released to the environment with the process wastes and emissions. This former practice is under severe pressure from environmental legislation. As end-of-pipe separation of heavy metals from voluminous waste streams is a costly affair which does not add any value to the product, attention is more and more being focussed on cleaner mineral processing technologies. Development of cleaner technologies is aimed at using raw materials and energy as efficiently as possible, whilst minimizing the production of emissions and wastes at their various sources within the process. It is this source oriented approach to achieve structural reduction of wastes and emissions which distinguishes clean technology from traditional environmental technology characterized by an end-of-pipe approach.

2 Aim

It is the objective of this study to picture the state of the art of clean technology in the chemical and metallurgical process industries, as far as prevention or structural reduction of environmental pollution by heavy metals is concerned. As pollution prevention requires insight in the sources of pollution, some processes are examined in detail to identify the source(s) of heavy metal emission, to describe the state of the art and to discuss the merits of different cleaner technologies for pollution prevention at the source, also taking the historic development of these processes and current research efforts into account. The processes selected for detailed examination are the production of zinc, phosphoric acid, titanium dioxide and aluminum. In addition to this process specific picture of clean technology, the fundamental differences and analogies between the various processes are examined in order to find out whether or not generic technological bottlenecks and solutions can be identified in the mineral processing industry.

3 General Aspects of Mineral Processing

Maximizing the extraction efficiency of valuable components from mineral ore bodies starts with the removal of undesired gangue materials which are generally disposed of at the mining site. Depending on the type of ore a variety of mechanical, physical and chemical separation techniques may be applied to enrich the ore. Rather than producing only one type of concentrate, selective separation of different concentrates may be practiced, each concentrate tailor-made for a different chemical or metallurgical process. Current ore enrichment practice is generally aimed at the production of selective concentrates or *mono-concentrates*, selectively enriched for subsequent extraction of one particular metal or mineral compound, as opposed to *bulk concentrates* which are enriched with respect to a combination of elements or minerals.

In the subsequent processing stages impurities remaining in the concentrate can either be recovered as valuable byproducts or must be disposed of as a waste. Given the still increasing regulatory pressure on waste prevention, more and more elements are separated and turned into a product rather than a waste. Long before environmental pollution became an issue, the recovery of side components as byproducts was catalyzed by the steady scaling up of mineral processing plants. With the increasing quantities of various side streams, economic recovery of byproducts came within reach. Where metals are concerned, however, this tendency is now obstructed by the low prices of most metals on the world market. Since the separation of heavy metals as a byproduct is often not attractive from an economic point of view, some countries, e.g. the Netherlands and Germany raise dumping costs to create an incentive for waste reduction.

In mineral processing two fundamentally different technologies can be distinguished: (i) *thermal* or *pyrometallurgical* processes and (ii) *wet chemical* or *hydrometallurgical* processes. In comparison with the hydrometallurgical or wet chemical processes, reaction rates in thermal or pyrometallurgical processes are in general substantially higher, resulting in rapid establishment of thermodynamic equilibrium. Hydrometallurgical processes often operate at non-equilibrium conditions as a result of slow reaction kinetics, thus necessitating voluminous processing equipment. The same parallel can be drawn between, on the one side, electrochemical processes in molten salts and, on the other side, electrochemical processes in aqueous media.

4 Mineral Ore Characteristics

Where metal ores are concerned the metal component is always in the cationic state, necessitating reductive treatment to derive the metal. Some ores, however, such as phosphates, are processed for their anionic component.

Table 1. The average composition (mg/kg)^a of several raw materials for some chemical and metallurgical processes.

	spalerite	apatite	ilmenite	anthracite	bauxite
desired element	Zn	P	Ti	C	Al ^e
concentration ^b	55	7 ^c	32 ^d	96	29 ^f
other elements					
Mg	320		900	2400	
Al			8700	29500	x
Ti			x	1230	12000
V			2000	48	56
Cr		200	550	26	230
Mn	250	20	14000	130	4900
Fe	80000	1500	290000	6470	42000
Co	<200				
Ni	< 50	50		25	
Cu	2500	50		15	
Zn	x	400		80	
Ga				8	80
As	1650	15		12	
Ag	<300				
Cd	1600	20		1	
Hg	< 5	0.02		0.3	
Pb	15000	2		22	
U		150		2	

source: [3,4] [5] [6] [7,8] [9]

^a The Table contains average data and is only presented for indicative purposes. Typically, each plant uses its own mixture of raw materials from several sources. Blank spaces do not mean that those elements are not present.

^b The numbers are given in weight percentages.

^c The P₂O₅ - content is typical 31 wt%.

^d The TiO₂ - content is typical 54 wt%.

^e Data for Jamaican bauxite.

^f The Al₂O₃ - content is 55 wt%.

In this paper four mineral processing industries are described. Table 1 presents an average composition of the mineral ores processed by these four industries. *Sphalerite* concentrate (mainly zinc sulfide) is the raw material for hydrometallurgical zinc production. Phosphoric acid and phosphate production are produced from *apatite* ores. Most phosphate is produced from fluoroapatite (a combined calciumphosphate/calciumfluoride mineral), although some companies process chloroapatite and hydroxyapatite ores. The mineral feed for titanium dioxide production is either *ilmenite* or *rutile*, depending on the type of process being operated. Aluminum production is invariably based on *bauxite* minerals.

Although Table 1 provides only a limited and generalized picture of the mineral ore composition, it is evident that all minerals depicted contain lots of impurities. Only a few of these are present in such quantities that their recovery as a by

product is economically feasible. The other impurities, some of which are toxic even at very low concentration levels, have to leave the process by definition as a waste. Toxic waste reduction and environmentally responsible waste treatment or disposal, particularly with regard to heavy metals, is a general problem in mineral processing industries.

Selection of the best processing route is largely dependent on the specific combination of impurities encountered in a particular ore. Between different mines, but also between different production sites of the same mine, significant differences in local ore composition are encountered. A more fundamental difference between mineral ores, which is of predominant influence on the process selection, is found in the way the impurities are bound to the ore. Some ores, such as apatite rock and in some cases rutile deposits, are essentially mono-mineral ores, whereas e.g., bauxite ore is an aggregate of several aluminous and other minerals. Selective digestion of the valuable component is not possible in the case of phosphate rock or zinc concentrate, since the impurities are trapped in the crystal lattice. Once the apatite structure is digested to release the phosphate, the impurities are inevitably released as well. This fact is responsible for contamination of the phosphoric acid product as well as the phosphogypsum waste product in wet phosphoric acid processes. In the case of bauxite, however, the situation is more favourable, as most of the non-aluminous minerals in the bauxite ore are not dissolved in the Bayer process liquor. Since these non-aluminous minerals are not chemically bound to the aluminous compounds of bauxite, and since the aluminous minerals themselves are relatively pure, a high quality alumina product can thus be obtained.

5 Cleaner Mineral Processing Technology Industrial Practice and New Developments

5.1 Zinc Refining

5.1.1 Introduction

More than 80% of the current primary zinc production capacity (7 million tpa) is based on the so called *Roast-Leach-Electrowinning (RLE) process* [10]. The second important process is the *Imperial Smelting Process (ISP)*. The latter is a pyrometallurgical process often combining zinc with lead production. For both economic and environmental reasons it is unlikely that in the foreseeable future new plants of the ISP type or any other pyrometallurgical zinc plant will be built. The vertical and horizontal retort processes are now becoming obsolete. This paper is therefore entirely focussed on the hydrometallurgical RLE process.

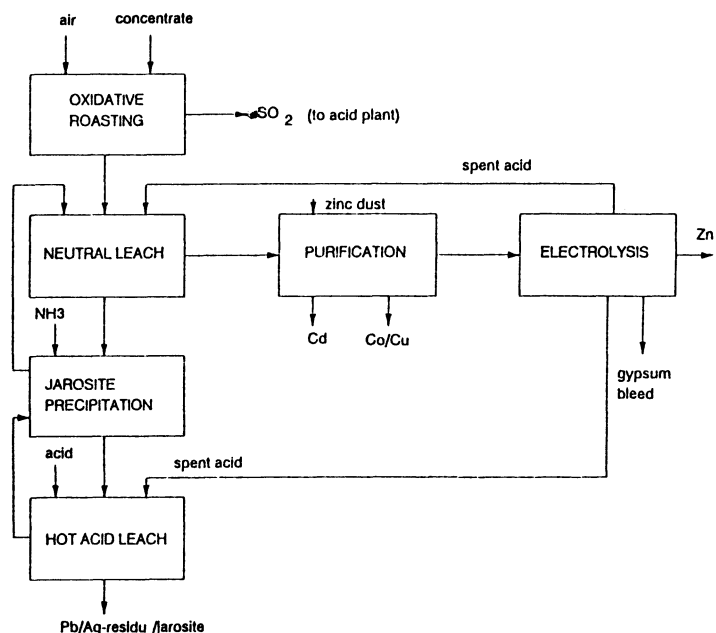


Fig. 1. Hydrometallurgical zinc refining plant

5.1.2 Process Description

Fig. 1 gives a general flow sheet of a modern zinc refinery. Sphalerite is a virtually insoluble compound. Although a process for direct dissolution has been developed, the majority of the world's zinc refineries exothermally convert the zinc sulfide with air to zinc oxide which is easily soluble in acidic solutions. The process is carried out in large fluidized bed ovens at 900 °C. Due to the presence of significant amounts of iron in the concentrate also up to 15 wt% zinc ferrite ($\text{ZnO} \cdot \text{Fe}_2\text{O}_3$) is formed. This unavoidable side reaction is highly unwanted as extra process steps are needed to extract the zinc from the stable zinc ferrite.

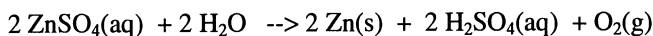
The sulfides are almost completely oxidized to sulfur dioxide. The off gas leaving the roast section is loaded with particulate matter which is removed in a large waste heat boiler designed as gravitational settler, subsequently in small-diameter cyclones and finally in an electrostatic precipitator. Mercury is separated from the gas phase and turned into a chloride compound [11]. The purified SO_2 -rich gas is then used as a feed for a double contact sulfuric acid plant. The small amount of heavy metals still present in the gas dissolve almost completely in the sulfuric acid so the emission to air is almost zero.

The zinc oxide particles (*calcine*) collected from the roaster and the gas cleaning section are combined and dissolved in sulfuric acid. This dissolution or *leaching* process proceeds in two steps. In the first step, the so called *neutral leach*, the zinc oxide is dissolved under relatively mild conditions (pH 3-5, 70 °C).

In the second step, the so called (*hot*) *acidic leach*, zinc ferrite is dissolved under more stringent conditions (pH 0.5-1.5, 95 °C). In addition to zinc also the iron is now released into solution. Before zinc electrolysis the iron needs to be separated from the zinc electrolyte.

Iron is removed by precipitation of *jarosite*, *goethite* or *hematite*, followed by filtration. The relatively small amount of dissolved iron present at the neutral leach stage can be removed as a $\text{Fe}(\text{OH})_3$ precipitate. The zinc electrolyte leaving the neutral leach is further purified by cementation of cadmium, copper, cobalt and minor amounts of other elements. This cementation process is performed in several steps to yield a number of valuable byproducts. After further upgrading pure cadmium is obtained (by electrolysis or distillation), a copper-cake (50 wt% Cu) as well as a cobalt-enriched cake.

The purified zinc sulfate solution is sent to the electrowinning plant where the following electrolysis reaction takes place:



The zinc metal is periodically stripped from the cathodes and further processed by melting and casting.

In the process outlined above insufficient outlet for magnesium, manganese and some other elements proved to be present. In order not to accumulate these elements in the leach electrolysis circuit, a *bleed* of spent electrolyte is applied. As this bleed is neutralized with lime, it finally yields a gypsum residue which is contaminated with heavy metals, zinc, magnesium and manganese.

5.1.3 Environmental Bottlenecks

Extraction Efficiency

Since up to 99% of the zinc content of the raw material is finally recovered as zinc metal, the zinc yield of the RLE process can hardly be improved. As evident from the process description and Table 1, however, major amounts of lead and small but valuable amounts of silver and sometimes gold are not recovered in most of the current zinc refineries. As a consequence these elements leave the process as a waste.

Solid Waste

By far the largest waste residue of hydrometallurgical zinc production is the iron precipitate in the form of jarosite, goethite or hematite (see Table 2 for some properties). Currently most refineries use the jarosite process mainly because of effectiveness, simplicity and relatively low costs. In particular the jarosite process, however, yields huge amounts of waste, in the order of 0.6-0.8 ton residue per ton of zinc metal produced. On the one side, the production of this waste residue is directly related to the iron content of the sphalerite concentrate. On the other side,

the high molecular weight of jarosite as such and the finely divided nature of the precipitate, resulting in a high water content of the residue, are factors responsible for the huge volume of waste residue. The jarosite is generally stored in ponds. . Since the jarosite is contaminated with several toxic elements such as lead, cadmium and arsenic, the dump sites have to be geohydrologically isolated and strictly controlled. This is not yet common practice. The iron precipitate problem is recognized as the most important environmental problem of the zinc industry [10].

In addition to the iron precipitate a less important gypsum waste stream is produced, resulting from zinc recovery from the spent electrolyte bleed and from neutralization steps in waste water treatment. Like jarosite, the gypsum waste is also contaminated with heavy metals and thus has to be stored in protected ponds.

Ground Water Protection and Effluent Treatment

Past experiences with jarosite residue storage have made it clear that the risk of leakage is substantial. In order to avoid groundwater pollution an effective monitoring system and drainage water treatment are required. Because of pollution prevention policies zinc companies in some countries are now facing deadlines for residue ponding or are being forced to process historical jarosite residues, the latter being the case in the Netherlands.

Table 2. Iron precipitate waste formed in hydrometallurgical zinc production

Composition % theoretical in practice			Amount (ton/ton zinc)	Extraction efficiency (Zn %)
<i>Ammonium jarosite</i> NH ₄ (Fe ₃ (SO ₄) ₂ (OH) ₆)			0.8 t (34 wt % H ₂ O)	96-99
Fe	37	25-30		
S	13	10-12		
Zn	-	4-6		
<i>Goethite</i> FeOOH			0.58 t (34 wt % H ₂ O)	97-98
Fe	63	40-42		
S	-	3-5		
Zn	-	5-9		
<i>Hematite</i> Fe ₂ O ₃			0.32 t (12wt % H ₂ O)	98-99
Fe	70	58-65		
S	-	1-1.7		
Zn	-	0.5-0.8		

5.1.4 Zinc Refining - Clean Technology Options

Extraction Efficiency

In order to optimize the recovery of valuable elements from sphalerite concentrates, extensive R&D programs were carried out over the past decades. As a result, up to 99% of the zinc content is now extracted as zinc metal. Despite this remarkable achievement research efforts towards a further enhanced zinc recovery are being continued.

In the ongoing research into recovery of other valuable elements, such as silver, a source oriented and an end-of-pipe oriented approach are clearly distinguished. Most studies are aimed at recovering precious (heavy) metals from the process streams within the zinc refinery. In addition, processes are being developed to reclaim valuable elements from previously ponded wastes. Examples of the first category are the processes suggested by Rodier [4], Rosato [12], Scott [13], Demarthe [14] and Huang [15]. The technologies suggested, and in some cases already applied, include thiourea leaching [1], solvent extraction [13] and optimized flotation [15]. The latter technology, in one case combined with sulfidization, was also suggested for removing silver from iron residues [16, 17].

It must be emphasized that the recovery of ore contaminants as valuable by-products is generally beneficial from an environmental point of view due to the fact that residual streams will be less polluted. Economic constraints are the main bottlenecks that prevent the implementation of these cleaner technologies.

Solid Waste

The need for jarosite treatment to either render it environmentally harmless or to give it a useful application has over the past fifteen years become more and more urgent. Although a final solution has not been found yet, some promising options have been identified. Even before 1980 the need for a cleaner iron residue was identified by Electrolytic Zinc of Australasia which developed the so called *Low Contaminant (LC) jarosite process* [18,19]. The LC process yields a somewhat cleaner jarosite. As the amount of waste is not reduced, however, this process has not found wide acceptance. A more promising solution is the *hematite process*. The impurity level of the hematite residue was sufficiently low to make it acceptable for application in the cement industry [20]. Impending stricter environmental legislation, the small market for this quality hematite and the higher costs of the hematite process have limited the number of hematite producers to a few, including e.g., Ruhr-Zink (Datteln, Germany) and Iijima (Japan). Current research efforts are aimed at reducing the sulfur and zinc content to such a level that the hematite can be processed in integrated steel plants [20].

Recently a new process has been developed for processing jarosite residues, including historical residues [21,22]. Upon treatment at 1300 °C in a flash furnace a stable slag and fly ash are formed. After treatment in a slag fumer, the inert slag can be used as a gravel substitute in concrete [23]. The fly ash which contains the

more volatile components such as lead, zinc, cadmium, arsenic and silver can be processed to recover valuable components. The only non-applicable waste product is a ferric arsenate residue. This process has been proposed as a solution for the jarosite problem in the Netherlands. The project has just been discarded, however, mainly because of the excessive costs involved.

Further reduction of impurity uptake in the iron residue is still a research topic. Recent studies have shown that the incorporation of zinc in jarosite is proportional to the supersaturation for jarosite precipitation [24]. This supersaturation can be controlled by dissolving zinc ferrite via a solvent-mediated process [25,26]. As a consequence, the supersaturation level is limited and the impurity uptake in jarosite is reduced.

The use of cleaner raw materials is, theoretically, a very effective approach to circumvent the iron precipitate problem. Availability of low iron sphalerite deposits is very limited, however, and higher costs are involved. For the majority of sphalerite mines the production of low iron concentrates is not feasible, unless a substantial loss of valuable zinc is accepted.

Ground Water Protection and Effluent Treatment

Waste water of the gas purification section and percolation water of the jarosite basins must be subjected to treatment before being discharged to surface water. For this purpose an elegant biological water treatment process has been developed by Budelco [27,28]. Under anaerobic conditions sulfate reducing bacteria are fed with ethanol to yield sulfide, forming virtually insoluble heavy metal sulfides. These sulfides are fed with the sphalerite concentrate into the roaster section of the zinc refinery. Zinc, cadmium, copper and cobalt are thus recovered.

Other Developments

An interesting alternative for the roast step in a fluidized bed is the *direct (pressure) leaching* process [37]. Oxidation of sphalerite takes place in an autoclave at elevated temperature and pressure. Under these conditions zinc ferrite is not formed. Instead of sulfur dioxide elemental sulfur is formed, thus eliminating the need for a sulfuric acid plant. At the proper reaction conditions most of the iron can be precipitated in the form of iron oxides (hematite) in the autoclave itself. As an alternative, iron can also be removed through the hematite process. In addition to elemental sulfur, lead and silver can be recovered with this process. The market for elemental sulfur is somewhat better than for sulfuric acid provided the sulfur is very pure.

5.2 Phosphoric Acid Manufacturing

5.2.1 Introduction

In phosphoric acid production wet processes dominate the market which is estimated at 50 million ton H_3PO_4 per annum [5]. Most of the wet process phosphoric acid is used to produce phosphate fertilizers. The phosphate rock raw material is mainly composed of apatite minerals, generally fluoroapatite. Since most of the ore impurities are trapped in the apatite crystal lattice, separation processes to remove impurities before the ore is digested in sulfuric acid are hardly effective. The process variants in use are named after the particular calcium sulfate modification ($\text{CaSO}_4 \cdot n\text{H}_2\text{O}$) which is precipitated during the apatite digestion stage in sulfuric acid. The modifications involved are calcium sulfate *anhydrite* (AH, $n=0$), *hemihydrate* (HH, $n=0.5$) and *dihydrate* (DH, $n=2$) [29].

Although some AH processes have been developed, commercial phosphoric acid plants either operate a HH or a DH precipitation in what is called a HH- or a DH-process, respectively. Apart from these straight-run processes, various process routes involving a calcium sulfate recrystallization step were developed, both with and without intermediate filtration of the calcium sulfate precipitate formed in the digestion stage. An example of these processes is the so called HDH-process.

5.2.2 Process Description - Wet Process

The aim of a phosphoric acid plant is to recover as much phosphate from apatite rock as possible, preferably at commercial product acid concentrations of 40-52 wt% P_2O_5 (or 50-65 wt% H_3PO_4). The efficiency of a plant is defined as the percentage of phosphate from the ore which is sold as acid. From the point of view of phosphate efficiency the so called HDH-process proved to be superior to the other processes. Additionally, the HDH-process (as in fact all processes precipitating HH in the digestion stage) directly produces acid of sufficient strength, so an evaporation step to concentrate the product acid is not required. Fig. 2 shows a flow diagram of a HDH-process. In the reaction section of this process HH is precipitated which is filtered, washed and subsequently recrystallized into DH. The phosphate incorporated in the HH during the digestion stage is released during recrystallization and can thus be recovered with the product acid. The DH is again filtered, yielding a relatively clean waste gypsum and reusable wash water.

5.2.3 Process Description - Electrothermal Process

An alternative process developed to yield extra pure phosphoric acid suitable for food grade phosphate production, is the so called *electrothermal reduction process* which produces pure elemental phosphorus as an intermediate. In this process

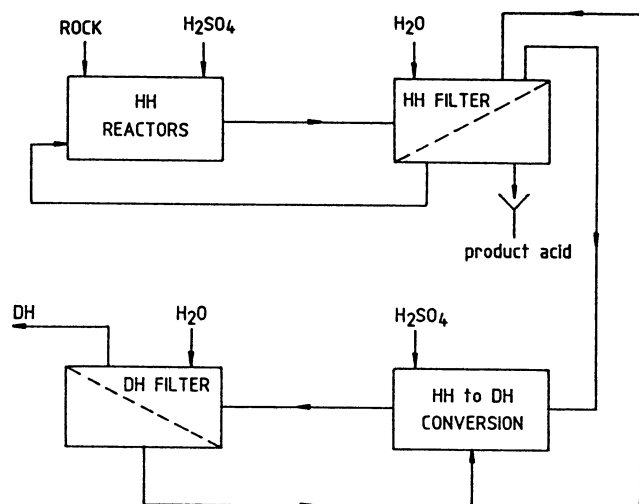


Fig. 2. A two-filter HDH wet phosphoric acid manufacturing process

phosphate ore is pelletized with clay and sintered. A mixture of the pellets with gravel and cokes is heated to 1400-1500 °C in an electrical furnace. The resulting product gas mixture from the furnace consists of CO (90%), P₄, SiF₄ and minor amounts of other volatilized components. Dust particles entrained with the furnace gas are separated in electrostatic precipitators. Due to condensation of heavy metals and radionuclides onto the particles this dust fraction, which is recycled to the pelletization section, is heavily contaminated. In order to prevent accumulation to hazardous concentration levels within the processing plant, some bleeding is required.

The phosphorus is condensed by spraying water. Silica fluoride is separated as a byproduct in wet scrubbers. The remaining CO gas can be used as a fuel gas. The pure phosphorus is converted to phosphoric acid by oxidation with air to phosphorus pentoxide which is subsequently absorbed in phosphoric acid. The phosphoric acid thus produced is far less contaminated with heavy metals than the wet process product acid. In the thermal process most of the heavy metals originally present in the ore are immobilized in an inert slag. The so called phosphorus slags find application as a gravel substitute in road and dike works.

In comparison with the wet process it is easier to control heavy metal emissions in the thermal process. Costs are much higher, however, mainly due to the high energy demand of the process. The product acid is largely used in foodstuffs and other speciality products. Since only a few thermal phosphorus plants are operated worldwide and production volumes are low in comparison with wet process plants, the thermal process is not discussed in more detail.

5.2.4 Environmental Bottlenecks

Phosphogypsum

The main waste stream of the wet phosphoric acid process is the so called *phosphogypsum* waste stream. The distribution of phosphate ore impurities over the calcium sulphate and phosphoric acid phase is to a large extent determined by the type of calcium sulfate modification which is precipitated. Incorporation of heavy metals, in particular cadmium, in the gypsum waste is a major environmental problem. Apart from the low market price of gypsum waste, two general reasons are discerned why phosphogypsum is discharged or ponded as a waste rather than being applied for building purposes. One of these reasons is the limited strength of the material as compared to natural gypsum. Another reason is the radio-activity of phosphogypsum due to the presence of uranium. The latter nuclide decays to radon gas which, if the phosphogypsum were applied in buildings, would pollute the indoor environment.

In the mid 1980's the *Rhine Action Programme* as well as the Port of Rotterdam Rhine research project identified the gypsum discharges of the Dutch wet phosphoric acid industries as the major point source of cadmium discharges to the Rhine River basin [30]. Although for the wet phosphoric acid industry in 1983 an exception was made in the EC-directive regarding maximum allowable aqueous emissions of cadmium [31], more and more pressure was exerted from the side of the Dutch government to reduce these cadmium emissions. The wet phosphoric acid industry in the Netherlands was thus forced to optimize its phosphate efficiency and to control its emissions of heavy metals via phosphogypsum. Since the heavy metals are neither desired in the gypsum waste, nor in the product acid, a difficult problem had to be solved. The industry's response is discussed below.

5.2.5 Wet Phosphoric Acid Manufacturing - Clean Technology Development

Phosphogypsum Waste

The easiest solution to prevent heavy metal contamination of phosphogypsum and product acid is found in the use of cleaner raw materials. This option is realistic, as far as cadmium is concerned. Two types of apatite ore are available on the market, one type of sedimentary, the other of magmatic origin. The sedimentary ores, an average composition of which is given in Table 1, contain in average much more cadmium than the igneous ores. Their lanthanide content, however, is generally less than 100 ppm (mainly cerium and yttrium). Igneous ores, although significantly less contaminated with cadmium (generally less than 1 ppm), may contain up to 1 wt% of lanthanides. The major reason, apart from the costs, why the use of these lanthanide-rich ores is unattractive, is that they hamper the recrystallization kinetics of calcium sulfates [5]. This adversely affects the plant production

efficiency, which is undesirable. In addition igneous ores are generally more heavily contaminated with uranium than sedimentary deposits.

A more elegant solution proposed is the precipitation of a cadmium-rich calcium sulfate modification, inhibiting cadmium to enter the product acid phase. After washing, the precipitate is recrystallized in such a way that the final calcium sulfate modification can reincorporate the cadmium only to a minor extent. Controlled recrystallization of calcium sulfate modifications to prevent heavy metal incorporation has extensively been studied by Witkamp [5]. In this particular recrystallization process the supersaturation for DH growth is limited and controlled by HH dissolution, following a solvent-mediated conversion. Cadmium remains in solution and may be removed by solvent extraction, sulfide precipitation, ion exchange or other techniques, although none of these methods is easily applied in phosphoric acid media.

Most of current R&D efforts into wet phosphoric acid production are aimed at inhibiting incorporation of heavy metals in calcium sulfate and at selective extraction of heavy metals and radionuclides from (diluted) phosphoric acid. In the past e.g., uranium extraction (as UF_6) from phosphoric acid has already been commercially practiced. Some wet process phosphoric acid is purified for speciality applications through selective extraction of impurities.

5.3 Titanium Dioxide Pigment Production

5.3.1 Introduction

The production of TiO_2 amounted to more than 3 million tpa in the early 1990's [38]. The most important application of TiO_2 is as a white pigment and filler in paint, plastics and paper. Approximately 10% of the TiO_2 produce is converted to metal which is used as a high quality construction material.

Only two commercial processes are currently in use to produce TiO_2 -pigment, being the *sulfate process* and the *chloride process* [32]. The latter accounts for more than 40% of current production. As most new plant facilities and extensions will be based on the chloride process, the sulfate process is soon expected to lose its dominant position.

Two ore types are used for TiO_2 pigment production: *rutile*, a pure natural TiO_2 compound (up to 98 wt% TiO_2) and *ilmenite*, a ferro-titanous compound (40-60 wt% TiO_2). Ilmenite can be used in the sulfate process but is without further treatment not suitable for the chloride process, with the exception of Dupont chloride processing technology being able to handle high grade ilmenites. As natural rutile deposits are scarce and expensive, much of the ilmenite is upgraded to either *synthetic rutile* (up to 98 wt% TiO_2) or *titaneous slags* (up to 90 wt% TiO_2) which can be utilized in both processes.

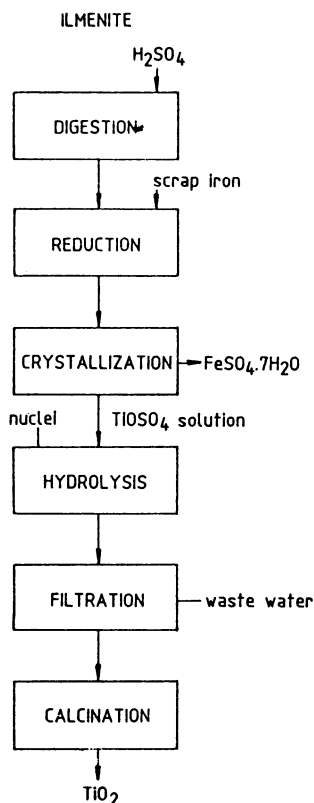


Fig. 3. Titanium dioxide - sulfate process

5.3.2 Process Description - Sulfate Process

The sulfate process, a flow sheet of which is presented in Fig. 3, was designed for ilmenite as a raw material. Ilmenite is first dissolved in sulfuric acid in a two-step leach: in the first step the ore is digested and in the second step scrap iron is added to reduce any iron to the ferrous state. From this solution ferrous sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) is precipitated by cooling and filtered. Titanium remains in solution as titanyl sulfate, $\text{TiO}(\text{SO}_4)$. By boiling the sulfuric acid solution titanyl sulfate is hydrolyzed yielding a TiO_2 -precipitate. The solids are filtered, washed, calcined and milled to give a crude TiO_2 -pigment which may be additionally coated. The major waste products are the impure ferrous sulfate pulp containing various other waste metal sulfates and large amounts of waste acid. Up to 7,500 kg of waste is thus produced in the sulfate process per ton of TiO_2 produced [42].

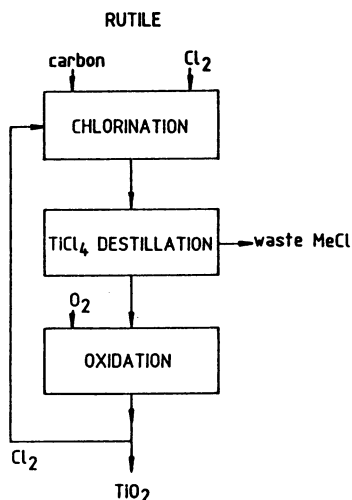


Fig. 4. Titanium dioxide - chloride process

5.3.3 Process Description - Chloride Process

The chloride process was originally designed for processing rutile ore which dissolves very slowly in sulfuric acid. The flow sheet is presented in Fig. 4. First, the rutile ore is mixed with coke. The solids react with chlorine in a fluidized bed chlorinator to form liquid TiCl_4 which is subsequently upgraded by distillation. In the next step, the pure TiCl_4 is oxidized at 1000°C yielding a raw TiO_2 pigment. Most of the chlorine is recovered and recycled to the chlorination step. Some of the chlorine is lost, however, due to chlorination of metal impurities. These metal chlorides, the quantity of which is determined by the raw material impurity content, constitute the most important waste stream of the chloride process.

5.3.4 Environmental Bottlenecks

Waste

In Table 3 a survey is given of the wastes produced in both processes.

It is evident that the chloride process produces substantially less waste than the sulfate process. This can partly be attributed to the fact that the wet chemical sulfate process yields large quantities of diluted acid, but also to the fact that the ilmenite ore used in this process is more contaminated than the rutile or slags used in the chloride process. Until recently this voluminous diluted acid waste stream was discharged to sea (if possible and permitted) or neutralized with lime yielding a contaminated waste gypsum. The acid waste problem cannot be solved by the use of higher grade raw materials in the sulfate process. In the chloride process, on

Table 3. Waste formation in titanium dioxide production (kg/ton TiO₂)

	sulphate process			chloride process		
	ilmenite	Sorel slag	ilmenite	RB-slag ^a		rutile
raw material	2 400	1 500		1 790	1 230	1 080
TiO ₂ -content (wt %)	45	70		59	86	97
sulphuric acid	4 500	4 000		-	-	-
chlorine ^b	-	-		1 872	1 881	1 858
waste	7 500	6 400		1 390	530	225
	(waste acid)			(waste chlorides)		
waste contents %						
acid	21	21	FeCl ₂	75	39	8
FeSO ₄	10,7	4,1	AlCl ₃	3	10	7
Cr, Al, V			C	8	18	39
			TiOCl ₂	4	4	4
			Unreacted	4	11	19

Source [39].

^a Richards-Bay slags.^b most of the chlorine is recovered in the process.

the contrary, the use of purer raw materials proves to be effective in waste reduction, as the metal chloride waste quantity is more than proportionally reduced in comparison with the sulfate process. In the past five years almost all newly constructed or announced plants throughout the world are based on the chloride route [40]. Environmental concerns about the acid waste of the sulphate process and the high costs involved in environmental protection are likely to continue this trend.

5.3.5 Titanium Dioxide Production - Clean Technology Options

Acid Waste

In order to reduce the acid waste generated by the sulphate process, maximized recovery of concentrated sulfuric acid is essential. Sulfuric acid recovery is most of all dependent on the filtration technology applied for separating freshly precipitated TiO₂ from its mother liquor. Belt filters with different compartments for filtration and washing are known to require less (wash) water than drum filters. Still, the acid as recovered contains only 18-25 wt% H₂SO₄ and needs to be upgraded to at least 70 wt% H₂SO₄ before reuse is technically feasible. This concentration step is a complicated and costly affair necessitating a high energy input. Due to the low market price of virgin sulfuric acid the process is not feasible from an economic point of view. Industrial applications of this technology are

enforced by environmental regulations [41]. A useful byproduct is a relatively clean ferrous sulfate which can be used as a flocculation agent in waste water treatment. The use of higher grade raw materials in the sulfate process does not apply as an effective strategy. With purer raw materials the iron influx decreases, more to the effect of reducing the amount of ferrous sulphate produced, however, than reducing the amount of acid waste.

Ferrous Sulphate

The amount of contaminated ferrous sulfate waste can be reduced by using Ti-slugs as a raw material instead of ilmenite in the sulphate process, not only because of the lower iron content of the slags but also because of the presence of Ti(III)-ions. These reduce the ferric ions to the ferrous state, eliminating the need for addition of iron scrap and thus reducing the amount of ferrous sulfate waste even further [39].

Metal Chlorides

To reduce the metal chlorides waste of the chloride process pure raw materials are essential. Rutile is therefore excellent as a raw material but prices are high and future availability is limited. As an alternative, (enriched) Ti-slugs can be used. These slags are produced from ilmenite or ilmenite/hematite ores through a pyrometallurgical process. After separation of silica and aluminum, these ores are reduced with cokes in an electric furnace, thus yielding a Ti-slag. The iron present in the ore can be separated as a byproduct finding application in the steel industry.

In addition, various processes are available to produce so called synthetic rutile (TiO_2 -content up to 98%) from ilmenite through selective chlorination or reduction with cokes followed by a wet leaching processes to remove iron [42]. In the latter case, however, aqueous waste products are produced. The waste problem is thus partly shifted from the pigment production site to the mining site.

As a remaining alternative, the metal chlorides can be processed after their formation in order to selectively extract valuable components. Selection of cleaner raw materials, especially (enriched) titanous slags or (natural) rutile, is still considered the best option for the chloride process.

5.4 Aluminum Refining Industry

5.4.1 Introduction

Aluminum is the most abundant metal in the earth's crust and aluminum ores are abundant as well. Aluminium is the most widely used non-ferrous metal with a world wide production of more than 14 million tpa (1992). Unlike the process diversity encountered with other mineral and metal products the commercial

production of aluminum always proceeds along the same processing route known as the *Bayer-Hall-Hérault* process, which was established more than a century ago. Although the process has been drastically improved since then, R&D efforts to further improve its performance are still being continued. In all commercial plants bauxite is used as a raw material. This ore is mainly composed of the aluminous minerals *gibbsite* ($\text{Al}(\text{OH})_3$), *boehmite* (AlOOH)₂ and *diaspore* ($\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$), totalling 40-60 wt% Al_2O_3 in commercial grade bauxites.

5.4.2 Process Description

In aluminum production two major processing steps are distinguished [33,34]. In the first step bauxite is processed to yield pure *alumina* (Al_2O_3). In the second step alumina is reduced to *aluminum metal* in a primary smelter. These processes are in general separated geographically, alumina being produced in the vicinity of the bauxite mining site, the smelter operation being performed at a site where cheap electricity is available.

The alumina plant is based on the *Bayer process*. Fig. 5 shows a simplified processing scheme. Whereas gibbsite is easily dissolved, boehmite and diaspore are known to dissolve slowly in strong caustic soda solutions, necessitating CaO addition to improve the leaching process. After digestion of the bauxite a settling and filtration operation is performed to separate undissolved silica, iron oxides and other non-amphoteric ore components from the process liquor. The bauxite residue is washed and disposed of in land fills. This voluminous waste stream is known as *red mud* because of its color and water content.

The remaining pregnant solution is subsequently cooled to create the supersaturation for gibbsite crystallization. Seed crystals are added in abundance to avoid massive scaling in the crystallizers. The gibbsite crystals are separated by filtration. The mother liquor filtrate is recycled to the ore leaching stage. The gibbsite is finally dried and calcined to obtain pure anhydrous (alpha-)alumina. Although some alumina (mainly gamma- Al_2O_3) is sold for speciality applications, more than 90 wt% of alumina produced is fed to aluminum smelters.

The smelting operation is known as the *Hall-Hérault process*. Alumina is dissolved in a bath of molten cryolite and electrolytically reduced to metallic aluminum. The carbon anodes are consumed in the process as their oxidation is part of the cell reaction, resulting in a CO/CO_2 off gas mixture. The liquid metal is periodically tapped from the cells and transported to the casting and alloying plant for further processing. As a result of the high purity of the alumina feed, both alumina and carbon anodes, pollution with heavy metals is kept to a minimum. The minor amounts of heavy metals (e.g. nickel) in the smelter off gas are captured in the gas cleaning section.

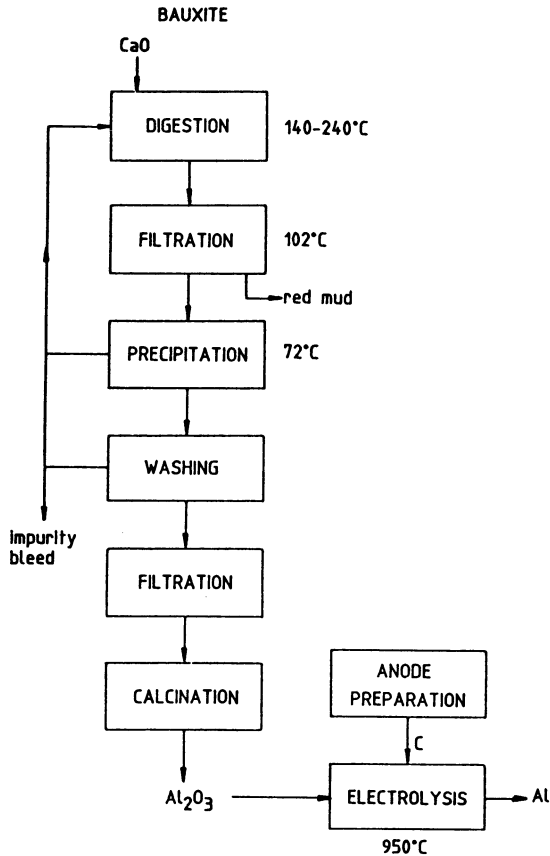


Fig. 5. A flow scheme for aluminum refining from bauxite

5.4.3 Environmental Bottlenecks

Solid Waste

The major environmental problem of aluminum production from bauxite, as far as heavy metals are concerned, is the red mud waste produced by the Bayer process [35]. Per ton alumina 0.4 to 1.4 ton red mud is produced containing 40-50 % water, at a pH value of 12 or even higher. The red mud contains a number of valuable components such as iron oxides (20-50%), titanium oxides (3-10%), as well as alumina (10-30% Al₂O₃) (all percentages on a dry weight basis). In general the red mud is stored in huge basins near the production site.

5.4.4 Clean Technology Options

Red Mud

None of the iron, silica, titanium and alumina compounds which could potentially be recovered from red mud are scarce or expected to become scarce in the near future [35]. Due to its poor physical properties, red mud is not suitable for civil engineering construction works. Current disposal practices are well controlled, including geohydrological isolation, ground water monitoring and drainage water treatment. By revegetation after top soil addition, lasting environmental damage is kept to a minimum. As an alternative, red mud may be sintered to yield brick, tiles or sorbent materials.

To date, an economically feasible alternative for the Bayer-Hall-Hérault process has not been identified and is not likely to be identified in the near future [43], in spite of massive research efforts in this field. Only one option that might in future drastically affect the aluminum industry, will be mentioned here. This option studied by Alcoa and the US Department of Energy is concerned with the carbothermic reduction of alumina-silica ores, directly yielding Al and Al-Si alloys in one step. This process would eliminate the need for intermediate alumina production and thus eliminate the red mud problem, as bauxite is directly fed with coke and clay to the carbothermic reactor. The process yields a Fe-Si slag and a Al-Si smelt. The latter is a useful product as such but can, if desired, also be processed in a membrane cell to obtain pure Al and Si products [43]. Major technical problems, however, still need to be overcome before this direct reduction process can become a commercial reality.

5.4.5 Technological Bottlenecks in Mineral Processing

A general feature encountered in mineral processing is the problem of solids handling. The raw material is encountered in the solid state and generally needs to be broken, crushed and ground before use. These comminution operations and the transportation of solids as such invariably give rise to dust formation. This is an obvious source of environmental pollution which can hardly be eliminated, unless the transportation and comminution systems are closed and equipped with filters, such as bag filters and electrostatic precipitators.

Dust problems are also encountered in thermal processing of mineral ores. Thermal processes generally involve large gas flows, leading to entrainment of particulate matter. Upon separation of the dust particles in e.g., electrostatic precipitators, metal vapours may condensate onto the dust particles. In thermal phosphorus production, for example, this gives rise to contamination of the phosphate dust particles with lead, zinc, mercury and radionuclides. Said metals accumulate in the process upon recirculation of the dust fraction to the feed preparation section of the process, necessitating regular bleeding of the dust

recycle stream and selective separation of hazardous heavy metals and radioactive components.

In general the concentration of the valuable component in the enriched ore (after removal of gangue material and subsequent ore dressing operations) is in the order of 50%, but sometimes in the order of a few percent or even less (copper, precious metals). This necessarily involves the production of huge quantities of waste. In thermal processing of mineral ores most of the undesired ore components end up in a slag. Depending on the nature of the slag, it may be used as a construction material or must be disposed of as a solid waste. In the Netherlands, however, forthcoming environmental legislation may drastically reduce the possibilities for slag utilization in road, dike and harbour constructions as the new leachability requirements are difficult to meet.

In hydrometallurgical processing the ore impurities are mostly separated by precipitation or crystallization, giving rise to large quantities of wet waste. Particularly when finely divided iron precipitates are concerned, as in the case of red mud in the Bayer alumina process or jarosite in the refining of zinc, the water content of the precipitate may be in the range of 30-60%. Both the water content and the leachability characteristics of these precipitates necessitate costly protective measures at the waste storage site: the storage site needs to be geohydrologically isolated from the environment and the drainage water must be collected and treated before discharge. Due to the high water content and the drying costs thus involved, subsequent processing of the precipitates to remove valuable components as byproducts is generally not economically feasible.

In addition to the wet waste disposal problem, another common environmental problem of hydrometallurgical processes and wet chemical treatment of minerals is the problem of waste water discharge. Ore digestion in these processes proceeds either in strongly acidic or strongly alkaline media, often necessitating neutralization of the waste water (in addition to other waste water treatment steps) before it can be discharged.

In most wet chemical and hydrometallurgical processes, either the waste or the major product is separated by precipitation or crystallization. When impurities are present in the mother liquor, as invariably the case in mineral processing, these will be distributed over the solid and the liquid phase, depending on the precipitation/crystallization kinetics and on thermodynamic equilibrium conditions. Whether the desired product is the liquid phase (phosphoric acid) or the solid phase (alumina), additional purification steps are generally needed after separation of the two phases by filtration.

It is almost common opinion that hydrometallurgical and wet chemical processes should be favoured over thermochemical and pyrometallurgical processes because of their lower energy demand. This opinion, however, is not justified by the facts. For example, the primary energy requirement of an average hydrometallurgical zinc process is 57.3 GJ/ton zinc [44], whereas zinc production in a blast furnace process requires only 40.6 GJ/ton zinc. In such comparisons a correct definition of the system boundaries is essential. On the one side hand, the energy efficiency of supporting processes, such as the production of electricity and cokes

from primary resources, must be included within the system boundaries. On the other side, credits for furnace gas and other byproducts should be taken into account. In the case of zinc, the high overall energy requirement of the hydrometallurgical process can largely be attributed to the high electricity demand of the process and the relatively poor energy efficiency of power stations (33-40%). The blast furnace, however, exhibits a much higher thermal efficiency (up to 80%). These factors require closer examination before a correct assessment can be made.

7 Discussion and Conclusions

Although only four major chemical/metallurgical production processes were discussed in this paper, a variety of unit operations was shown to be applicable for reducing heavy metal emissions to the environment. These include: leaching, solvent extraction, flotation, slag fuming, precipitation and recrystallization, ion exchange, filtration, distillation and evaporation. The apparent variety of technological solutions, however, cannot obscure the fact that a number of common problems in mineral processing are solved in a similar way.

Wet Processes

In almost all hydrometallurgical and wet chemical mineral processing routes crystallization and/or precipitation steps play a prominent role. The examples from industrial practice described in this paper, though ranging from zinc hydrometallurgy and wet process phosphoric acid production to alumina production in the Bayer process, all involve one or more (re)crystallization steps to achieve selective separation of valuable and undesired ore components. In all three examples the supersaturation for precipitation or crystallization is controlled at a low level to avoid massive uptake of impurities and to control the size and habit of the crystals for optimum filtration properties. This essential limitation of the supersaturation is either effected by seeding or, in a more sophisticated way, by applying the solvent-mediated conversion principle.

The importance of the filtration and washing operations following crystallization or precipitation cannot be underestimated either. The Bayer process, for example, is based on the elegant principle of selective digestion of aluminous minerals in caustic. The non-aluminous and non-amphoteric ore components remain undissolved. The selectivity of the Bayer process, however, is not utilized to its full extent, as substantial amounts of valuable alumina still end up in the bauxite residue (red mud) with adherent process liquor. Since direct carbothermic reduction of bauxite is not within technical reach yet, further improvement of filtration technology is needed to improve the efficiency of the Bayer process. Also in wet phosphoric acid production the performance of e.g., the two-filter HDH-process with respect to phosphate yield and phosphogypsum impurity content is largely determined by the efficiency of filtration and washing operations.

Filtration technology is of similar importance in the sulfate process for production of titanium dioxide and in hydrometallurgical zinc production processes.

Although crystallization process control and solid/liquid separation technology still offer ample scope for improvement, two major drawbacks of hydrometallurgical and wet chemical processes will inevitably remain:

1. Effective control of crystal size and habit during crystallization or precipitation steps in mineral processing requires tailormade solutions:
crystallization processes are very sensitive to minor amounts of impurities in the mother liquor. Impurities, including heavy metal ions, can influence the crystallization process as nucleation and growth retarders, habit modifiers etc. As the actual effect of one specific impurity on a specific crystallization process is already difficult to predict, the combined effect of a mixture of impurities in industrial crystallization practice is only empirically determined. The effect of impurities is further known to be largely different on different modifications of the same salt, as has been established for e.g., the dihydrate, hemihydrate and anhydrite modifications of calcium sulfate. As each natural mineral ore contains its own unique mixture of impurities (that could be considered as a fingerprint of the mine), it is evident that effective control of the size and habit of the crystals and thus of their filtration properties requires a tailormade approach for each individual ore.
2. Stoichiometric amounts of an inorganic waste will be formed:
most minerals are processed either for their cationic or for their anionic component only. In hydrometallurgical and wet chemical processes the undesired ore component is separated and disposed of mostly as an inorganic salt. In general these salts as such are environmentally harmless. Environmental hazards, however, arise from the additional presence of toxic components such as heavy metals, and from adhering process liquor which is either a strongly acidic or a strongly alkaline solution. Since even minor amounts of impurities can pose serious environmental risks, it is highly unlikely that the mineral processing industries will succeed in improving the quality of their wet inorganic wastes to such a level that direct discharge to surface waters can be permitted.

Thermal Processes

Pyrometallurgical and thermochemical plants have long been considered notorious polluters, mainly because of the dust problems that were not effectively coped with in the past. Heavy metal (amongst other components such as fluorine) contaminated dusts emitted by historical smelters were traced as a source of adverse health effects to workers in the smelter and the people living in the vicinity. This problem has virtually been eliminated in most Western countries. Dust particles are now effectively separated and recycled to the feed section of the process. Accumulation of toxic elements is limited by regular bleeding of the dust recycle, also enabling selective extraction of valuable components from the enriched dust fraction.

Unlike the wet mineral processing routes, the thermal processes are usually quite flexible with regard to the composition of the mineral ore being processed. This is explained by the fact that the core of these processes is a relatively simple liquid/gas (liquid slag and furnace gas) or solid/gas (calcine and roast gas) separation step, which is not sensitive to ore impurities, mostly followed by selective separation of valuable components from the gas phase. The high volatility of hazardous (heavy) metals such as lead, zinc, cadmium and arsenic and of most (heavy) metal chlorides enables their selective recovery by gas phase condensation or distillation.

The slags formed in thermochemical and pyrometallurgical processes can sometimes be used as a raw material in e.g., the steel industry. If not, the slags can be used as construction materials in civil engineering projects. In case the slag is not sufficiently inert to allow for direct use, without measures for environmental protection, a slag fuming treatment can be applied.

From the viewpoints of effective raw material utilization and cleaner production technology it is surprising that the interest in thermochemical and pyrometallurgical processes is declining rather than growing, in favour of the wet chemical and hydrometallurgical processes. This declining interest can likely be attributed to the high energy demand, labour and maintenance costs of the thermal processes. Upon closer examination, however, as mentioned in the previous section, the energy demand often appears to be comparable with the wet processes, or often even lower when waste heat is effectively recovered.

It is thus concluded that thermochemical and pyrometallurgical mineral processing routes are not less promising for the future than wet chemical and hydrometallurgical processes, both from the viewpoint of cleaner production and from the viewpoint of effective utilization of mineral resources. In general, thermal processes are better suited to cope with the lower grade mineral ores that will be processed in the future. Due to the depletion of richer ore deposits, more bulk concentrates are likely to be processed in time. Whereas most wet chemical and hydrometallurgical processes are designed to process relatively clean mono-concentrates, the thermal processes are generally better equipped to handle bulk concentrates, thus reducing waste production at the mining site as well. Particularly with respect to material problems and the present lack of insight in the behaviour of high temperature reaction media, however, some major technological problems still need to be overcome before a wider application of cleaner pyrometallurgical and thermochemical mineral processing technology can be effected.

For wet chemical and hydrometallurgical processes the present high selectivity will need further improved with a view to expected decline of ore grades in the future. Membrane technology and solvent extraction are promising options.

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14 Contaminated Aquatic Sediments and Waste Sites: Geochemical Engineering Solutions

Ulrich Förstner

Hamburg-Harburg University of Technology, Environmental Engineering Section,
P.O.Box 90 10 52, 21071 Hamburg, Germany

Abstract

Three geochemical concepts demonstrate the advantage of a long-term strategy compared to the traditional approaches in waste management: (i) the mobility concept, (ii) the concept of capacity controlling properties, and (iii) the concept of final storage quality, the first being relevant for process studies, the second for effect evaluations and the third for problem solutions. "Final storage quality" indicates the ultimate goal of geochemical engineering and can be reached either by incineration and post-treatment (municipal solid waste) or by incorporation into low-temperature mineral formations which remain stable over geological times.

14.1 Introduction

In modern waste management, the fields of geochemically oriented environmental technology include:

- the study of material fluxes within and between the anthroposphere and different "geospheres";
- the optimization of elemental distribution at high-temperature processes (e.g. incineration of solid waste materials);
- the selection of favourable milieu conditions for the deposition of large-volume wastes, such as dredged materials,
- the selection of additives for the solidification and stabilization of hazardous waste materials,
- the development of test procedures for long-term prognoses of pollutant behaviour in all kinds of waste depositories.

Inclusion of the time factor moves beyond a traditional chemical approach. It also transcends the civil engineering approach in waste management, which usually devotes little attention to long-term emissions from waste disposal sites. "Because we have become accustomed to considering the filling period as the most important phase in landfill operation, we have forgotten that subsequent to the active working period there is the infinitely long time in which the site has to function as a depository for all materials unwanted in the biosphere" (Stief, 1987).

14.2 Geochemical Concepts for Metal Pollutants in Solid Wastes

Environmental geochemistry, since about 30 years, is concerned with human impact on the element cycling in air, water, soil and also on biota. More recently, geochemical experience has been introduced into engineering practice. Three geochemical concepts demonstrate the advantage of a long-term strategy compared to the traditional approaches in waste management:

14.2.1 Mobility Concept

For systems involving solution/solid interactions, "mobility" typically reflects the flux of metal species in a certain medium, which contains both accelerating and inhibiting factors and processes. Accelerating factors comprise effects of pH-lowering, redox changes, inorganic and organic complexation, and microbially mediated species transformations such as biomethylation. Within the spectrum of "barriers", physical processes include adsorption, sedimentation, and filtration; chemical barriers comprise mechanisms such as complexation and precipitation; and biological barriers are often associated with membrane processes, which can limit translocation of metals (e.g., from plant roots to the shoots and fruits). "Complexation" in its various forms can both inhibit and accelerate metal fluxes, particularly in biological systems consisting of different types of membranes. With respect to the behaviour of toxic metals it has been stressed by Salomons (1985) that from an impact point of view it is important to know whether the concentrations in the pore waters are determined by adsorption/desorption processes or by precipitation/dissolution processes. If the latter is the case the concentrations in the pore waters of pollutants should be widely independent from the concentrations in the solid phase.

Including new experience from impact evaluations related to capacity controlling properties, the mobility concept of environmental geochemistry can be implemented into waste management practice by different ways of optimizing barrier systems. As shown from the examples of large-mass wastes - dredged material, mining residues and municipal solid waste, long-term immobilization of critical pollutants can be achieved by promoting less soluble chemical phases, i.e., by thermal and chemical treatment, or by providing respective milieu conditions. A common feature of geochemically-designed deposits is their tendency to increase overall stability in time, due to the formation of more stable minerals and closure of pores, thereby reducing water permeation.

14.2.2 Storage Capacity Controlling Properties

This conceptual approach has been developed in the framework of the concept of "chemical time bombs". To make the scientific objectives clearer, it is useful to distinguish between two different mechanisms (Stigliani, 1992): The first is direct saturation, by which the capacity of a soil or sediment for toxic chemicals becomes exhausted. The second way to "trigger" a time bomb is through a fundamental

change in a chemical property of the substrate that reduces its capacity to adsorb (or keep adsorbed) toxic materials. Within a scientific perspective of the chemical time bomb concept the aspect of the storage capacity controlling properties (CCPs) of solid substrates will play a key role. In this respect, the potential of sediments, soils and waste materials to immobilize toxic chemicals is conceived as a first and in most cases preferential barrier against dispersion of these substances in both ground and surface waters or their transfer to terrestrial or aquatic biota.

14.2.3 Final Storage Quality

The final storage approach is one way to develop and control landfills on a conceptual basis. It has been defined by the Swiss Federal Government in 1986 (Anonymous, 1986) and received wider attention by the book edited by Peter Baccini on Landfills - Reactor and Final Storage (Baccini, 1989): "Landfills with solids of final storage quality need no further treatment of emissions into air and water". Final storage properties can be achieved by using with typical geochemical engineering techniques such as:

- selection of favourable milieu conditions for the deposition of large-volume wastes such as dredged materials,
- selection of additives for the solidification and stabilization of hazardous waste materials,
- and optimization of elemental distribution at high-temperature processes, e.g. incineration of solid waste materials.

14.3 Mobility of Metals and Assessment of Long-Term Effects

14.3.1 Metal Mobilization from Aquatic Sediments and Waste Sites

Sediments. Release of potentially toxic metals from contaminated sediments pose problems both in aquatic systems and subsequent to land deposition of dredged materials. Examples are given by various authors, indicating the major factors, processes and rates of metal mobilisation:

- Field evidence for changing cadmium mobilities was reported by Holmes et al. (1974) from Corpus Christi Bay Harbor: During the summer period when the harbor water was stagnant, cadmium precipitated as CdS at the sediment/water interface. In the winter months, however, the increased flow of oxygen-rich water into the bay resulted in a release of the precipitated metal.
- In the St. Lawrence Estuary, Gendron et al. (1986) found evidence for different release mechanisms near the sediment-water interface - the profiles for cobalt resemble those for manganese and iron with increased levels downwards, suggesting a mobilization of these elements in the reducing zone and a reprecipitation at the surface of the sediment profile. On the other hand, cadmium appears to be released at the surface, probably as a result of the aerobic remobilization of organically-bound cadmium.

- Biological activities are typically involved in these processes - remobilization of trace metals has been explained by the removal of sulphide from pore waters via ventilation of the upper sediment layer with oxic overlying water, allowing the enrichment of dissolved cadmium that would otherwise exhibit very low concentrations due to the formation of insoluble sulphides in reduced, H_2S -containing sediments. Emerson et al. (1984) suggest a significant enhancement of metal fluxes to the bottom waters by these mechanisms. It was evidenced by Hines et al. (1984) from tracer experiments that biological activity in surface sediments greatly enhances remobilization of metals by the input of oxidized water. These processes are more effective during spring and summer than during the winter months.
- From enclosure experiments in Narragansett Bay, Hunt and Smith (1983) estimated that by mechanisms such as oxidation of organic and sulphidic material, the anthropogenic proportion of cadmium in marine sediments is released to the water within approximately three years. For remobilization of copper and lead, approximately 40 and 400 years, respectively, is needed, according to these extrapolations.
- Prause et al. (1985) studied the release of Pb and Cd from contaminated dredged material after dumping in a harbour environment. During an observation period up to 24 h no significant Cd or Pb release could be found from the dredged sludge, but during the long term experiments extensive Cd remobilisation was recognized. The contact of the polluted freshwater sediments with seawater finally cause the release of 1-2 mg Cd per kg solids. It is suggested that the reaction kinetics, mainly with respect to the initial mobilization of metals from solids, are controlled by microbial activity.
- Metal release from tidal Elbe River sediments by a process of "oxidative remobilization" has been described by Kersten (1989). Short (30 cm) sediment cores were taken from a site, where diurnal inundation of the fine-grained fluvial deposits takes place. In the upper part of the sediment column, total particulate cadmium content was approximately 10 mg kg^{-1} , whereas in the deeper anoxic zone the total particulate concentration of Cd was 20 mg kg^{-1} . Sequential extractions indicate that in the anoxic zone 60-80% of the Cd was associated with the sulphidic/organic fraction. In the upper - oxic and transition - zone the association of Cd in the carbonatic and exchangeable fractions simultaneously increase up to 40% of total Cd. This distribution suggests that the release of metals from particulate phases into the pore water and further transfer into biota is controlled by the frequent downward flux of oxygenated surface water. From the observed concentrations, it would be expected that long-term transfer of up to 50% of the Cd from the sediment subsurface would take place either into the anoxic zone located further below the sediment-water interface or released into the open water.

Typical early diagenetic geochemical changes and subsequent element mobilization via the porewater result from dredging activities. A study performed by Darby et al. (1986) in an artificially created estuarine marsh demonstrates characteristic effects of oxidation (Table 1):

Table 1 Mobilization of Metals During Dredging (after Darby et al., 1986). Concentrations in mg/l.

Metal	Pore-water (a)	River Water (b)	a/b	Effluent at An Artificial Marsh		
				Expected Conc.	Measured Conc.	% Change
Mn	6.94	0.03	230	1.34	1.19	- 11
Fe	57.3	0.26	220	11.12	6.01	- 46
Ni	0.054	0.001	54	0.011	0.035	+ 218
Pb	0.077	0.002	38	0.016	0.142	+ 788
Hg ($\mu\text{g/l}$)	3.2	0.26	12	0.82	2.0	+ 144
Cd	0.009	0.001	9	0.0025	0.019	+ 660
Cu	0.012	0.004	3	0.0055	0.051	+ 827
Zn	0.12	0.052	2	0.065	5.30	+ 8069

Compared to the river water concentration, the channel sediment porewater is enriched by a factor of 200 for iron and manganese, 30-50 for nickel and lead, approx. 10 for cadmium and mercury, and 2-3 for copper and zinc. When the expected concentration of metals following hydraulic dredging, which were calculated from a rate of porewater to river water of about 1:4, were compared with the actual measurements at the pipe exiting the dredging device, negative deviations were found for iron and manganese, suggesting reprecipitation of Fe/Mn-oxide minerals; the positive deviations of zinc (factor 80), copper, lead and cadmium (factors 7-8) indicate that during dumping of the sludge-water mixture significant proportions of these elements were mobilized and transferred into the effluent water.

The acidification of the sediment/water system begins after hydrogen ions are generated during the oxidation (e.g., during dredging or resuspension of mainly fine grained material containing less carbonate than needed for long-term neutralization (Breemen et al., 1984).

Pore water data from dredged material from Hamburg Harbor indicate typical differences in the kinetics of proton release from organic and sulphidic sources. Recent deposits are characterized by low concentrations of nitrate, cadmium and zinc; when these low-buffered sediments are oxidized during a time period of a few months to years, the concentrations of ammonia and iron in the pore water typically decrease, whereas those of cadmium and zinc increase (with the result that these metals are easily transferred into agricultural crops!).

The different steps are schematically given in Figure 1. Oxidation of sulphides during stage B strongly increases the concentrations of cadmium and zinc in a relative short time. When acidity is consumed by buffer reactions (phase C), cadmium and zinc concentrations drop, but are still higher than in the original sulphidic system. In phase D, oxidation of organic matter again lowers pH-values and can induce a long-term mobilization of Zn and Cd.

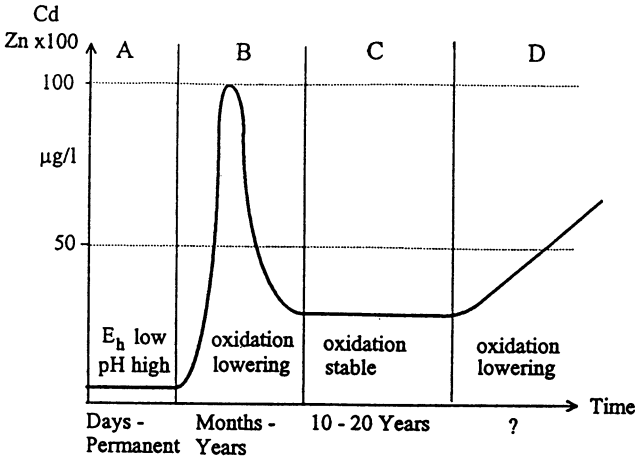


Figure 1: Schematic Diagram Illustrating Different Phases of Metal Release from Land-Disposed Dredged Material (Maaß and Michlich, 1988)

Waste Sites. In municipal solid waste landfills, initial conditions are characterized by the presence of oxygen and pH-values between 7 and 8. During the subsequent "acidic anaerobic phase", the pH drops to a level as low as 5 because of the formation of organic acids in an increasingly reducing milieu; concentrations of organic substances in the leachate are high (Figure 2).

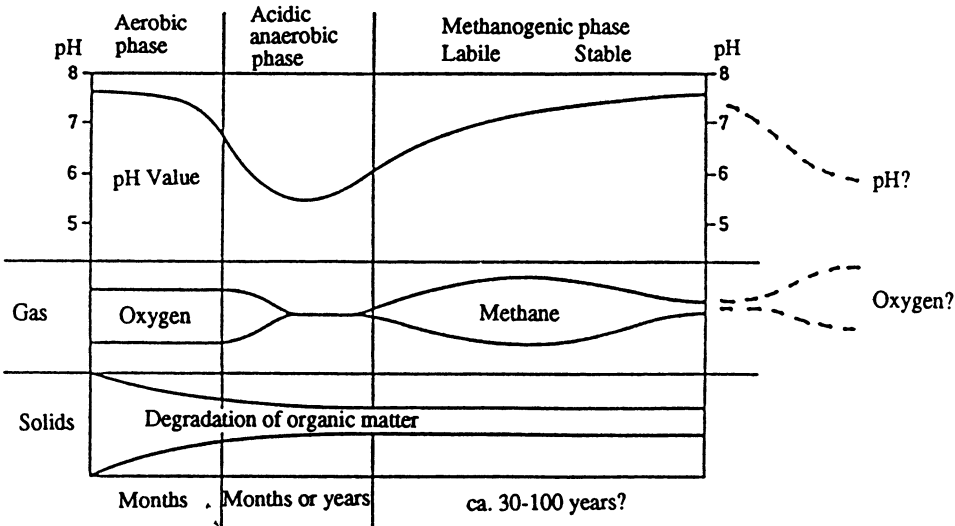


Figure 2 Scheme of the Chemical Evolution of Municipal Solid Waste Landfills (Förstner et al., 1991)

In a transition time of one to two years, the chemistry of landfill changes from acetic to methanogenic conditions. Typically increased concentrations of metals have been found for iron, manganese and zinc in leachates during the acidic decomposition phase compared with the methanogenic phase.

There is not much experience with landfill evolution subsequent to the initial 30 years. What could happen is that the landfill is again oxidized. It has been inferred that oxidation of sulphidic minerals by intruding rainwater may mobilize trace metals. The impact on the underlying groundwater could be even higher if a chromatographic process, involving continuous dissolution and reprecipitation during passage of oxidized water through the deposit, were to preconcentrate critical elements prior to final release with the leachate.

Comparison of inorganic groundwater constituents upstream and downstream of 33 waste disposal sites in Germany (Arneith et al., 1989) indicates typical differences in pollutant mobilities, which may partly be related to releases during the acidic phase of the landfill development. High contamination factors ("contaminated mean"/"uncontaminated mean") have been found for boron, ammonia, and arsenic; heavy metals such as cadmium, chromium, lead and copper are significantly enriched in the leachates as well.

In the study on the material management within a fictitious region "Metaland" (Baccini and Brunner, 1991), an estimation was made by Baccini et al. (1992) on the release of contaminants from landfills subsequent to a 50-year reactive period, for the case that all barriers will have failed at this time. Population in Metaland was assumed as being 1 million on an area of 2.500 km², each producing 40 tonnes of waste within a 40 years time span. Table 2 indicates, that a very significant input of TOC (and of ammonia), with an annual increase of 50% compared to the uncontaminated groundwater will occur, and it has been suggested that this input will last over a period of approximately 1000 years.

Table 2 Effects of Landfill Leachate on Chemical Composition of a Groundwater Reservoir in the Metaland Model Study (Baccini et al., 1992). Specific Leachate Flux to a Groundwater Reservoir of 2·10⁹ m³ was taken as 0.02 L per kg of Waste Material and Year (Net Precipitation: 1000 mm/Year)

	C _{org} [mg/L]	Cl	Zn	Cd	Hg
				[µg/L]	
Mean leachate concentration after 50 years landfill operation	600	500	600	2	0.1
Mean concentration in the uncontaminated groundwater	0.5	3	5	0.02	0.005
Mean annual increase of concentration in groundwater	0.24	0.2	0.24	0.008	0.00016
<i>Mean annual increase in %</i>	<i>50%</i>	<i>7%</i>	<i>5%</i>	<i>4%</i>	<i>3%</i>

14.3.2 Prognostic Tools for the Behaviour of Metals in Wastes

Acid Producing/Neutralizing Capacity. Long-term release of protons can be expected even from the relatively low organic carbon ashes and slags from municipal waste incineration, as has been suggested by Krebs et al. (1988). Microbial degradation of 1 - 2 % of residual organic carbon will produce approximately 1 mol H^+ per kg bottom ash, which is about equivalent to the acid neutralizing capacity of this material (but several orders of magnitude higher than the H^+ -input from acid precipitation). The acid-neutralizing capacity is defined operationally by the amount of acid required to reach pH 7; Figure 3 presents titration curves of typical bottom ashes from municipal solid waste incineration (Belevi et al., 1992).

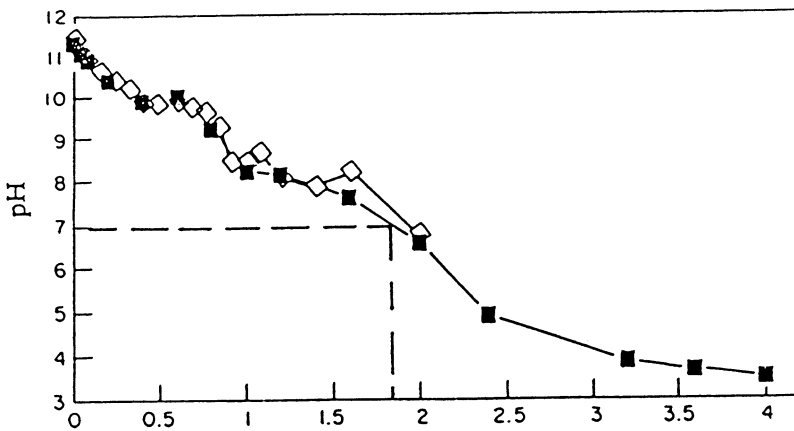


Figure 3: Titration of Bottom Ash Samples. Full Signature: Extraction Time 48 h; Open Signature: 197 h (Belevi et al., 1992)

Laboratory experiments by Belevi et al. (1992) suggest that non-metal fluxes by leachate (such as chloride, sulphur and DOC fluxes) would adversely impact the environment for years to decades after disposal. Heavy metal fluxes by leachate are expected to be compatible with the environment; however, additional laboratory and field studies are necessary to assess their behavior over longer time periods.

Experimental Design for Long-Term Metal Release. With an experimental approach, which was first used by Patrick et al. (1973) and Herms and Brümmer (1978), metal mobility of industrial waste materials has been studied in a circulation apparatus by the controlled intensification of significant release parameters such as pH-value, redox-potential and temperature. Here, an ion-exchanger system is used for extracting and analyzing the released metals at an adequate frequency (Figure 4).

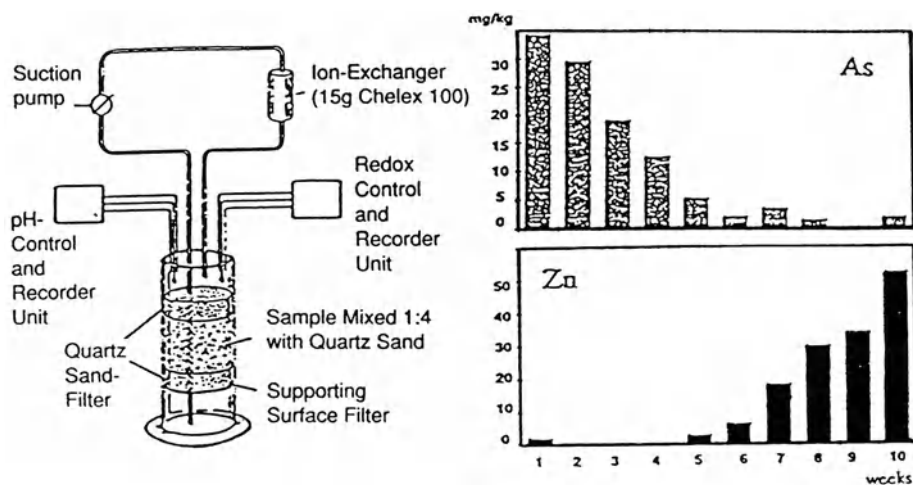


Figure 4 (Left): Experimental Design for Long-Term Prognosis of Metal Release (Schoer and Förstner, 1987)

Figure 5 (Right): Release of Arsenic and Zinc from Industrial Solid Waste in a Long-Term Circulation Experiment (Förstner et al., 1991)

In a series of experiments, a number of industrial waste materials of different types, intended for co-disposal in borrow pits, were investigated with this method. In these experiments, special attention was given to the efficiency of individual components with respect to long-term behavior of critical trace elements in such mixed deposits. The kinetics of element release from "conditioned" waste material (i.e., treated with high-pH additives) is shown in Figure 5 for As, and Zn. By treatment with pH 5 solutions, mobilization of As is essentially completed after the initial five weeks of the experiment. Mobilization of Zn is strongly enhanced toward the end of the study period. Regarding the latter element, it can be expected that the cumulative percentage of release from the treated material would significantly be enhanced upon continuation of the experiment.

Chemical Characterization of Dredged Material. With regard to the selection of disposal options for dredged materials, the study of the water phase only with not be fully satisfying. While most of the actual situation would be reflected in these data, the potentialities of future adverse effects as well as the possible measures for reducing such hazards cannot be predicted. In this respect, extractability of pollutants with chemical agents of different strength will provide more reliable information of the potential release of these substances under typical environmental conditions.

Elutriate Test. To estimate short-term chemical transformations, the interrelations between solid phases and water has been increasingly subjected to laboratory experimentation. The advantage of such experiments is that especially important parameters can be directly observed and particularly unfavourable conditions simulated. The Army Corps of Engineers and the U.S. Environmental Protection Agency have developed an elutriate test that is designed to detect any significant release of chemical contaminants in dredged material. This test involves the mixing of one volume of the dredged sediment with four volumes of the disposal site water for a 30- min shaking period. If the soluble chemical constituent in the water exceeds 1.5 times the ambient concentration in the disposal site water, special conditions will govern the disposal of the dredged material (Lee and Plumb, 1974).

Sequential Extraction. In connection with the problems arising from the disposal of solid wastes, particularly of dredged materials, chemical extraction sequences have been applied which are designed to differentiate between the exchangeable, carbonatic, reducible (hydrous Fe/Mn oxides), oxidizable (sulphides and organic phases) and residual fractions. The undisputed advantage of this approach with respect to the estimation of long-term effects on metal mobilities lies in the fact, that rearrangements of specific solid "phases" can be evaluated prior to the actual remobilisation of certain proportions of an element into the dissolved phase (Förstner, 1985). One of the widely applied extraction sequences of Tessier and co-workers (1979) has been modified by various authors. Examples are presented in Table 3, e.g., standard sequence by the Community Bureau of Reference (EC).

Table 3 Sequential Extraction Scheme for Partitioning Sediment Samples

Fraction	Extended Version (Kersten & Förstner, 1986)	EC/BCR-Version (Ure et al., 1993)
Exchangeable Ions	1 M NH ₄ OAc	0.5 g sediment - 5 h - 20 ml acetic acid 0.11 mol/l
Carbonate-Associated Metals	1 M NaOAc, pH 5 w/ HOAc	
Easily Reducible (Mn-Oxides)	0.01 M NH ₂ OH HCl w/ 0.01 M HNO ₃	Residue from above; 20 ml NH ₂ OH HCl 0.1 mol/l (16 h), HNO ₃ pH 2
Moderately Reducible (Amorph. Fe-Oxides)	0.1 M Oxalate Buffer pH 3	
Sulphidic/Organic	30% H ₂ O ₂ pH 2/0.02 M HNO ₃ extr. 1 M NH ₄ OAc, 6% HNO ₃	10 ml hydrogen per- oxide 8.8 mol/l (2x); 50 ml NH ₄ Ac/HOAc
Residual	Hot HNO ₃ conc.	Lithogenic Material

Metal Transfer between Inorganic and Organic Substrates. It seems that thermodynamic models are still restricted because of various reasons: (i) adsorption characteristics are related not only to the system conditions (i.e., solid types, concentrations and adsorbing species), but also to changes in the net system surface properties resulting from particle/particle interactions; (ii) influences of organic ligands in the aqueous phase can rarely be predicted as yet; (iii) effects of competition between various sorption sites, and (iv) reaction kinetics of the individual constituents cannot be evaluated in a mixture of sedimentary components.

At present, experimental studies on the dissolved/solid interactions in such complex systems seem to be more promising. One approach uses a multi-chambered device (Calmano et al., 1988), where the individual components are separated by membranes, which still permit phase interactions via solute transport of the elements; in this way, exchange reactions and biological uptake can be studied for individual phases under the influence of pH, redox, and ionic strength (Figure 6a).

A mass balance for the element copper in Figure 6b indicates that only 1.3 % of the inventory of Cu of the sludge sample is released when treating with seawater. Only one third stays in solution, equivalent to approx. $40 \mu\text{g l}^{-1}$, and there is no significant difference to the conditions before salt addition. Two thirds of the released copper is readsorbed at different affinities to the model substrates. The dominant role of organic substrates in the binding of metals such as Cd and Cu is of particular relevance for the transfer of these elements into biological systems. It can be expected that even at relatively small percentages of organic substrates these materials are primarily involved in metabolic processes and thus may constitute the major carriers by which metals are transferred within the food chain.

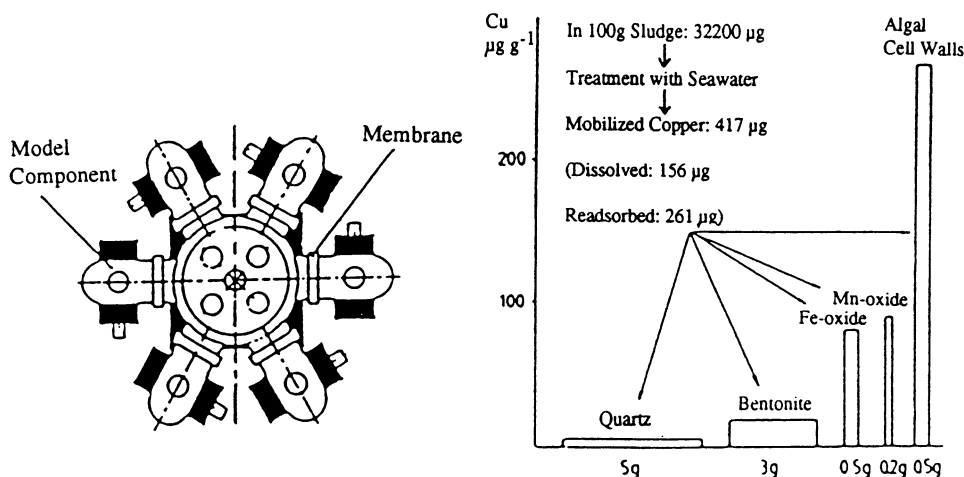


Figure 6: Metal Transfer Between Sedimentary Components. 6a: Schematic View of the Multichamber Device. 6b: Transfer of Copper from Anoxic Harbor Mud into Different Model Substrates after Treatment with Artificial Seawater (Calmano et al., 1988)

14.4 Remediation Procedures

"Geochemical and biological engineering" emphasise the increasing efforts to use natural resources available at the disposal site for reducing the negative environmental effects of all types of waste material, in particular of acid mine wastes (von Michaelis, 1988; Kalin and Everdingen, 1988).

"Geochemical engineering", a new and challenging field in environmental geochemistry (Salomons and Förstner, 1988; Schuiling, 1990) applies geochemical principles (such as concentration, stabilization, solidification, and other forms of long-term, self-containing barriers), and provides new perspectives to traditional technological disciplines (Figure 7).

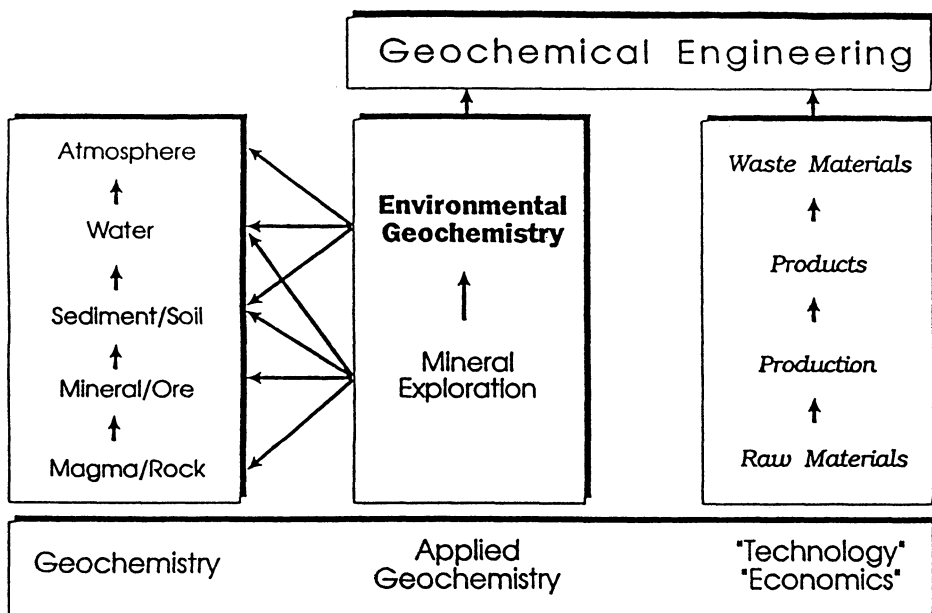


Figure 7 New Developments in Environmental Geochemistry

14.4.1 Storage Under Permanent Anoxic Conditions

Regarding the various containment strategies it has been argued that upland containment (e.g., on heap-like deposits) could provide a more controlled management than containment in the marine environment. However, contaminants released either gradually from an imperfect impermeable barrier or catastrophically from failure of the barrier could produce substantial damage (Kester et al., 1983). On the other hand, near-shore marine containment (e.g., in capped mound deposits), offers several advantages, mainly with respect to the protection of groundwater resources, since the underlying water is saline and inherent chemical processes are favourable for the immobilisation or degradation of priority pollutants.

In a review of various marine disposal options, Kester et al.(1983) suggested that the best strategy for disposing of contaminated sediments is to isolate them in a permanently reducing environment. Disposal in capped mound deposits above the prevailing sea-floor, disposal in sub-aqueous depressions, and capping deposits in depressions provide procedures for contaminated sediment (Bokuniewicz, 1982). In some instances it may be worthwhile to excavate a depression for the disposal site of contaminated sediment which can be capped with clean sediment. This type of waste deposition under stable anoxic conditions, where large masses of polluted materials are covered with inert sediment became known as "subsediment-deposit". The first example was planned for highly contaminated sludges from Stamford Harbour in the Central Long Island Sound following intensive discussions in the U.S. Congress (Morton, 1980).

Under sub-sediment conditions there is a particular low solubility of metal sulphides, compared to the respective carbonate, phosphate, and oxide compounds. One major prerequisite is the microbial reduction of sulphate. Thus, this process is particularly important in the marine environment, whereas in anoxic freshwaters milieu there is a tendency for enhancing metal mobility due to the formation of stable complexes with ligands from decomposing organic matter. Marine sulphidic conditions, in addition, seem to repress the formation of mono-methyl mercury, one of the most toxic substances in the aquatic environment, by a process of disproportionation into volatile dimethyl mercury and insoluble mercury sulphide (Craig and Moreton, 1984). There are indications that degradation of highly toxic chlorinated hydrocarbons is enhanced in the sulphidic environment relative to oxic conditions (Sahm et al., 1986; Kersten, 1988).

14.4.2 Chemical Stabilisation by Additives

In general, solidification/stabilization technology is considered a last approach to the management of hazardous wastes. The aim of these techniques is a stronger fixation of contaminants to reduce the emission rate to the biosphere and to retard exchange processes. Most of the stabilization techniques aimed for the immobilization of metal-containing wastes are based on additions of cement, water glass (alkali silicate), coal fly ash, lime or gypsum (Malone et al., 1982; Wiedemann, 1982; Goumans et al., 1991).

Laboratory studies on the evaluation and efficiency of stabilization processes were performed by Calmano et al.(1988) on Hamburg harbor mud, using acid titration curves for limestone and cement/fly ash stabilizers. Best results are attained with calcium carbonate, since the pH-conditions are not changed significantly upon addition of CaCO_3 . Generally, maintenance of a pH of neutrality or slightly beyond favours adsorption or precipitation of soluble metals (Gambrell et al., 1983). On the other hand it can be expected that both low and high pH-values will have unfavourable effects on the mobility of heavy metals.

Experimental studies of the processes taking place with mixed residues from lignite coal incineration indicate favorable effects of incorporation of both chloride and heavy metals in newly formed minerals (Figure 7).

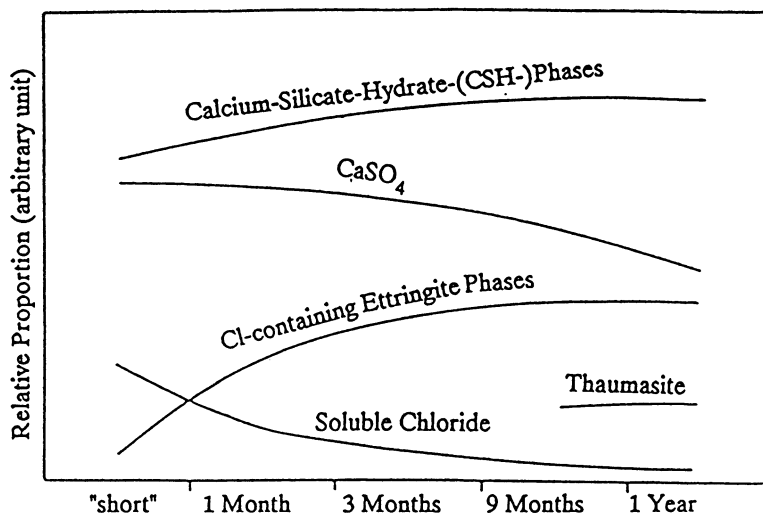


Figure 8: Schematic Representation of Mineral Formations in "Stabilisates" from Coal Residues (Bambauer, 1992)

Ettringite (i.e. calcium-aluminate-monosulphate-hydrate phases) in particular, can act as "storage minerals" for chloride and metal ions. The former may be incorporated at up to 4 kg CaCl_2 per m^3 of the mineral mixture. Calcium-silicate-hydrate phases may be formed in a subsequent process, and by filling further pore space these minerals can significantly reduce permeability of the waste body for percolating solutions. Experimental studies of the leachability of salts and trace elements from samples of "stabilisates", with a pressure-filtration method, indicate relative high rates of release for sulphate ions, but not for zinc and cadmium in the eluate (Bambauer, 1992).

In general, microscale methods, e.g., formation of mineral precipitates in the pore space of a waste body, will be employed rather than using large-scale enclosure systems such as clay covers or wall constructions (Wiles et al., 1988). An overview on various fields of environmental research and management to which mineralogical methods can be successfully applied has been given by Bambauer (1991).

14.4.3 Final Storage Quality of Municipal Solid Waste Materials

From a geochemical point of view the "reactor landfill" is characterized by labile conditions during the initial aerobic and acid anaerobic phases, the former mainly due to uncontrolled inter- actions with organic solutes (see above). Particular problems occur when leachate collection pipes are plugging during the acidic decomposition period. Sludge-only landfills have even lower permeabilities and interparticular porosities than municipal solid waste landfills.

On the other hand, solid residues with final storage quality should have properties very similar to the earth crust (natural sediments, rocks, ores, soil; Table 4). This can be achieved in several ways, e.g., by assortment or thermal, chemical and biological treatment. In most cases this standard is not attained by simple incineration of municipal waste, i.e., by reduction of organic fractions only. There is, in particular, the problem of easily soluble minerals such as sodium chloride. At present, bottom ash cannot be considered as a material of final storage quality. It should either be disposed into monofills with leachate collection and treatment systems or be treated prior to disposal (Belevi et al., 1992, see below).

Table 4: Comparison of Inventories of Chemical Components in the Two Landfill Alternatives and in the Earth Crust (Förstner et al., 1989)

Reactor Landfill	Final Storage	Earth's Crust
<i>Major solid constituents</i>		
Solid "inert" waste	Silicates, oxides	Quartz, Fe-oxide, clay, carbonates
Putrefactive waste	[Gypsum, NaCl] ^a	(Gypsum, NaCl)
Grease trap waste	(Char) ^b	Kerogenic compounds
<i>Minor solid constituents</i>		
Organic micropollutants	Organic micropollutants	-
Metals in reactive chemical forms	Metal-bearing minerals, mainly oxides	Metals mainly in inert forms
<i>Dissolved constituents</i>		
Protons, electrons	(Protons)	(pH; acid rain)
Organic compounds	(Organic residues)	(Humic acids)
Dissolved salts	[Dissolved salts] ^a	(Dissolved salts)

^a Partial extraction during pretreatment ^b Minor constituent

Measures before incineration include the separate collection of (organic) kitchen and garden wastes (containing chlorine and sulfur), which can be transferred into compost; a major decrease of chlorine content, however, would require a significant reduction of PVC in municipal solid waste. After incineration washing of the residues can be performed either with neutral or acidified water. Future efforts should be aimed for optimizing the incineration process in a sense, that critical components are concentrated in the filter ash and in the washing sludge, whereas the quality of the bottom ash is improved - by application of high-temperature procedures (Faulstich, 1989) - in a way, that deposition is facilitated and even a reuse of this material is possible due to either the low concentrations or chemically inert bonding forms of metals (Brunner, 1989).

Recent advances mainly concern the application of high temperature techniques for re-melting precipitator ashes and flue gas purification product. An example is the RedMelt-process, designed by Faulstich and colleagues (Faulstich et al., 1992), which - in a reductive milieu - influences differentiation into three phases: (1) metal-rich (Fe, Cu) bottom phase; (2) "condensate" phase with enrichment of zinc, lead and cadmium in the flue gas (from where metals can be recovered and transferred to a base metal smelter); and (3) relatively metal-poor silicate phase, which can easily be used for construction purposes. Table 5 summarized available leaching data on different materials and treatments municipal solid waste incineration products. All values relate to the pH-4 conditions as prescribed by the Swiss Guidelines in the Technical Advice on Solid Waste Materials (1991). While untreated and even washed electrostatic precipitator dusts do not meet the requirements given by the TVA-supplement, cement-solidified ashes are near the limit. Satisfying results can only be reached by using high-temperature processes, and best results are shown by the RedMelt procedure. With regard to energy consumption, initial data suggest, that the average consumption is in the range of 1-2 kWh/kg residue, and this is nearly equivalent to the energy content of the original municipal solid waste material.

Table 5: Leachabilities of Residues from Municipal Solid Waste Incineration (IMRA, 1991, extended)

	Lead [ppm]	Cadmium [ppm]	Zinc [ppm]	Copper [ppm]
Untreated Electro Precipitator Ash - MSWI Oberhausen	4,2	4,5	133	1,7
Washed Electro Precipitator Ash + Wet Washing Residues	0,77	0,94	57	0,26
TVA-(Swiss)-Guidelines Leaching Values (pH = 4)	1	0,1	5	0,5
Cement-Solidified Precip. Ash + WWR (g), Addit./Ash = 1:2	0,14	0,08	5,1	0,05
Electro Precipitator Ash Treated by 3R-Process	0,1	0,02	0,7	0,08
Vitreous Residue from ABB-(Asea-Brown-Boveri) Process	<0,040	<0,030	0,11	<0,040
Silicate Phase from RedMelt-Process (Faulstich et al.,)	0,004	<0,001	<0,020	0,005

Outlook

The enormous problems arising from the historic thoughtless dissipation of chemicals in the environment has become obvious in the last ten years, and especially with the opening of eastern Europe. The detection of extremely toxic chemicals at Love Canal, Lekkerkerk and Georgswerder are only a few of the harsh lesson. After solving a few spectacular cases with intensive efforts, it now seems that financial restrictions may inhibit the use of many newly developed remediation techniques (such as chemical extraction, high-temperature incineration, and some biological procedures) to sanitize contaminated land on a large scale (i.e., for areas of hundreds of square kilometers. Although this relates primarily to parts of Eastern Europe, the tens of thousands of old landfill sites which must be excavated, treated and recultivated will soon strain even more prosperous economies. It may well be, that economic considerations will strengthen the popularity of geochemically engineered solutions in these situations, as well as for large waste masses such as mine residues, dredged materials and filter ashes described here. But even if traditional engineering continues to dominate practical solutions the specific potential of geochemistry to provide instruments for long-term assessment of processes should be used and expanded.

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III Specific Examples of Metal Polluted Areas

15 Engineering Aspects of Pollution in View of Case Studies Carried Out in Poland

A. Lewandowski¹ and J. Przewłócki²

¹ GEOMOR Geoscience and Marine Research Consulting Co. Ltd,
ul. Zeromskiego 8 81–826 Sopot, Poland

² Institute of Environmental Protection, Warciana 39 a, 54–128 Wrocław,
Poland

1 Introduction

The engineering aspects of pollution should imply three activities: inventory (to recognize the situation), impact assessment (to determine whether the recognized pollution has a negative impact on environment), and remediation (to find a way to improve the situation).

The inventory is sampling and analyzing, the impact assessment is modeling to forecast the influence, remediation is mainly engineering activity to improve, minimize, or rehabilitate the existing or predicted influence of pollution on environment.

The aim of this chapter is to show these engineering aspects via case studies being carried out now (or to be carried out) on a different scale – starting from the scale of the Southern Baltic to a regional or town scale.

2 Geochemical Mapping of the Southern Baltic

It is a large-scale project not only to recognize the pollution of Southern Baltic sediments, but also to describe directions of sediment spreading, learn the rate of accumulation, and find hot-spot regions.

The inventory part of the engineering activity was to produce a geochemical map of the Southern Baltic on a scale of 1:500 000. Initial results were presented during a joint meeting of SETAC-EUROPE and AEHMS at Potsdam (Lewandowski 1992). In that paper only some figures were presented (Figs. 1, 2) showing the area covered and methodology used.

The results will present concentrations of respective elements as shown in Fig. 3.

The project is carried out by the State Geological Institute, Marine Branch, in Sopot, and totally financed by a Polish budget.

The cost up till now has been USD 200 000 and to complete the whole project the same amount again would be necessary.

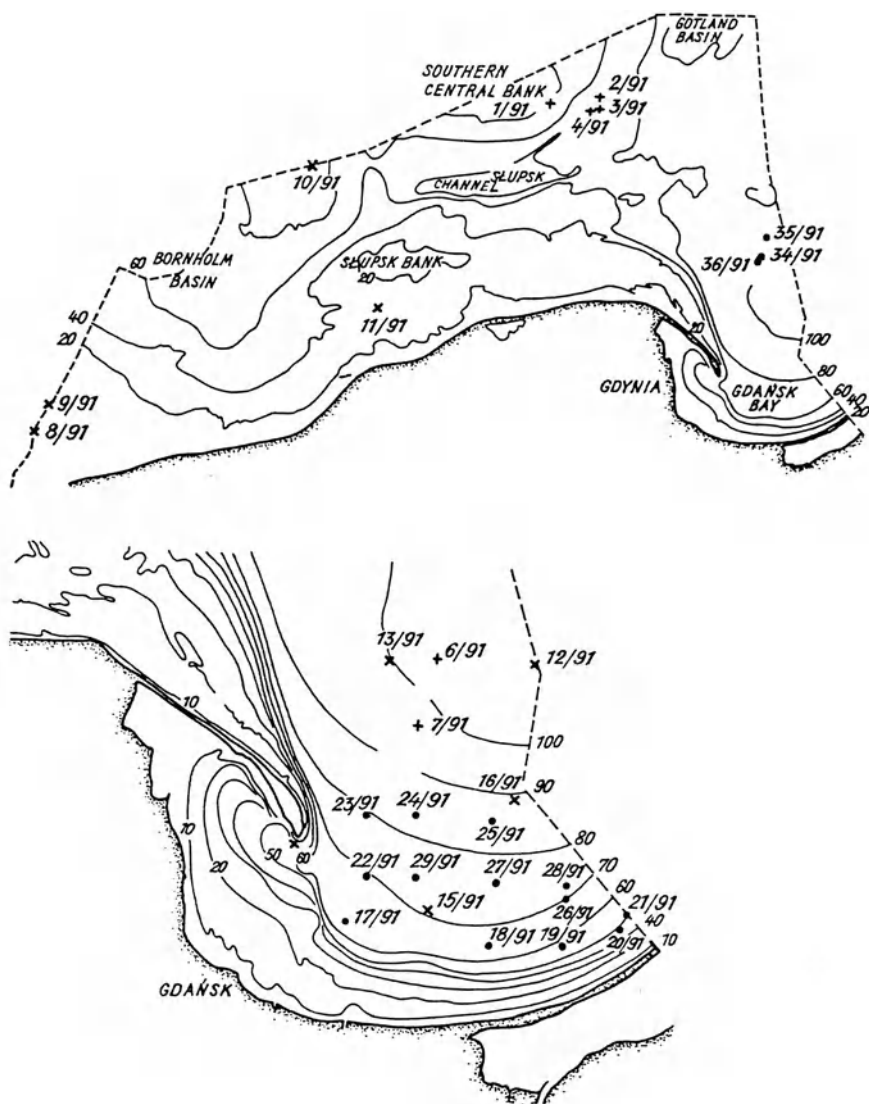


Fig. 1. Sampling stations in 1991

Unfortunately, there is no possibility to carry out analyses of aliphatic and aromatic hydrocarbons – samples are available. Moreover, there is still lack of standards concerning the permissible concentration of chemical components in the sediments of the Baltic Sea.

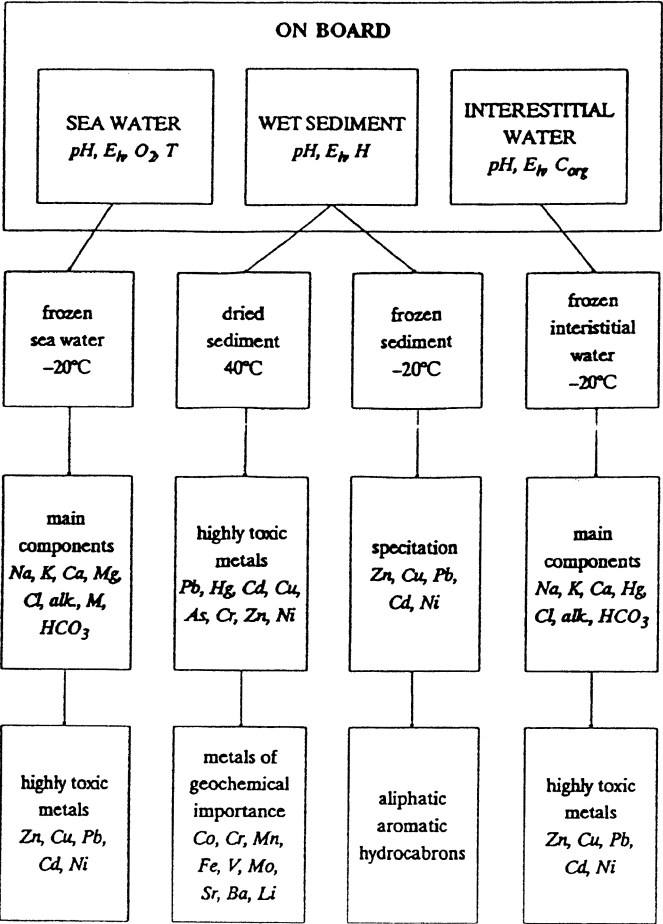


Fig. 2. Scheme of sample analysis

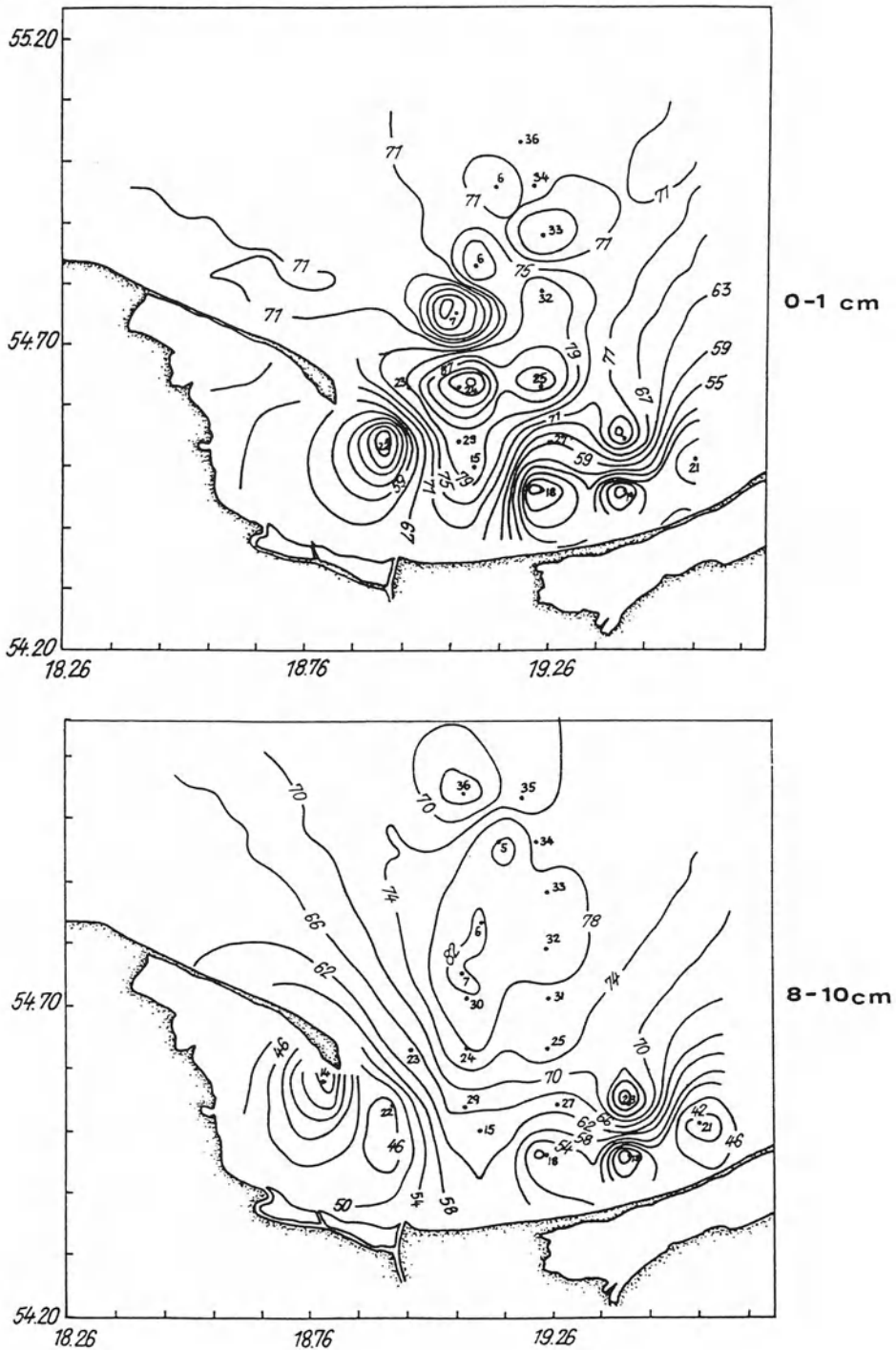


Fig. 3. Concentrations of lead (Pb) in Gdansk Bay sediments at 0-1 cm and 8-10 cm depth

3 Odra Project

The total area of the Odra drainage basin is equal to 120 000 km² and the river length is 859 km.

More than 115 cities, inhabited by more than 10 million people, are located in the area. Over 3.5 million m³/day of the municipal waste water was discharged from the cities in 1990, including 2.8 million m³/s (79%) from Poland. Only 73% of the total waste water volume was treated, including 36% that undergoes only primary treatment.

Basic loads and their structure within the upstream part of the river drainage basin are presented in Table 1.

Municipal waste water is the main source of organic pollutants and nutrients. These waters contain significant loads of heavy metals coming from industries located in the cities and discharging their pretreated waste water into municipal sewage systems.

Industrial waste water discharged directly into the river is the source of the greatest part of heavy metal loads and salinity.

The most significant part of the total nitrogen load comes from rural areas.

From monitoring results, it is known that zinc provides 82.4% of the total load of heavy metals prevailing in industrial waste water. The rest is copper load, which comes from the copper and artificial fertilizer industries, and lead load which is, however, three times less than that of copper. For instance, in 1990 the copper mills Glogow I and Glogow II discharged 279 kg Zn/day, 178 kg Cu/day, and 88 kg Pb/day.

Heavy metal concentration in the water of the Odra river is caused not only by discharges from point sources but also by those from diffused sources (atmospheric precipitation polluted with heavy metals, as well as sources such as highways and railways).

In 1990 the average heavy metal load discharged via the Odra river into the Baltic Sea was equal to 2.5 t/day.

The heavy metal deposition region is located in the Szczecin Lagoon, resulting in a significant (38%) decrease in fish production over 15 years.

Table 1. Structure and origin of principal pollutants discharged into the Odra river drainage basin waters in 1990 including Czech and German parts of the area

Pollution sources	BOD ₅		N _{tot}		P _{tot}		Heavy metal		Cl ⁻ + SO ₄	
	t/day	%	t/day	%	t/day	%	t/day	%	t/day	%
Industry	170	23	37	8	9.8	13	2.6	59	3614	83
Municipalities	585	77	246	53	64.7	83	1.8	41	449	10
Agriculture	—	—	184	39	3.8	4	—	—	307	7
Total	752	100	467	100	78.3	100	4.4	100	4370	100

According to the surface water monitoring program, Zn, Cu, Pb, Ni, Cd, and Hg were determined twice a week in 1990 in water samples extracted from five cross sections (Odra in Chalupki, Wroclaw, and at the mouth of the Szczecin Lagoon and the outlets of the Nysa Luzyczna and Warta rivers).

For the remaining basic cross sections, only Zn, Cu, Pb, Cd, and Hg were monitored during that period.

The average concentrations of zinc, copper, and lead in Odra, along the river run at the average yearly water flow in 1990, are presented in Fig. 4 (scenario 0). They were based on the data from monitored cross sections (12 data per year).

The total concentration of the heavy metals has exceeded the admissible level (0.3 g/m^3) only in the upstream part of the Odra as a result of the high transborder pollution load (see Fig. 4).

Also lead concentrations never exceed the admissible level (0.05 g/m^3) along the river flow within Polish territory.

On the other hand, there are bilateral agreements on Odra protection as well as a program concerning Baltic protection. According to these, it is expected that Poland will decrease the load discharged to the Baltic Sea by 50% by 1997.

The limited financial resources for water protection purposes call for a new and suitable investment strategy, including evaluation of the necessary waste water treatment efficiency and of a waste water treatment plant construction and development program.

That is why during 1991–1992, the prefeasibility study concerning the water quality of the Odra was carried out with the financial support of the World Bank.

Using the numerical model, it was possible to simulate a scenario (Fig. 4, scenario 1) assuming reduction of heavy metals to 80% in the steel works, 85% in the copper mills, and 98% in the chemical factories at the upstream region of the Odra (Slask region).

In order to achieve such reductions, a waste water treatment should be developed that would cost up to USD 250 million.

Then heavy metal loads at the Odra river mouth would decrease to only 12.5% (down to 4039 kg/day) for the sum of metals and 29% for Pb (4039 kg Pb/day).

The improvement of the Odra water quality is expected as a result of the construction and development of municipal wastewater treatment plants, which are planned for 29 municipalities but would cost 0.9–1.2 billion USD.

However, a satisfactory situation in this region cannot be achieved without significant reduction of heavy metal influxes from the diffused sources by applying more effective filters for industrial exhaust gases.

4 Rega Project

The Rega river project is a small-scale project in comparison to the Odra or Vistula river projects.

The project itself reflects the changes which are now taking place in Poland – not only political and economical, but also changes in the way of thinking. The community, represented by the mayors of the small cities located along the river run and at the river estuary, decided to have the river water clean.

They also want beaches which are really attractive with fine yellow sand, as well as sea water clean enough to make bathing possible close to the river mouth.

For this reason they have formed the Rega Union, which handles all matters concerning environmental protection in the Rega Region on behalf of the municipalities.

The Rega river is situated in the northwestern part of Poland in the provinces of Szczecin and Koszalin. The catchment area of the river is about 2700 km² and the approximately 140 000 inhabitants discharge their municipal and industrial waste water into the 200-km-long Rega river. The river falls into the Baltic Sea with an average discharge of approximately 21 m³/s.

The river is heavily polluted, as the waste water in most cases is cleaned only mechanically. In large areas of the towns, waste water is connected to the storm water systems, and it is therefore discharged into the Rega river without any cleaning.

A total of 11 municipalities discharge rain and waste water into the Rega river or its tributaries.

Thus all municipalities need new sewage and rainwater systems in addition to the fact that the existing sewage piping the latter is in most cases either inadequate or too old, so that its proper function cannot be assessed.

Most towns need new or modified municipal waste water treatment plants. In some cases, it is also necessary to design and build industrial waste water treatment plants.

This aim may be achieved by the methods: inventory, impact assessment, remediation.

Thus inventory, which is now being realized, includes biological and chemical analysis of river and seawater as well as hydraulic parameters of the river and hydrodynamic parameters of the coastal seawaters at the Rega mouth.

Such data will make it possible to start numerical modeling of the river (MIKE 11; Fig. 5) and the river estuary simulating a wide range of biochemical interaction processes, varying in complexity from simple BOD calculations to multicomponent simulations including heavy metals, nutrients, phosphorus, oxygen, and their interaction with biomass.

The results of numerical modeling will allow determination of the possible load discharge to the river by the sewage treatment plants to be built or to be modified (remediation), as well as the impact on the coastal waters at the region of the river mouth (MIKE 21; Fig. 5).

In total, this project includes 11 waste water treatment plants of which 2 are new, 5 are plants which are in either the planning or the construction stage, and the remaining 4 are industrial waste water treatment plants.

Initially, the project will concentrate on treatment plants and the associated sewage piping in the towns located close to the Rega river, while environmental

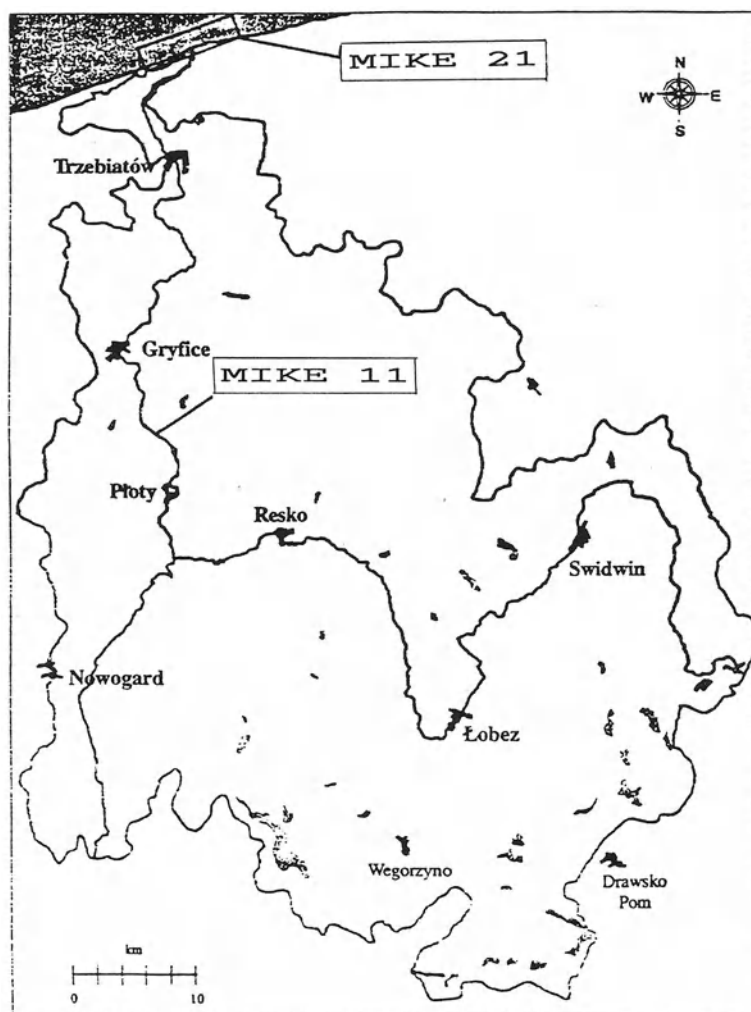


Fig. 5. Modelling applied at Rega river basin

solutions/projects in the less populated areas will be postponed. Approximately 80 000 people are living in the towns, where also approximately 90% of the total amount of industrial waste water in the region is produced.

The inventory and impact part of the project is financed by subsidies designated by Danish Government for environmental activities in Eastern Europe countries and amounts ca. 7 million Dkr.

Based on very rough estimates, the total investment is 148 million USD (83 million USD for waste water treatment plants and 65 million USD for sewage systems, including design, supervision, training of staff, commissioning, etc.). The investments are scheduled to begin in 1994.

The construction of sewage treatment plants will be performed using foreign and Polish means.

5 Coal Fly Ash Projects Utilization in Gdansk – Town Scale Project

The Gdansk Power Plant (EC II) currently produces 220 000 tonnes of coal fly ash annually. In addition to this, more than one million tonnes of fly ash have been stockpiled temporarily in the middle of Gdansk. The ash is causing severe dust problems and must be removed.

Coal fly ash contains a number of soluble salts and partly leachable trace elements which may also pose a potential threat to the environment if the ash is not utilized or disposed of properly. There is, therefore, an immediate and continuous need to manage substantial amounts of coal fly ash in an environmentally acceptable manner.

In Gdansk, coal fly ash has traditionally been considered and treated as a useless waste product which should be landfilled, but coal fly ash may be regarded as a valuable secondary raw material which can replace increasing scarce natural raw materials, e.g., in cement and concrete and in construction works like roads, ramps, and land reclamation projects, provided the necessary environmental precautions are taken.

That is why the project is divided into two parts:

- a general investigation,
- an environmental investigation.

Part 1 of the project, the general investigation and evaluation of ash management in the Gdansk area, will include an overview of the existing ash management situation, chemical, mineralogical, and geotechnical characterization of the coal ashes produced in the area, performance of a critical review relating the available ash management options to the local conditions, review and evaluation of in-plant ash handling, and performance of field demonstration tests. A hierarchy of coal ash management options will be recommended.

Part 2 of the project is a study of the environmental and geotechnical implications of a marine land reclamation site at the coast of the Gulf of Gdansk in the immediate vicinity of Gdansk (see Fig. 6). The total capacity of the land reclamation site will be 2–4 million tonnes of ash, which will be placed at water depths up to approximately 6 m.

The study is site-specific, but the methodology will to a large extent illustrate general aspects of the ash utilization/disposal and will be applicable to other projects as well.

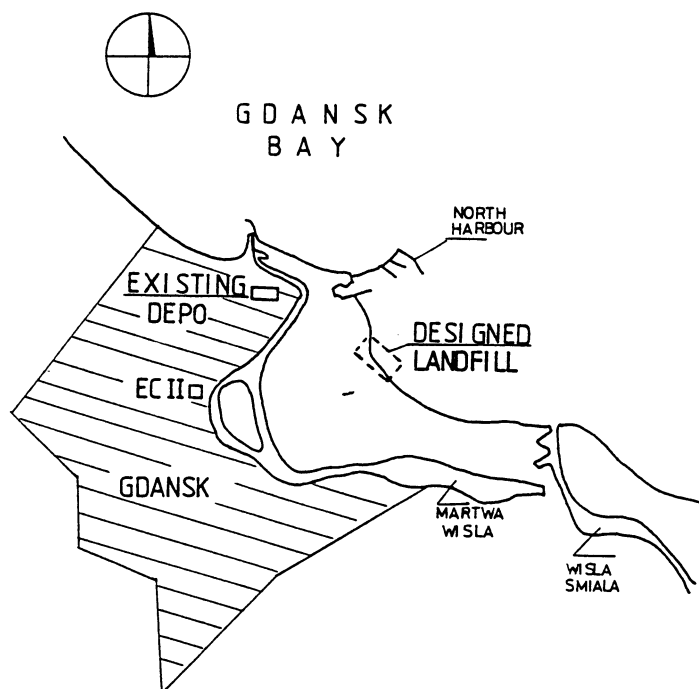


Fig. 6. General layout of fly ash reclamation site

Five 20-m drillings, which have already been completed, revealed an impervious clay layer covered by a 5-m-thick stratum of fine- to medium-grained sand.

Under such favorable conditions the leachates would be transported to the sea – not to the groundwater aquifer.

A number of laboratory leaching tests will be performed in order to determine the potential and actual leaching of selected contaminants from the coal fly ash both in the short and the long term. Based on previous experience in a marine environment, the most leachable contaminants are expected to be As, Cr, Mo, Se, and V. The leaching of inorganic salts (sodium, potassium, calcium, sulfate, etc.) has no significant environmental implications in marine surroundings.

Using a mathematical simulation model and the leaching properties determined in the laboratory, the potential emission of contaminants resulting from the contact between water and ash and the subsequent flow of water (rainwater and/or seawater) through the ash will be estimated.

The dilution of the produced leachate in the surrounding marine environment has been determined by dynamic mathematical model simulations. A combination of two models was used:

- two-dimensional mathematical hydrodynamic model (MIKE 21 already used in Rega project) for simulation of the current field, and

- Lagrangean type mathematical transport-dispersion model for simulation of the associated concentration fields.

An environmental impact assessment of the various coal fly ash land reclamation scenarios was then performed, based on the results of the estimated emission and dilutions of leachate/contaminants, the ecological baseline conditions, and existing legal regulations. Recommendations were made of possible techniques which may be expected to reduce or minimize the anticipated environmental impact.

Recommendations concerned also a future monitoring program.

The activity described above was realized together with Danish institutions and financed from the same subsidies as the Rega project.

The estimated project cost is USD 400 000.

The whole budget of the project including a construction of breakwaters and filling up the lagoon is estimated to reach USD 7 million.

6 Future Projects

The future efforts should concentrate at the Szczecin Lagoon (Odra mouth), the Gdansk Bay and the Vistula Lagoon (branched Vistula mouth).

Such studies should take into account the results of prefeasibility studies for the Vistula and Odra (financed by World Bank), as well as the results of geochemical mapping.

It is necessary to put into motion the pictures of sediment geochemical mapping and water quality studies using hydrodynamic, water quality, and eutrophication models to find pollution pathways.

The sediment studies seem to be important because even when water quality is improved, the contaminated sediment will remain. Dredging and separation techniques will not solve the problem.

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16 Environmental Impact of The Mining Industry in Poland

E. Helios Rybicka

University of Mining and Metallurgy, 30-059 Krakow, Al. Mickiewicza 30, Poland

1 Introduction

Elevated contaminant concentrations, in particular heavy metals, in natural soils and water systems derived from industrial sources pose a severe threat to the environment (Förstner and Wittmann 1981). Biological (microbiological, solubilization, biomethylation), chemical (pH and Eh changes, variations in concentrations and types of complexing ligands) or physical (river erosion) remobilization of metals accumulated in sediments may have very serious effects on river biota (Krabe 1988) as well as on the quality of surface waters and alluvial aquifers (Förstner 1989). Many studies have been undertaken to ascertain the sources and in particular the chemical behavior and speciation determining the toxicity and mobilization mechanisms of metals in natural waters (Salomons and Förstner 1984).



Fig. 1. Occurrence of principal mineral raw materials in Poland. (Kozłowski 1983). Hard coal districts: 1 operating; 2 designed. Brown coal districts: 3 operating; 4 designed. (1 Turoszow; 3 Konin; 4 Belchatow); 5 petroleum and gas districts, metallic ore districts: 6 operating; 7 designed (1 copper; 2, 3, 4, 4 Pb-Zn), chemical raw material districts: 8 operating; 9 designed (1 sulfur; 2, 3 rock salt); industrial stones: 10 operating; 11 designed

Poland is relatively rich in mineral raw materials (Fig. 1). From about 80 mineral commodities exploited recently the most important are:

- hard and brown coals,
- copper, zinc, and lead ores,
- native sulfur and rock salt.

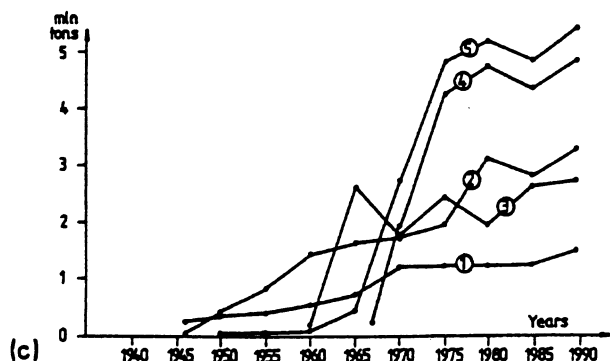
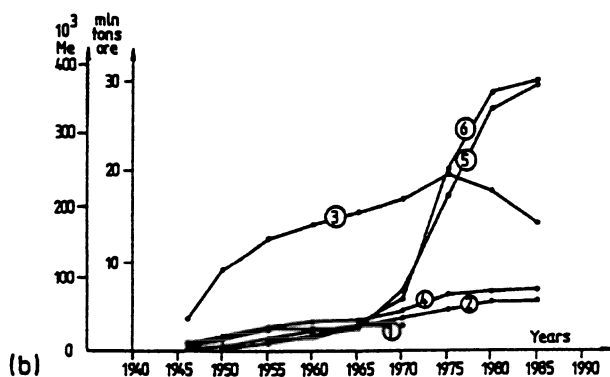
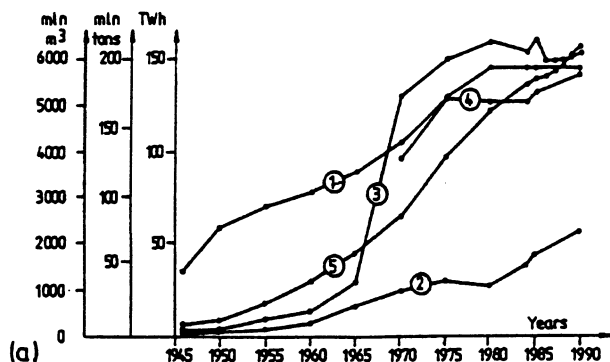


Fig. 2 a–c. Run-of-time output and final production of selected mineral raw materials and elements in 1945–1985 (1990) years. (Guziel 1988). **a** 1 Hard coal; 2 brown coal; 3 natural gas; 4 conventional fuel; 5 electric power. **b** 1 Iron ore; 2 zinc-lead ore; 3 zinc metal; 4 lead metal; 5 copper ore; 6 electrolytical copper. **c** 1 Rock salt; 2 salt in brines; 3 sulfur ore; 4 sulfur, underground melting; 5 total sulfur

Production of most important mineral raw materials in Poland for the period 1945–90 is shown in Fig. 2 a, b, and c.

Mining activity imposes negative, usually irreversible effects on the natural environment. The most serious are:

- changes in hydrogeological systems,
- hydrological transformations of soils and surficial flows,
- contamination of soils and surficial water reservoirs,
- chemical pollution of the atmosphere.

2 Hard Coal

Hard coals have been recently mined in Poland in the three districts: Upper Silesian Coal Basin (USCB) (Katowice, Rybnik areas), Lower Silesian Coal Basin (LSCB) (Walbrzych and Nowa Ruda areas) and Lublin Coal Basin (LCB) (area east from Lublin). Negative effects of mining activity are especially well recognizable in the Upper Silesian Coal Basin, as coal has been intensively exploited here for about 150 years.

The hydrological system of the USCB is influenced mainly by mineralized and polluted waters which originate from dewatering of mines, and are discharged to the surficial flows. In 1989, the 65 operating coal mines in the USCB supplied about 720 000 m³ of water per day from 83 discharge points. These waters are rich in Cl⁻ and SO₄²⁻ and contain high amounts of heavy metals and radium (Guziel 1988, Wilk et al. 1990). The total amount of chloride and sulfate ions released to the USCB surficial flows reached 8000 Mg per day in 1990, from which 5000 Mg were finally transported to the Vistula River and remaining 3000 Mg to the Odra River.

The influence of mineralized mine waters on the end parts of main rivers in the USCB (at average flow rates) is shown in Table 1 (Wilk et al. 1990).

The data prove an increase of chlorine and sulfate ion concentrations in the rivers to over 0.3 g/dm³ over remarkable distances: in the Odra River from the Olza tributary mouth to the town of Opole and in the Vistula River between the mouths of the Gostynia and Dunajec tributaries.

The key point for the protection of hydrogeological system of the USCB appears to be the discharge of waters from the two particular mines: Piast and Ziemowit, which hoist totally 3908 Mg of Cl⁻ per day, i.e., 60% of the total load for the USCB.

Mineralized waters in the USCB coal mines show high concentrations of natural radioactive isotopes (Ney et al. 1988; Wilk et al. 1990). It is caused by the reducing environment predominating within the coal formations. Under such conditions, some elements (e.g., radium) are selectively leached from the wall rocks, which result in high excess of Ra over U and Th in the mine waters. Concentrations of ²²⁶Ra in waters discharged mainly to both the Vistula and Odra Rivers

Table 1. Water salinity of upper part of main streams in the USCB

Stream	Load of Cl+SO ₄ ions in g/dm ³
Vistula catchment area	
Gostynia	10.429
Mleczna	9.494
Szarlejka	2.029
Czarna Przemsza	1.687
Brynica	0.889
Przemsza	0.588
Rawa	0.755
Bobrek	0.453
Odra catchment area	
Kłodnica	2.121
Bytomka	1.380
Olza	1.077
Bierawka	1.027
Ruda	0.740

vary from 0 to 28.1 kBq/m³. Highest Ra contents were found in waters of highest TDS originating from ten mines.

Another important problem is the pollution of both the bottom and flood-plain sediments with heavy metals (Fig. 3) derived from mine waters as well as released by ore (mainly Zn and Pb) processing and smelting plants. Highest concentrations of Zn (11 580 ppm), Pb (1745 ppm, and Cd (200 ppm) were reported from the overbank alluvial (Macklin and Klimek 1992), as well as up to 500 ppm Cd, 2500 ppm Pb, and 11660 ppm Zn in bottom sediments of the Przemsza River (Helios Rybicka 1992).

The subsidence affected mining fields of 43 USCB mines and gave rise to the formation of 322 ponds (data for 1987). Total submerged areas reaches about 8 km², and this land is completely excluded from any utilization.

Mining activities yield a huge volume of wastes. Figure 4 (GUS 1991) shows the highest amount of industrial wastes in the USCB and LSCB coal mining countries (Katowice, Walbrzych), the copper LCD mining district (Legnica) and the sulfur mining district (Tarnobrzeg).

Two types can be distinguished: spoils and cleaning wastes. It is estimated that production of 1 ton of hard coal is accompanied by an additional 0.4 ton of various wastes. From this figure, 46% remains underground and the rest (54%, cleaning wastes) is dumped on the surface. Petrographically, the wastes are Carboniferous claystones, mudstones, sandstones, and gravelstones/conglomerates, all containing variable amounts of heavy metal sulfides. Ashes and slugs from power stations constitute a relatively small percentage of the wastes (2–3%).

In the USCB about 140 waste dumps have been located, some of them outside the mining fields. Although land rehabilitation has been completed for most of the dumps, the pollution of groundwaters due to the leaching of soluble components

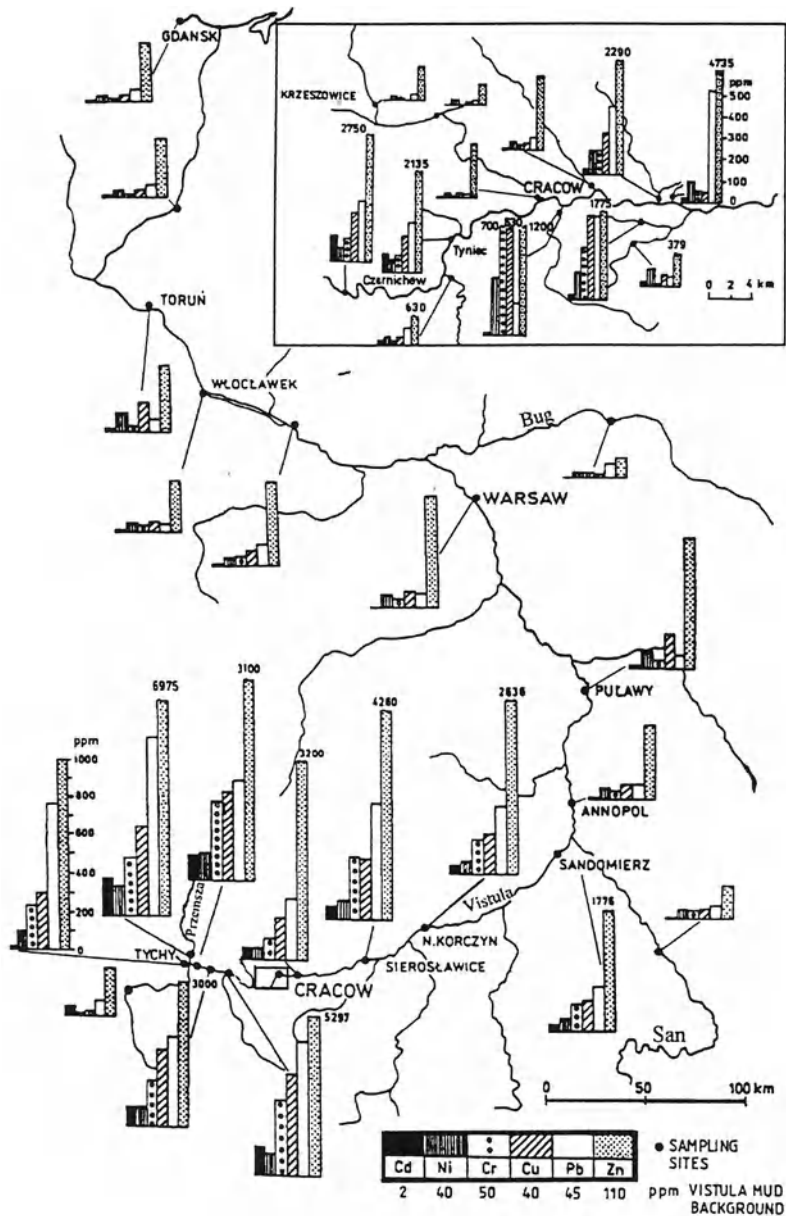


Fig. 3. Concentrations (ppm) of heavy metals in sediments of the Vistula River and its tributaries, Poland (fr. j 63 μ). (Helios Rybicka 1992)

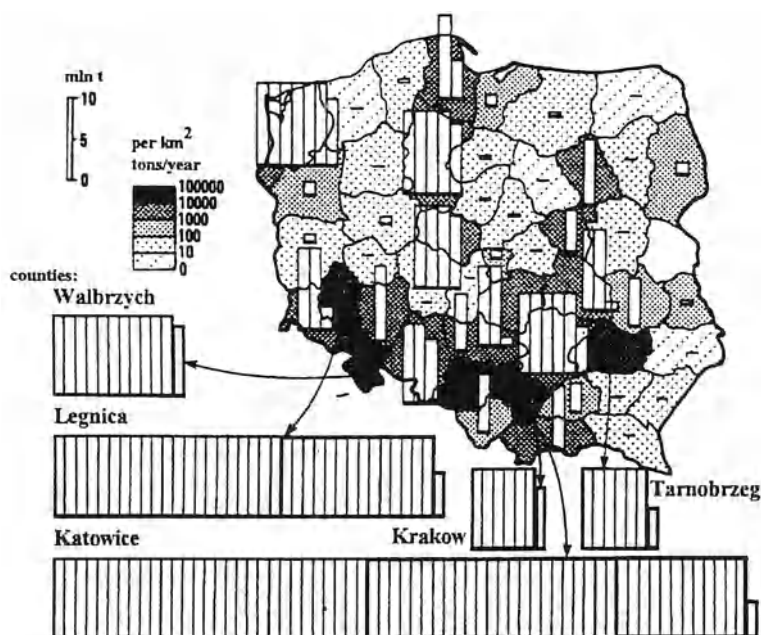


Fig. 4. Accumulated industrial wastes (end of 1990) by counties in Poland. (GUS 1991)

by percolating meteoric waters still continues. Thus, despite their age, the dumps are classified as potential pollution sources for surficial and groundwaters. The most destructive effects of waste dumps are:

- negative changes of the landscape,
- partial or complete removal of soils,
- pollution of atmosphere, vegetation and soils in adjacent areas with gases (spontaneous combustion) and dusts (aeolian erosion),
- changes in soil chemistry of the surrounding areas due to erosion of dumps,
- pollution of groundwaters.

One of the most dangerous environmental hazards caused by waste dumps is the pollution of surficial and groundwaters by soluble solids leached from the wastes. It is supported by studies of pore solutions derived from the Carboniferous spoils and of waters seeping from the dumps (Twardowska et al. 1988). The results proved the presence of solutions highly contaminated with the products of sulfide weathering/decomposition in the full thicknesses of typical spoil dumps of various ages. In solutions collected from 7–15-year-old spoils, concentrations of sulfate ion exceed by 10–80 times the standards for potable waters. Formation of especially dangerous, highly acid waters (pH below 4) appears to be a common process. The leaching time of sulfides from fine-grained, oxygenated spoils is estimated to be about 11 years, on average. In dumps, this process is much slower, due to the coarse fraction of spoils and limited volumes of meteoric waters avail-

able. However, some spoils can be persistent sources of pollution with products of sulfide oxidation which may affect the environment for decades.

Mining activity may result in the formation of subsidence troughs, occasionally or permanently filled with surficial or groundwaters. This leads to the formation of large waste lands. Moreover, exploitation causes drainage of the surrounding areas by dewatering of mines and excessive salinity of surficial flows by waters hoisted from mine workings.

In the LSCB the total volume of soluble solids released to the surficial flows with the mine waters reached 180 Mg per day in 1989. The mine waters are of poly-ionic, $\text{SO}_4^{2-} - \text{HCO}_3^- - \text{Mg} - \text{Ca} - \text{Na}$ type with local admixture of Cl^- . High contents of sulfate in ground waters result from infiltration of industrially contaminated, meteoric waters, from leaching of numerous spoil dumps, and from long-lasting residence of ground waters in abandoned workings. Potential pollution sources of waters infiltrating into the LSCB mines are 17 dumps collecting various types of spoils of various age.

In the LCB the negative effects of coal mining are still relatively insignificant because of a short period of exploitation. However, discharge of mine waters to the Swinka River caused apparent deterioration of water quality although quality class standards have not been exceeded, as yet. Total load of Cl^- and SO_4^{2-} ions in hoisted waters reached 11.1 Mg per day (Wilk et al. 1990).

3 Brown Coal

The total area affected by damage from brown-coal open-pit exploitation amounts to 60 000 hectares and is largest in the whole open-pit mining industry in Poland. Three mining districts are at present in operation: Belchatow, Mid-Poland (Konin, Turek) and Turoszow. Negative environmental effects caused by brown-coal open-pit mining are irreversible and affect waste areas. The common term "moon landscape" perfectly illustrates the resulting changes.

Apart from geomechanical processes which lead to the complete destruction of soils and irreversible changes in the landscape, the drainage of open pits influences hydrological systems (e.g., Belchatow). Both surficial flows and underground (shallow and deep) reservoirs are affected by:

- formation of depression cones (Fig. 5), which results in lowering of shallow and deep water tables,
- changes in watersheds and divides.

Dewatering of open pits results in a deficiency of water in farm lands and forest districts. Mine waters of brown-coal pits are generally uncontaminated and commonly meet the standards for potable waters.

Environmental problems caused by brown-coal mining are inevitably linked to those produced by adjacent power stations which utilize most of the output. Combustion of brown coal results in mass emission of gases (CO_2 , SO_2 , nitrogen ox-

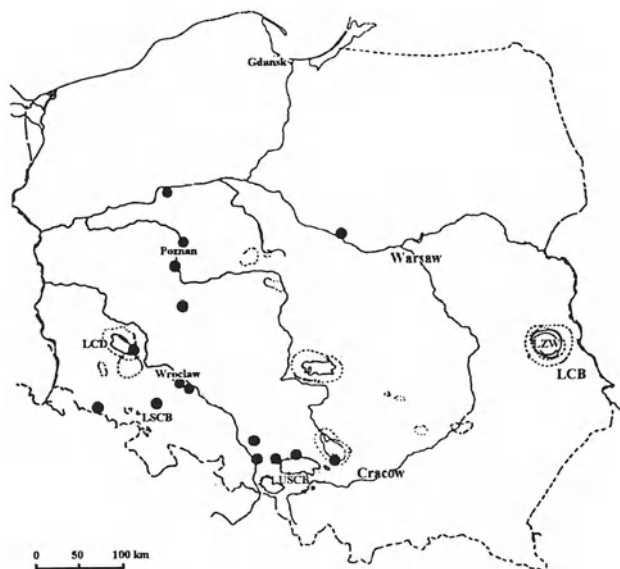


Fig. 5. Ranges of depression cones in the mining districts in Poland (Wilk 1990). • Localization of selected sources of contaminated groundwaters. (Błaszyk 1991)

ides) and dusts (composed mostly of SiO_2 , CaO , Al_2O_3 , and Fe_2O_3) with admixture of heavy metals (Zn, Pb, Cd). Brown coals mined in Poland show sulfur contents between 0.5 and 1.1%. As this sulfur is organic-bonded, its removal before combustion is impossible. Huge amounts of SO_2 are thus released to the atmosphere (Fig. 6) giving rise to acid rains and, consequently, to the degradation of soils by acidification.

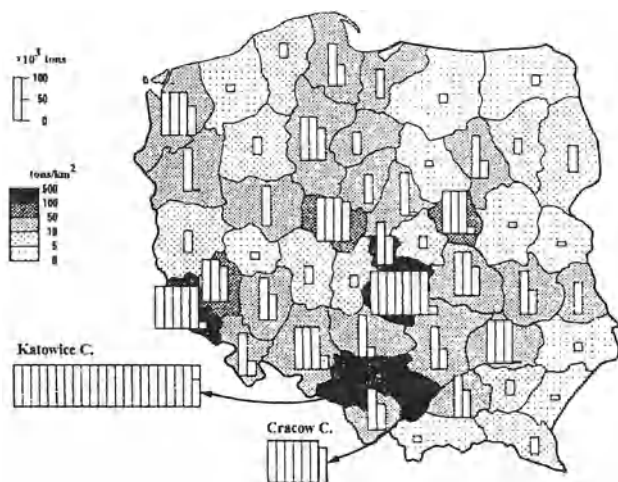


Fig. 6. Emission of SO_2 equivalent in 1990, by counties in Poland. (GUS 1991)

4 Base Metal Ores

Two areas of metallic ore mining have recently become active in Poland: the Upper Silesian Zn-Pb District (USD) (Bytom, Chrzanow, and Olkusz) and the Lubin Copper District (LCD) (Fig. 1).

In the Upper Silesian Zn-Pb District, the principal environmental problem is the formation of depression cones due to the dewatering of mines (Fig. 5). In the Bytom subdistrict, where ores have been worked since the 12th century, the static waters have been almost completely drained off from the mining fields and adjacent areas. Although Bytom mines have been inactive since 1989, the water is still hoisted and discharged to the surficial flows (mainly to the Brynica River). This discharge supplies 100 Mg of TDS per day (90% sulfates) and some amounts of base metals (up to 2 mg/cm³, mostly Zn and Pb). Mine waters commonly contain phenols (1–2 mg/dm³) which originate from infiltration of surficial contaminations.

In the Lublin Copper District mine and industrial waters are purified before discharge to the Odra River, which prevents deterioration of the quality class. Periodically, during high river flows, waters of increased TDS (14.5 g/dm³) are released at the rates below 70 m³/min. The load supplied to the Odra River in 1984 included 66000 Mg chlorides, 21000 Mg sulfates, 3.6 Mg Cu, 3.0 Mg Pb, and 3.2 Mg Zn (Wilk et al. 1990).

In the LCD, the ore mines are accompanied by processing plants and smelters which contribute significantly to the overall pollution. The soils in the vicinity of copper smelters are rich in heavy metals. The amount of Cu in the upper soil layer may reach 7400 ppm, and Pb 2000 ppm.

The Polish base metal ores are relatively low grade. Hence, the wastes (mostly tailings) constitute 90–98% of the total run-of-the-mine. The volume of wastes produced allow placing the base metal industry in second position just after the coal (and power) industry. The wastes are deposited in dumps and tailing ponds. Especially the latter are sources of environmental hazards due to the rise in the groundwater table in the adjacent areas (in some cases up to several meters). It results in excessive moisture content of soils and formation of marshes and ponds.

It must be emphasized that waters percolating from tailing ponds are highly polluted and, depending on contaminants, may affect the groundwaters and soils. In the LCD, waters in tailing ponds contain high amounts of Cu, Zn, and Pb sulfates and chlorides as well as organic compounds. If it contaminates groundwaters, these cannot be utilized as potable waters and, moreover, can also be harmful for vegetation. Expansion of contaminants around huge tailing ponds in the LCD (Gilow and Zelazny Most) became a serious problem as pollution affected an area of about 12 m². The industrial waters are commonly discharged to the surficial flows after clarification in the tailing ponds. Such waters may contain up to 300 mg/dm³ sulfate ion and 3 mg/dm³ Zn and Pb ions. An example is the strongly degraded Luszowka Stream (tributary of the Vistula River) which receives 2.2 Mg of sulfates and 22 kg of Zn + Pb per day.

Table 2. Range concentrations of Pb, Cd, Zn, Cu, Cr, and Ni in the soils in Pb-Zn-mining regions (Katowice county, Kucharski and Marchwinska 1990)

Locality	Metal concentration (mg/kg)					
	Pb	Cd	Zn	Cu	Cr	Ni
Olkusz	12–820	.X–17	24–1400	.X–46	.X–17	.X–32
Bukowno	46–1520	1–42	90–920	1–19	.X–25	1–29
Slawkow	37–352	2–16	148–2960	10–39	1–15	2–17
Klucze	4–258	1–9	33–540	1–20	.X–24	.X–61

Industrial waters discharged from Zn-Pb ore processing plants as well as mine waters and meteoric waters infiltrating the waste dumps are principal pollutants of the Przemsza River (tributary of the Vistula River, see Fig. 3).

Dewatering of mines significantly lowers the water table. In the USD hydrological system has been affected in an area of about 1000 km².

Soils in the neighborhood of metal mines and smelters show metal concentrations exceeding up to 100 times the background (Table 2). One of the vital environmental problems in Poland appears to be the contamination by cadmium and lead.

The metal industry releases noxious gases; sulfur and nitrogen oxides, fluorine, and others. In the neighborhood of the Miasteczko Slaskie Zn-Pb smelter, forests and other vegetation have been almost completely destroyed.

5 Rock Salt

Exploitation of rock-salt deposits causes subsidence and soil destruction due to excessive salinity. Production of a metric tons of sodium carbonate yields about 11.3 m³ of wastes released to settling ponds. The wastes contain CaCO₃, CaSO₄, Ca(OH)₂, Fe(OH)₃, silicates, aluminosilicates, and sewage composed of KCl, NaCl, NH₄Cl, Na₂SO₄, MgCl₂ and CaCl₂ (Wilk et al. 1990).

Industrial water carrying fine-grained wastes to the ponds partly infiltrates the bedrock and percolates through the embankments rising water table and contaminating the surficial flows and soils with the soluble solids. High concentration of some solids (mainly NaCl and CaCl₂) exceeding 12 mg/dm³ damages the structure and chemical composition of soils. In the Kujawy salt mining area, an additional source of pollution are common damages of pipelines and leakages of brine which causes expansion of pollution and enlarges the damaged areas.

6 Sulfur

The destructive effects of the sulfur industry on the natural environment are well known and can be classified into the three groups:

- atmosphere pollution with dusts (native sulfur, superphosphate, cryolite),
- atmosphere pollution with gases (sulfur oxides, nitrogen oxides, sulfuric acid) released during technological processes.
- contamination of surficial flows by mine and industrial waters (total volume of $89.4 \times 10^6 \text{ m}^3$ in 1986, from which 10% are potable waters).

Limits for these substances have been exceeded over the distance of 15 km. The Sulfur Company Siarkopol succeeded in significant reduction of pollutants, e.g., dust emission dropped from 11904 tons per year in 1980 to 2667 t/a in 1986 and hydrogen sulfide emission has been lowered from 86 t/a in 1980 to only 2 t/a in 1986.

Contaminants of surficial flows are: suspension (3243 tonnes in 1986) and chlorides (131410 tonnes in 1986). Mine waters originating from Machow and Jezioro Mines along with industrial waters and sewages produced during sulphur refining are discharged to the Mokrzyszowka stream (tributary of the Vistula River) and cause complete degradation of water quality. In the Vistula River, concentrations of sulfate and chloride ions raised at the rate of dozen to some tens of mg/dm^3 (Wilk et al. 1990).

Sulfur mining and refining decrease groundwater reserves due to dewatering and consequent depression cones and contaminates Quaternary water aquifers which are the main sources of potable waters. As destruction affects aquifers in the highly urbanized areas, the new water intakes must be made far distant from the pollution sources, which raises costs.

Flotation of sulfur ore produces troublesome suspended tailings which are deposited in the ponds, which at present occupy over 400 hectares. The planned area of waste land (including tailing ponds, dumps, open pits) is estimated at 4000 ha.

Native sulfur is the main contaminant causing destruction of soils. Rapid oxidation produces sulfuric acid, which reduces the pH of soils to 1.2–2.5. The sulfur content in topsoil measured in mining fields, and commonly in surrounding areas, exceeds 0.1% and may reach even 5% in the Grzybow Mine.

It is estimated that complete destruction of soils caused by exploitation by the underground melting method may finally affect an area of 5–6000 ha.

7 Summary

The mining industry causes tremendous devastation of the natural environment. The main problem appears to be the destruction of the hydrologic system. Impor-

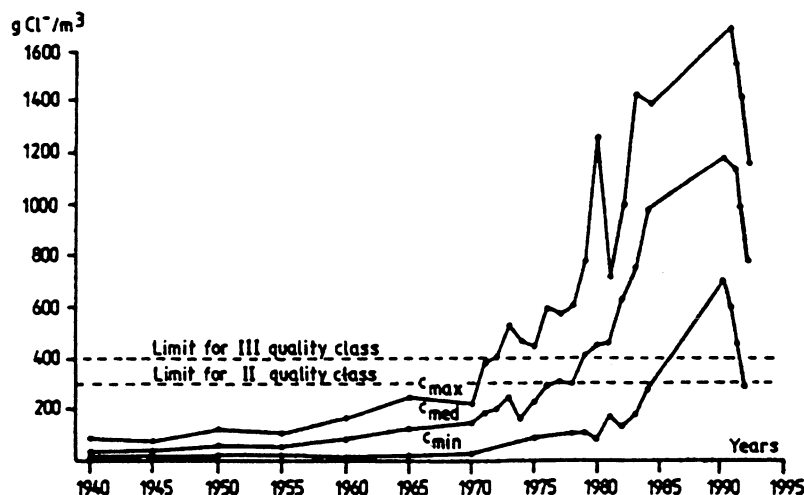


Fig. 7. Concentrations of Cl^- ions in Vistula River water (1940–1984), in Bielany/Krakow. (Kurbiel and Rybicki 1987)

tant factors are, e.g., formation of depression cones around dewatered mines and an increasing number of pollution sources for groundwaters.

The mostly endangered surficial flows are the upper course of both the Vistula (and its Upper Silesian tributaries) and the Odra Rivers, where the increase of contaminants (especially in the last years) must be regarded as alarming. Most of the polluting substances originate from highly mineralized waters hoisted from the Upper Silesian coal mines. An example of a drastic increase of pollutants is the distribution of chloride concentrations in the Vistula River near Krakow in the years 1940–92 (Fig. 7)

Both the Vistula and Odra Rivers are simultaneously important sources of water for domestic and industrial purposes. The Vistula River supplies about 0.5 billion m^3 of water along the 550-km long upper and middle courses (to the mouth of the Bug River) which covers nearly 35% of the total water consumption in Poland. The Odra River yields an additional 300 million m^3 downstream to the mouth of the Nysa Luzycka River (i.e., about 2% of the total consumption). Progressing overmineralization of both rivers (and their tributaries) is a real peril, and may lead to an ecological catastrophe.

From the surficial flows included in the water quality classification, about 50% do not even meet the standards for third quality class (Fig. 8).

The total load of domestic and industrial sewages transported to the Baltic Sea by rivers from Polish drainage basin includes among others (averages in tons per year estimated for 1988–89, data from State Bureau of Statistics, 1991):

Nitrogen	–	207 326
Phosphorus	–	15 584
Zinc	–	3331
Lead	–	448

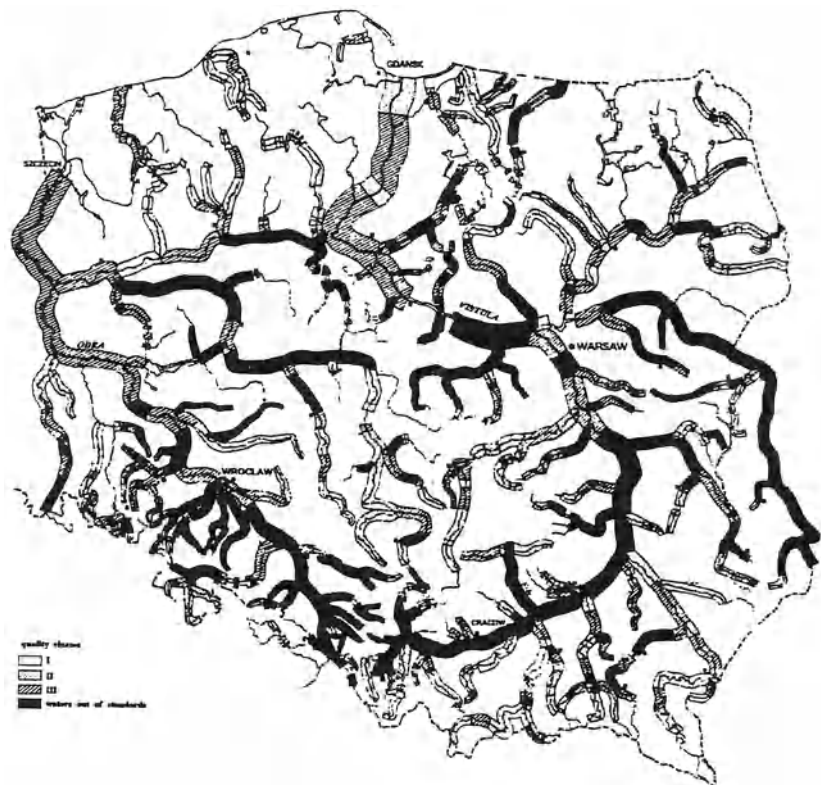


Fig. 8. Quality classes of stream waters in Poland in 1988. (GUS 1991)

Copper	—	515
Cadmium	—	40
Mercury	—	90
Chromium	—	443
Nickel	—	284

Other important sources of pollution are the wastes produced by the mineral industry. In 1990, the volume of such wastes included (data after State Bureau of Statistics, 1991) 660.5 million tons of spoils (from which 31.3% was dumped) and 490.7 million tons of tailings and cleaning wastes supplied by coal, barite, native sulfur, and base-metal processing plants (from which 69.3% was dumped).

The hard-coal mining yields the largest volume of wastes. It is estimated that in the period 1984–2000 about 900 million m³ of spoils will be dumped in the USCB area alone (Witczak and Szczepanska 1987). The annual load of chlorides in these spoils reaches 40000 tons. Such a volume is sufficient to contaminate 133 million m³ of water at concentrations exceeding the quality standards.

Most of the pollutants originate from the weathering of sulfides contained in spoils, precisely from their decomposition into sulfates and/or sulfuric acid. Under

full oxygenation, the decomposition of sulfides may yield 450 000 tons of sulfates per year (Twardowska et al. 1988) – a volume high enough to pollute 2300 million m^3 of water (i.e., twice the annual consumption of the whole Katowice county) at a level exceeding quality standards. Many dumps may produce highly acid waters of pH below 4.

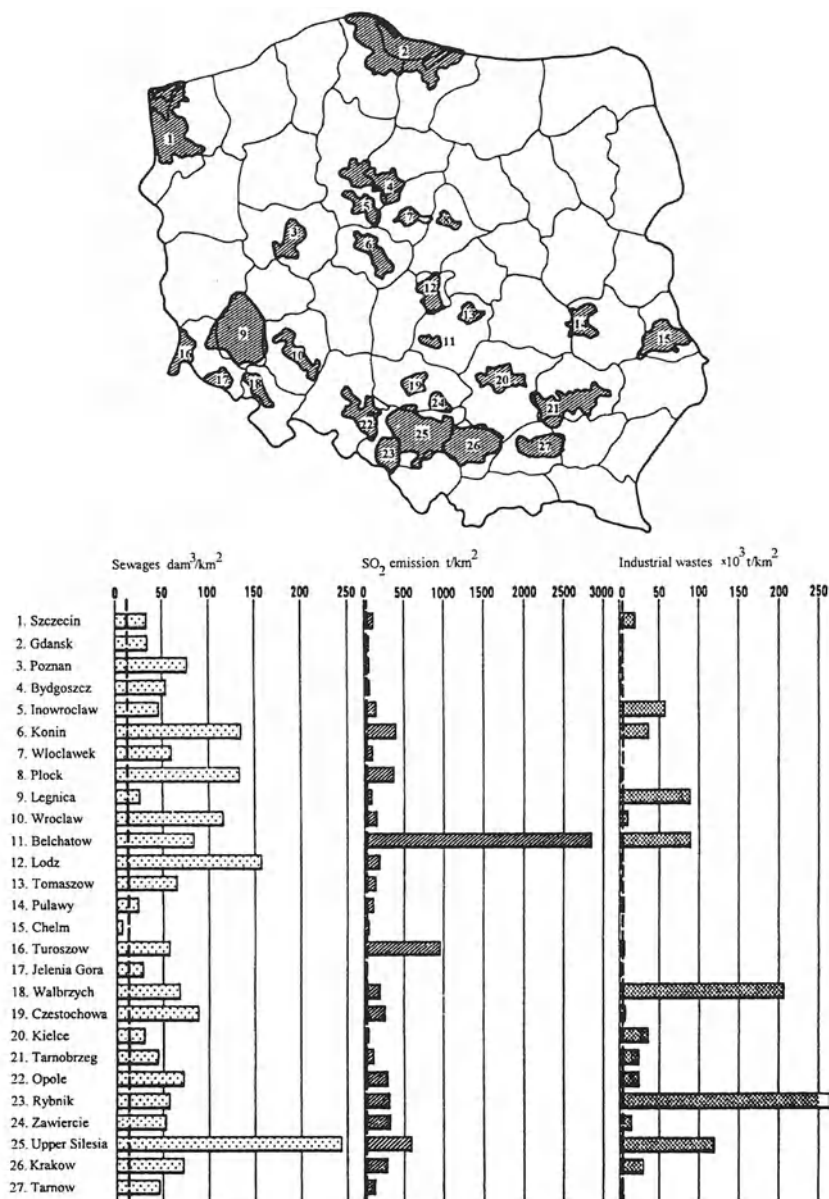


Fig. 9. Ecologically endangered areas in Poland (data for 1990). (GUS 1991)

Taking into account the volume of sewage which should be purified, the emission of dusts and gases (in SO₂ equivalent), and the volume of dumped wastes (per km³), 27 ecologically endangered regions have been distinguished (Fig. 9). Almost half of this figure corresponds to the mining districts.

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17 The Problems of Heavily Polluted Soils in the Czech Republic: A Case Study

J. Kozák, J. Janku, and J. Jehlicka

University of Agriculture, Prague 6, Suchbát, 165 21, Czech Republic

1 Introduction

Soil can be considered as a very important "ecological crossroad" in the landscape. From this point of view adequate attention has not been paid to it in our country during the last 40 years. Soil was mainly considered as a source for yields of agricultural crops and as a sink for placing different wastes. On the other hand, we meet many very biased assays of soil contamination, which do not reflect reality. The results of many research studies show that point contamination of our soils represents a bigger problem than diffuse contamination.

The aim of this chapter is:

- to describe the severe contamination of selected area
- to show some results of the new methods for evaluation of soil contamination.

2 Description of the Contaminated Locality

More than 120 ha of alluvial soils (fluvisol) in a locality near the town of Píbram were contaminated. There are two main sources of contamination. First, near the above-mentioned locality, the lead-smelting works are situated. The total amount of Pb emissions is estimated to be 220 t a^{-1} . The other source of contamination is the ore-cleaning plant. Liquid and solid wastes from this plant are stored in settling pits. The walls were broken and the contents were deposited by water of the Litavka river during floods. In Fig. 1, a map of the flooded area is shown. The numbers show the places where samples were taken.

The contamination in this area is so high that almost no plant can grow there, only some grass species (mainly fescue) during the spring period, high in precipitation, could survive. The situation is apparent in Fig. 2.

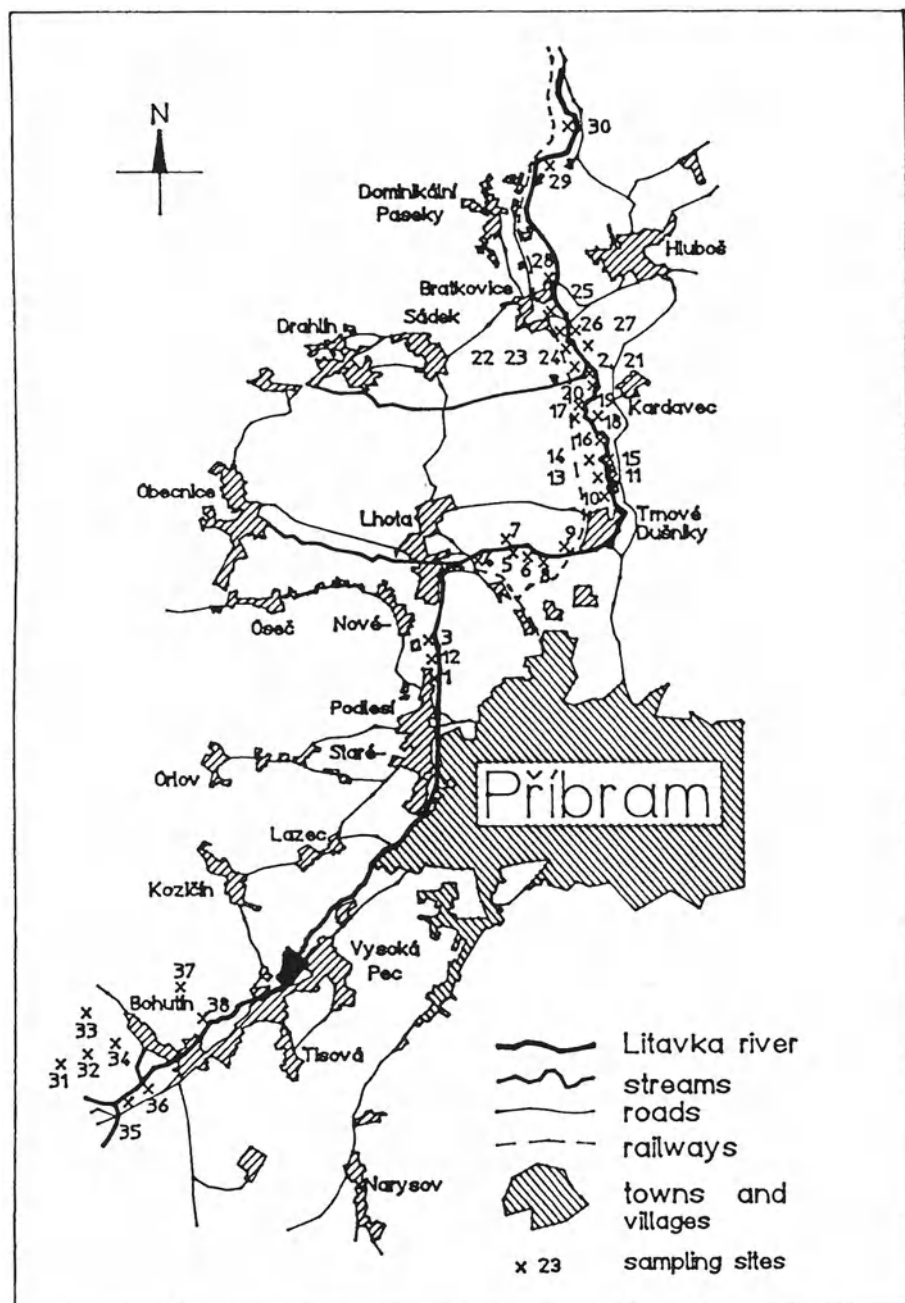


Fig. 1. Map of alluvium of the Litavka river



Fig. 2. View of the flood area of the Litavka river

3 Methods

The soil samples were taken from 5–40-cm depths. Altogether, 28 sampling sites were situated in the area, where plants showed a high degree of soil toxicity (samples 1–28), 10 sites in the surrounding area without toxicity symptoms (samples 29–38).

Nine trace elements were determined, among them Pb, Cd, and Zn by means of AAS in 2M HNO_3 extracts. The total contents of Ni, Cr, Cu, Co, Sn, and V were determined by emission spectroscopy in mixture with LiCO_3 and Ge and Pd as internal standards.

At 14 places, whose numbers correspond to those of the soil samples, samples of plants were also taken. The plant samples were washed in distilled water, dried at 105 °C, ashed at 450 °C, and the ash was dissolved in diluted HCl (1:1). The following elements were determined by means of AAS: Zn, Cd, Pb, Mn, and Cu.

The contaminated soil samples were treated by sequential extraction to determine the contents of heavy metals present in different forms. Details of the extraction procedure are given in Spevacková et al. (1989).

Analytical data were evaluated by classical statistical methods. Two methods of multidimensional statistical analysis were applied to analytical data of the top layer: factor analysis (FA) and correspondence analysis (CA). The computation

procedure of FA developed by Macháček (1987) was used. Details are given in Pavel and Kozák (1988). CA is a less-known multivariate method, which makes it possible to discover "hidden" relations both between variables (dimensions) and samples (factors). Correspondence analysis combines the advantages of both the R and Q techniques of main component analysis. The computation procedure was described, e.g., by Reyment (1963), Cubbit and Henley (1978), and Hebák and Hustopecky (1988). The common graphical presentation of projection of both dimensions (columns) and samples (rows) is very useful. A short distance between points (projections) related to each dimension indicates the similarity of its characteristics or behaviour. The distance between points related to samples indicates its similarity or differences in the group under study.

4 Results and Discussion

4.1 The extent of the Soil Contamination

Concentrations of nine elements in soil samples taken from 5-cm depth are given in Table 1. It is apparent from these data that in the case of Pb, Cd, Zn, and Sn, the enrichment in the soil was extremely high. Even long-lasting contamination by emissions from the Pb smelting work could not contribute substantially to the concentrations found in the samples under study. The soil samples from the sites where no toxicity symptoms were found showed considerably lower concentrations of Cu, Cd, and Sn.

Table 2 gives data on the concentration of the same nine elements found in soil samples taken from the 40-cm depth.

Soil samples taken from the deeper layer were also heavily contaminated. This fact could be used as evidence that the contamination of the area had occurred many times in the past. The concentrations of heavy metals show that the source of contamination was the same.

4.2 Speciation of the Heavy Metals in the Soil

The contaminated samples were treated by means of the sequential extraction to determine contents of heavy metals present in different forms. The following elements were determined: Cd, Cu, Pb, and Zn.

The following fractions were separated:

- fraction 1 – exchangeable forms;
- fraction 2 – forms bound in carbonates;
- fraction 3 – forms bound in Fe, Mn oxides;
- fraction 4 – forms bound in soil organic matter;
- fraction 5 – silicate matrix.

Table 1. Concentrations of nine elements in the soil samples taken from 5-cm depth (mg kg⁻¹)

Sample no.	Element								
	Pb	Cd	Zn	Ni	Cr	Cu	Co	Sn	V
1	2500	32.0	2615	39.8	65.8	140.6	16.5	348.9	115.3
2	5400	41.0	5850	17.8	55.2	237.8	8.8	271.4	64.1
3	2300	13.0	6750	15.6	52.9	98.6	10.4	66.1	70.7
4	6400	40.0	3375	18.9	52.9	334.6	12.4	416.8	61.7
5	2180	4.0	2200	6.8	33.0	103.9	5.6	83.2	49.2
6	3400	7.0	7100	7.4	33.0	111.0	7.7	211.2	54.8
7	3000	18.0	1250	20.1	49.0	144.3	12.3	220.2	63.5
8	1800	23.0	2250	23.7	60.3	160.3	14.5	220.2	66.7
9	2820	34.0	925	15.8	45.5	156.2	8.6	301.4	60.5
10	2600	46.0	4700	28.2	62.3	237.8	16.5	327.7	70.0
11	3760	35.0	2810	15.4	68.8	169.0	13.5	22.5	60.5
12	6900	33.0	1850	19.4	50.6	30.6	12.6	19.3	62.9
13	2740	39.0	3800	33.3	55.9	231.6	16.2	341.7	77.1
14	3400	37.0	2900	18.9	55.3	126.6	13.3	107.0	65.4
15	2480	10.0	9770	10.0	50.6	113.9	9.7	304.5	54.8
16	2900	75.0	5500	20.8	45.5	171.2	23.7	137.5	62.9
17	2900	86.0	5000	22.9	47.5	150.1	22.8	100.5	61.1
18	3700	37.0	5470	17.6	51.8	214.1	12.3	167.8	65.4
19	5000	59.0	7150	16.9	50.6	241.0	16.4	265.8	75.0
20	2600	23.0	2500	13.1	40.0	111.0	9.1	141.9	45.1

Table 1 (continued)

Sample no.	Element								
	Pb	Cd	Zn	Ni	Cr	Cu	Co	Sn	V
21	3460	33.0	3750	14.6	46.4	133.4	11.7	198.3	66.7
22	1500	21.0	2350	16.1	46.5	91.1	10.2	118.8	42.5
23	1120	14.0	1065	23.2	63.0	27.9	11.3	16.6	89.4
24	1220	14.0	1250	19.1	54.6	37.8	10.7	58.9	56.1
25	3900	34.0	3900	24.2	65.8	133.4	14.2	117.6	91.2
26	3000	2.6	199	15.0	41.7	29.9	6.7	15.3	47.4
27	5200	5.9	380	10.6	33.9	31.5	6.5	16.7	46.5
28	1880	24.0	2300	12.5	39.2	112.5	8.9	110.6	48.8
29	1300	3.0	8800	15.2	45.9	6.7	6.7	1.2	56.4
30	1000	2.0	4600	12.1	47.8	7.8	6.2	0.8	50.7
31	1300	1.3	7000	13.5	38.8	6.9	7.6	0.1	49.3
32	3300	2.1	1400	34.0	69.5	46.3	13.9	116.5	101.0
33	3300	1.8	1200	20.2	52.6	10.7	10.4	4.7	74.4
34	2300	2.8	7500	22.6	44.4	11.3	25.0	0.7	70.2
35	1750	1.0	4600	12.4	48.3	13.0	11.4	3.1	63.8
36	3080	1.7	7300	16.6	33.9	13.5	7.3	1.4	56.9
37	5400	1.0	3600	20.3	52.6	34.0	11.8	15.8	60.3
38	1740	4.0	3500	14.9	56.1	50.7	10.8	11.8	73.0

Table 2. Concentrations of nine elements in the soil samples taken from 40-cm depth (mg kg⁻¹)

Sample no	Element								
	Pb	Cd	Zn	Ni	Cr	Cu	Co	Sn	V
1	8700	32.0	6000	18.3	80.9	349.0	20.7	1050.0	59.1
2	4200	41.0	4900	33.8	59.8	176.5	15.5	0.1	67.5
3	1400	13.0	8000	15.2	52.6	62.3	10.1	47.8	50.7
4	6700	38.0	8000	15.4	60.5	253.0	11.2	750.8	52.7
5	5500	15.0	4000	8.0	30.9	25.0	7.4	0.4	39.9
6	4700	33.0	2300	8.5	28.2	22.5	7.0	14.9	39.6
7	3500	22.0	1150	14.6	53.2	111.0	11.0	94.9	67.6
8	4200	35.0	2900	11.1	35.7	190.7	10.5	284.2	46.6
9	3500	41.0	4400	17.6	50.4	155.2	8.7	186.5	56.9
10	3000	60.0	4200	13.7	53.4	193.9	11.7	148.3	58.1
11	2700	32.0	3000	9.4	41.8	90.9	9.0	70.2	47.8
12	5100	56.0	3600	13.0	51.7	98.3	10.5	117.9	62.8
13	2700	42.0	3700	15.0	52.8	235.8	13.0	140.8	88.1
14	4400	42.0	3400	13.0	57.6	118.0	11.3	145.2	67.9
15	6100	32.0	5900	9.4	52.8	382.2	8.1	648.0	38.8
16	3700	41.0	3700	13.7	50.6	153.2	130	125.5	60.4
17	8700	44.0	4700	15.7	66.1	372.0	6.1	397.8	71.8
18	6200	35.0	5000	14.7	51.1	220.9	9.7	229.4	55.4
19	12400	44.0	8000	15.9	73.2	595.6	6.8	648.1	66.6

Table 2 (continued)

Sample no	Element								
	Pb	Cd	Zn	Ni	Cr	Cu	Co	Sn	V
20	2200	46.0	2300	8.4	85.4	80.8	8.7	129.6	48.3
21	1670	33.0	2250	12.9	38.7	46.1	8.9	42.6	48.3
22	6200	6.5	3000	10.2	39.6	28.8	8.6	0.3	53.2
23	1030	16.0	1200	17.7	53.9	46.7	7.3	13.4	73.3
24	1500	19.3	1300	10.6	41.3	53.9	9.2	36.1	50.7
25	4900	51.0	3700	16.8	70.1	141.7	18.5	88.2	66.6
26	2100	3.3	50	9.3	41.5	10.9	6.5	8.8	58.7
27	3900	5.6	170	5.9	37.9	16.7	5.8	2.7	43.8
28	1880	26.0	1400	8.7	54.5	7.3	9.5	49.3	49.3
29	5700	3.0	3400	13.1	54	7.3	6.1	0.1	53.2
30	4800	0.5	3500	16.8	71.8	7.5	19.9	7.4	56.4
31	3500	0.3	2300	13.0	44.0	4.8	5.2	2.3	44.0
32	26.6	0.2	2000	13.1	49.4	11.3	4.7	4.6	51.2
33	2800	0.2	2500	19.2	68.1	6.4	13.3	2.1	54.8
34	3500	1.9	1040	18.4	64.2	12.3	22.8	0.2	67.9
35	25.5	0.4	7800	11.9	82.1	5.7	8.8	0.1	78.1
36	39.2	0.3	2300	6.6	40.0	2.9	4.1	0.1	55.3
37	2600	4.0	6000	13.9	66.3	21.6	12.6	5.4	73.3
38	1040	3.2	3000	8.0	47.9	28.5	8.3	4.7	72.6

Cd was present mainly in fraction 1 in the case of contaminated soils (30–40%), in the case of noncontaminated soils mainly in fraction 3.

Cu was present mainly in fraction 4 (30–40%)

Pb was found in fractions 2 and 3 in the contaminated soils (50%) and in the case of noncontaminated soils mainly in fraction 3 (75–90%).

Zn was found mainly in fraction 3, in the case of contaminated soils also in fraction 2. Details are given in Spevackova et al. (1989).

4.3 Contamination of Plants Grown on the Polluted Soils

In plants, samples taken at sampling sites with the same numbers as soil samples, the following elements were determined: Zn, Cd, Pb, Mn, and Cu. The results of the plant analysis are given in Table 3.

The extremely high concentrations, especially of Zn, Cd, and Pb, in many localities showed that these metals could be concentrated in plants to a large extent. The symptoms of soil toxicity could be easily explained by this fact.

4.4 The Application of Factor Analysis (FA) and Correspondence Analysis (CA) to the Analytical Data

Two methods of multidimensional statistical analysis were applied to the analytical data: factor analysis and correspondence analysis. Analytical data – contents of 9 metals in 38 soil samples taken from the top layer (5 cm) were used.

Dimensions of columns are represented by concentrations of Pb, Cd, Zn, Ni, Cr, Cu, Co, Sn, and V. Dimensions of rows are represented by contents of all the

Table 3. The concentration of selected heavy metals in plants grown on polluted soils. The numbers of samples correspond to the numbers of soil sampling sites

Sample no.	Element				
	Zn	Cd	Pb	Mn	Cu
7	1631	7.76	478	372	16.1
12	3107	3.8	1159	814	63.7
13	603	3.1	126	339	5.7
15	379	0.5	30.8	3.9	2.2
17	472	1.8	176	289	5.5
27	193	0.5	56	66	7.2
29	336	1.3	25	126	4.7
32	72	0.6	24.4	179	31
37	88	0.6	65	384	7.6
40	179	1.0	279	548	8.7
3	1396	11.5	691	498	28.4
22	496	3.0	152	331	6.9
36	373	2.2	218	875	13.5
11	438	0.9	37.2	82	14.6

Element	Pb	Cd	Zn	Ni	Cr	Cu	Co	Sn	V
Average concentration	3013.947	22.689	4006.816	18.408	50.197	107.437	11.953	133.803	64.508
Standard deviation	1441.736	21.261	2427.274	6.961	9.694	83.412	4.644	122.629	15.276

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Table 6. Scores of factors for dimensions

Factor		Score of factors for dimensions								
1	0.352	0.396	-0.032	1.063	1.912	0.483	0.946	0.397	1.513	
2	-0.599	-0.350	-0.459	0.978	1.804	-0.557	0.146	-0.363	1.761	
3	1.021	-0.139	-1.202	-0.071	0.542	0.151	-1.066	0.137	-0.157	
4	-1.006	-0.340	0.287	-0.094	1.155	0.315	-1.287	0.560	0.468	
5	1.329	-0.373	0.918	-0.028	0.508	-0.157	-0.430	-0.032	1.406	
6	0.012	-0.294	-0.153	1.190	-3.936	-0.039	0.274	0.339	0.689	
7	-0.188	0.605	0.028	-0.115	-1.429	-0.022	-1.289	-0.237	2.289	
8	-0.135	-0.230	-0.339	-1.806	-0.583	0.178	0.996	0.086	2.123	
9	0.115	0.283	-0.052	-0.448	0.380	-0.976	0.074	0.624	-0.048	

easier by exploiting the auxiliary computations, e.g., averages and variations of respective dimensions of the group of samples.

Based on the combination of these methods, we suggested the following interpretation:

Factor 1 (41.5%) – as a degree of the homogeneity of the spatial distribution of metal under study in soils.

Factor 2 (21.5%) – as a measure of the contamination (non-contaminating elements versus contaminating ones).

Factor 3 (12.7%) – as a measure of the soil contamination mainly by Pb versus soil contamination mainly by Zn.

Factor 4 (9%) – as a measure of the soil contamination mainly by Sn.

The projections of dimensions (elements) – represented by numbers, and of samples (soils) – represented by points into two planes declined by the first four factors are given in Figs. 3 and 4.

The following conclusions could be made. In the soils under study is most homogeneously distributed Cr, followed by V; less evenly distributed was Ni and Co. The distribution of the other elements is very heterogeneous. The degree of heterogeneity for Cd and Sn is similar (the coincidence of factor 1 for dimensions 2 and 8), Cu a little less, and Pb more. The distribution of Zn showed very high heterogeneity.

Cr and V, to a lower degree Ni, were found predominantly in normal concentrations. As the contaminating elements could be considered those with negative value of the factor 2, forming a cluster on Fig. 2, e.g., Pb, Cu, Zn, Cd, and Sn. The distribution of projections of samples (points) according to the first two factors is very heterogeneous – no dense clusters were formed. In the diagram samples could be distinguished in which the contents of elements is homogeneous and noncontaminated and those in which the contents of elements is uneven and contaminated.

The third factor distinguished samples which are contaminated mainly by Pb from those contaminated mainly by Zn. Both elements showed the highest concentrations (see Table 4).

The fourth factor distinguished samples with contamination by Sn.

Heavy metals in 38 samples

Dimensions: 1-Pb, 2-Cd, 3-Zn, 4-Ni, 5-Cr, 6-Cu, 7-Co, 8-Sn, 9-V

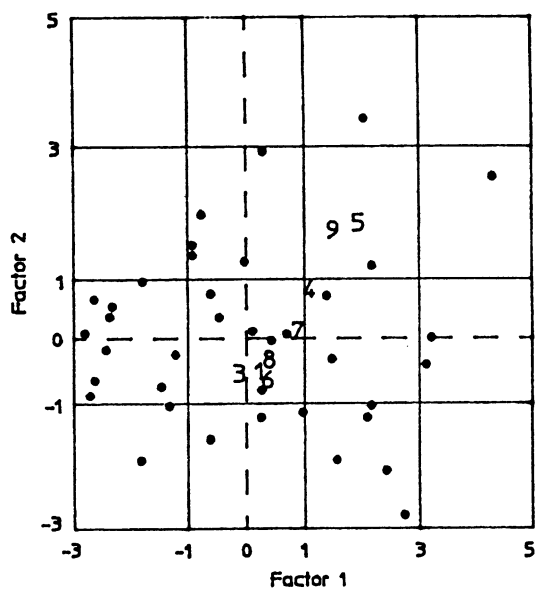


Fig. 3. Correspondence analysis

Heavy metals in 38 samples

Dimensions: 1-Pb, 2-Cd, 3-Zn, 4-Ni, 5-Cr, 6-Cu, 7-Co, 8-Sn, 9-V

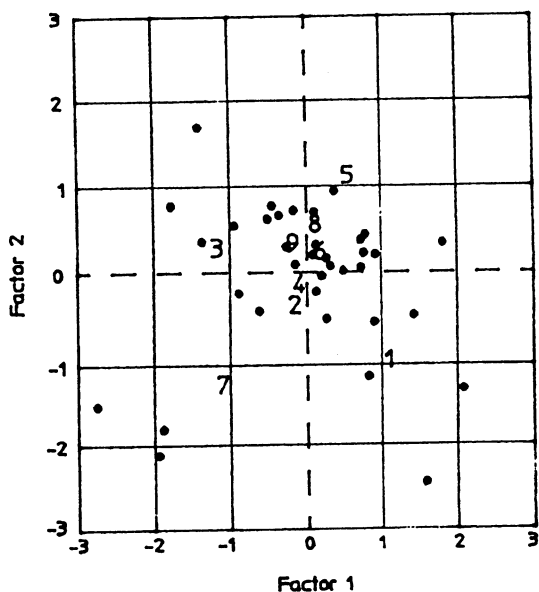


Fig. 4. Correspondence analysis

Heavy metals in 38 samples
Dimensions: 1-Pb, 2-Cd, 3-Zn, 4-Ni, 5-Cr, 6-Cu, 7-Co, 8-Sn, 9-V

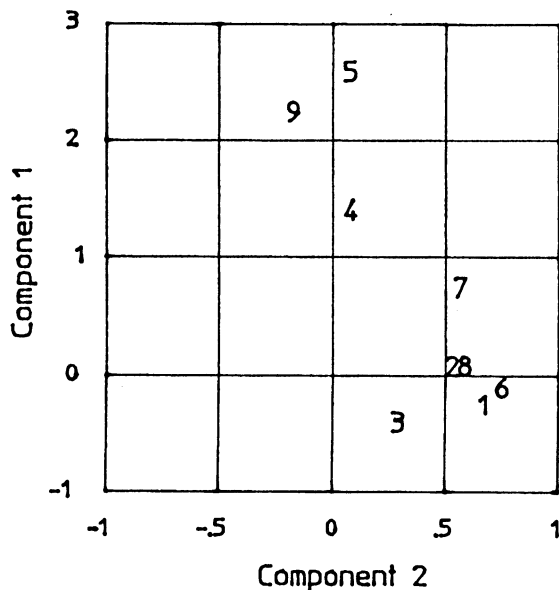


Fig. 5. Analysis of main components (rotated axis)

The projection of samples and dimensions into the plane F3–F4 formed a more compact cluster than in the case of the plane F1–F2. Approximately one third of the projections is situated further away. Those samples could be identified as samples with extreme heavy metal chemistry.

The analysis of the main components with rotation of axis (Fig. 5) was performed to verify the interpretation of the factors. The noncontaminating elements ($\text{Cr} > \text{V} > \text{Ni}$) are cumulated along the first axes, the contaminating elements ($\text{Cu} > \text{Pb} > \text{Cd} = \text{Sn}$) along the second axes. Weakly contaminating Co is situated between both axes and also strongly contaminating Zn, but with a negative value for the first main component. Also in this case Cd and Sn have an identical position in the projection plane, their projections coincide.

5 Conclusions

The results showed that soils extremely contaminated by heavy metals exist in the Czech Republic. It is clear enough that point contamination of the soils under study has occurred several times.

The interrelation between contaminating elements was evaluated by means of two multivariate statistical methods. The above described method proved to be more useful to distinguish between contaminated and noncontaminated area.

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18 Heavy Metals in the Danube River in Yugoslavia

P. Marjanovic, M. Miloradov, Z. Cukic

Tempus Center, University of Novi Sad Yugoslavia, Trg Dositeja Obradovica 6,
21000 Novi Sad, Yugoslavia

1 Introduction

An evaluation of the potential ecological impact of heavy metals which are not essential for biological communities, such as lead, cadmium, and mercury, clearly illustrates the transpositional problems associated with the by-products of modern society. While some environmental contamination results from the natural leaching of geological formations, the most significant redistribution of toxic trace metals, with the exception of mercury, occurs as a result of societal activities such as mining and fossil fuel combustion. Mercury is continuously evaporating from the Earth's surfaces and then being washed back to the surfaces through rain and snow; this naturally occurring redistribution of mercury is greater than the redistribution due to societal activities. These materials cannot be easily removed once they are released into the environment. However, they are reactive under certain conditions, and various physical and biological processes (bioaccumulation, biomagnification, etc.) may act to alter their form and distribution.

While the risk assessment process and ecological impact assessment will benefit from efforts to develop improved analytical and toxicological techniques, the process of risk management will transcend scientific analyses since the question of acceptable risk is a social rather than a scientific determination. Societal activities are largely responsible for the movement of heavy metals away from their natural geological locations. Subsequent changes in metal speciation, environmental distribution, exposure, and bioavailability are scientific issues of great concern. However, public policy decisions must incorporate not only quantitative risk assessment data and scientific judgement but also the cost-benefit analyses of various management strategies.

Management strategies may often only result in the redistribution of metals from one environmental compartment to another or from one location to another. For example, the collection and disposal of fly ash particles into surface water systems reduce the potential atmospheric exposure of terrestrial organisms, including man, but increase the potential heavy metal stress in the exposed aquatic biota. The biological treatment of municipal wastewaters effectively reduces the total metal input into surface waters, but the subsequent application of sewage sludges to agricultural land may reintroduce these metals directly into the human food chain. Similarly, the pollution of aquatic systems in one region may with time relocate the problem to a different downstream location if conditions (e.g., reservoirs on the streams, etc.) favor such a relocation.

Field studies which critically evaluate the effects of heavy metals on an ecosystem's structure and function are of particular research interest. A body of evidence indicates the development of metal tolerance in a number of plant and animal populations. Investigation of such resistant populations has been suggested as a useful approach to monitoring environmental contamination.

There is an increasing need to study the factors which influence human exposure to metals and the associated stress in the human response. In this respect the development of validated monitoring programs, the use of sentinel species in environmental monitoring, and the development of toxicity test procedures with species representative of the sensitivity of natural ecosystems are especially important.

However, there are two important problems encountered when trying to understand and prevent any harmful environmental contamination. One is the problem of identifying the causes of environmental contamination, and the other, the uncertainties involved in extrapolating the results from relatively simple laboratory studies to the more complex field situation.

With all of the above in mind, we have tried to look at the problem of evaluating the state of heavy metal pollution in Yugoslavia. As far as we know, no systematic studies of country- and basin-wide levels of pollution have been conducted so far, and efforts are presently under way to develop integral environmental quality monitoring programs in Eastern Europe. The transboundary aspects of heavy metal pollution in the Danube river basin and the profound need for international cooperation in the study of this problem are stressed.

2 Yugoslav Sector of the River Danube

The Danube watershed covers a total area of 817 000 km² with a population of approximately 90 000 000 people, living mostly in urban centers. Most of the Danube watershed (70%) is located upstream of the Iron Gate reservoir (an over 300-km-long reservoir constructed for the purpose of power production by Yugoslavia and Romania in the late 1970s) and is within the industrially and agriculturally developed countries of Germany, Austria, the Czech and Slovak Republics, Hungary, Romania, and Yugoslavia. The pollution from these countries and settlements is then discharged into the river Danube and even though some of it is transformed and stabilized before it reaches the Iron Gate reservoir, a significant amount reaches the reservoir and settles at the bottom. The variety of pollutants that are discharged into the waters of the Danube is largely due to many different types of polluters in the watershed. Besides organic pollution, specific pollutants such as heavy metals, mineral oils, and pesticides are also present, and in the past few years radioactive pollution has become an additional threat because of the number of nuclear power plants that exist in the watershed. Furthermore, the widespread use of chemicals and fertilizers in the agricultural areas of the wa-

tershed make agriculture a significant contributor to the total pollution of the Danube.

The main tributaries of the Danube river in Yugoslavia are the rivers Sava, Drava, Tisza, Tamis, Morava, Timok, Mlava, and Pek. All of them discharge their waters into the Danube as it flows through Yugoslavia and also brings along the pollution which originates in the neighboring countries.

Upon crossing the Yugoslav-Hungarian border, the Danube slowly flows through the Yugoslav Pannonian plain, passes two major Yugoslav urban centers, Novi Sad and Belgrade, and enters the Iron Gate Gorge near the town of Golubac. Once a wild stretch of the Danube and the most difficult part to navigate, it is today as calm as though nature intended not to disturb the remains of one of the oldest cultures and prehistoric human populations that lived on its banks. However, when one comes out of the Iron Gate Gorge, only then does one realize that the human hand played a major role in creating this idyllic scene. The Iron Gate Dam stands across the Danube and connects the people of Romania and Yugoslavia as a symbol of cooperation and many years of hard joint work.

The dam brought prosperity to the surrounding communities in more ways than one, but it also eliminated need for some people and brought hardship to others. The increased water level could be felt all the way to Novi Sad and the effects of the dam can be regarded as both positive and negative. Whatever one's opinion, the dam has made the Danube different, both upstream and downstream.

The waters of the Danube leave the Iron Gate clearer and cooler than before, to enter the reservoir of the Iron Gate II power plant (another joint Yugoslav-Romanian project) before the river leaves the territory of Yugoslavia on its way to the Black Sea, its final destination.

Of the Danube's 2192-km-long trip to the Black Sea, 358 km are in Yugoslavia, 230 km of which represents the border between Yugoslavia and Romania. It crosses the Yugoslav-Hungarian border with an average flow of $2413 \text{ m}^3/\text{s}$, while its average flow equals $5840 \text{ m}^3/\text{s}$ after leaving Yugoslavia. More than 50% of the Danube's water is in the Danube on Yugoslav territory but not all of this water originates in Yugoslavia.

All of the left-bank tributaries to the river Danube come from Hungary and Romania. The largest one is the river Tisza, with a watershed area of $157\,200 \text{ km}^2$ and an average discharge of $830 \text{ m}^3/\text{s}$. It enters Yugoslavia from Hungary near the village of Djale and joins the Danube near Slankamen. The biggest tributary of the river Tisza in Yugoslavia is the river Begej (average discharge = $26.5 \text{ m}^3/\text{s}$). Another tributary of the Danube is the river Tamis, which enters Yugoslavia from Romania near the village of Jasa Tomic and joins the Danube near the town of Pancevo, downstream of Belgrade (average discharge = $48 \text{ m}^3/\text{s}$). On the left bank of the Danube, a number of other streams bring approximately $40 \text{ m}^3/\text{s}$ of water on average to the Danube (the rivers Brzava, Moravica, Karas, and Nera are tributaries of the Danube with the largest part of their watersheds on Romanian territory). Of the $950 \text{ m}^3/\text{s}$ of water which left-bank tributaries bring to the Danube, only around $40 \text{ m}^3/\text{s}$ comes from the Yugoslav territory.

In Yugoslavia, the largest right-bank tributary of the Danube is the Sava. It drains over 35% of what was once Yugoslav territory and has a watershed area of 96 400 km². At the Serbian border, the river Sava has an average flow of 1200 m³/s while at its confluence with the Danube, after receiving the waters of the rivers Drina, Bosut, and Kolubara, its average flow amounts to 1640 m³/s. The length of the river Sava on Serbian territory is 206 km.

The river Drina, which is the largest tributary of the river Sava, has a watershed area of 19 570 km² and an average discharge at the mouth of 400 m³/s; 220 km of this river represents the border between Bosna and Hercegovina and Serbia. The river Lim is the major tributary of the river Drina with an average discharge of 110 m³/s.

The Kolubara is the last big tributary of the river Sava with a watershed area of 3641 km² and an average discharge of 22.5 m³/s.

Yet another major right-bank tributary of the river Danube in Serbia is the river Morava, with a watershed area of 37 400 km² and average discharge of 240 m³/s. The river Morava watershed drains most of Central Serbia and is formed from the Western and Southern Morava rivers.

Downstream of the river Morava, the Danube received 61.5 m³/s from four relatively small tributaries, i.e., the rivers Mlava, Pek, Porecka, and the Timok. The river Mlava has a watershed area of 1864 km² and an average discharge of 12 m³/s. The river Pek has a watershed area of 1237 km² and an average flow of 13 m³/s, while the Porecka river has a watershed area of 520 km² and an average discharge of 3.5 m³/s.

The river Timok drains most of the Eastern part of Central Serbia and has a watershed area of 4630 km² and an average discharge of 33 m³/s. Part of the river Timok represents the border between Yugoslavia and Bulgaria.

3 Iron Gate Reservoir

The Iron Gate Dam has been constructed to operate at a maximum water level of 69.5 m above sea level. However, the maximum water level at which the dam operated during the first few years was kept at 68.00 m, to evaluate and control the complex impacts of the reservoir upon the flood plain. The water level at the dam is a function of the water flow at the mouth of the river Nera [Observation station Back Planaka (km 1076+650)] located 133.5 km upstream of the dam (Fig. 1).

Figure 2 shows the longitudinal water level profile for natural conditions as well as for the backwater effect conditions for high river water flows occurring once in 100 years ($Q_1\%$). Also shown are the longitudinal profiles for the water regimes 68/63 and 69.5/63.

The modified water flow regime along the length of the reservoir brings about a number of other significant changes in the morphological characteristics of the river reservoir channel, the transport and sedimentation of particulate matter and sediment, the oxygen content and dynamics, the phytoplankton population struc-

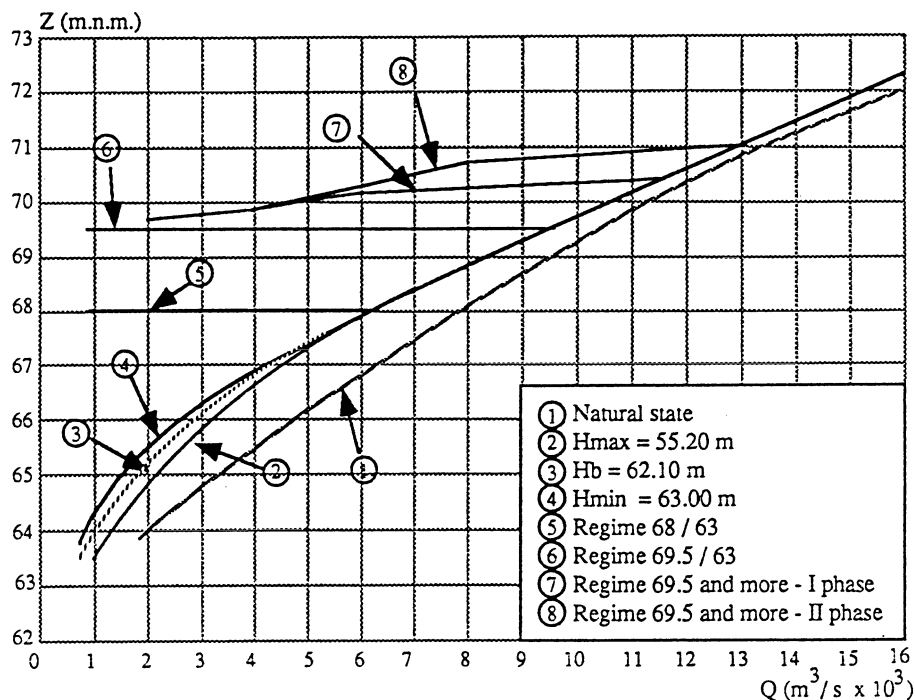


Fig. 1. Water discharge curves for the Danube river at river 1076 + 650 (River Nera)

ture and dynamics, and a series of other physicochemical characteristics and processes, all of which have a profound effect upon the water quality of the river Danube, both upstream and downstream of the dam.

The changes in the water regime, which are a function of the water level control at the dam and the incoming river flows, result in changes of the flow velocities and consequently in changes in the sediment transport characteristics of the river Danube. These changes and the relevant processes have profound effects on a number of qualitative characteristics of the river: the assimilative capacity of the river and the oxygen budget are modified, sediment deposits at the bottom of the river may cause the reduction of the cross sectional area of the reservoir, while waste materials coming from upstream may accumulate at the bottom of the reservoir, and the infiltration capacity of the river bottom and the associated groundwater recharge may be reduced due to the increased resistance of the bottom and this may reflect in the changed water regime in the associated flood plain etc.

The sediments budget has been continually monitored since 1974 at the following stations:

1. Station at the most upstream point of the reservoir.
2. Stations at the mouth of the rivers Sava, Tisza and Morava.

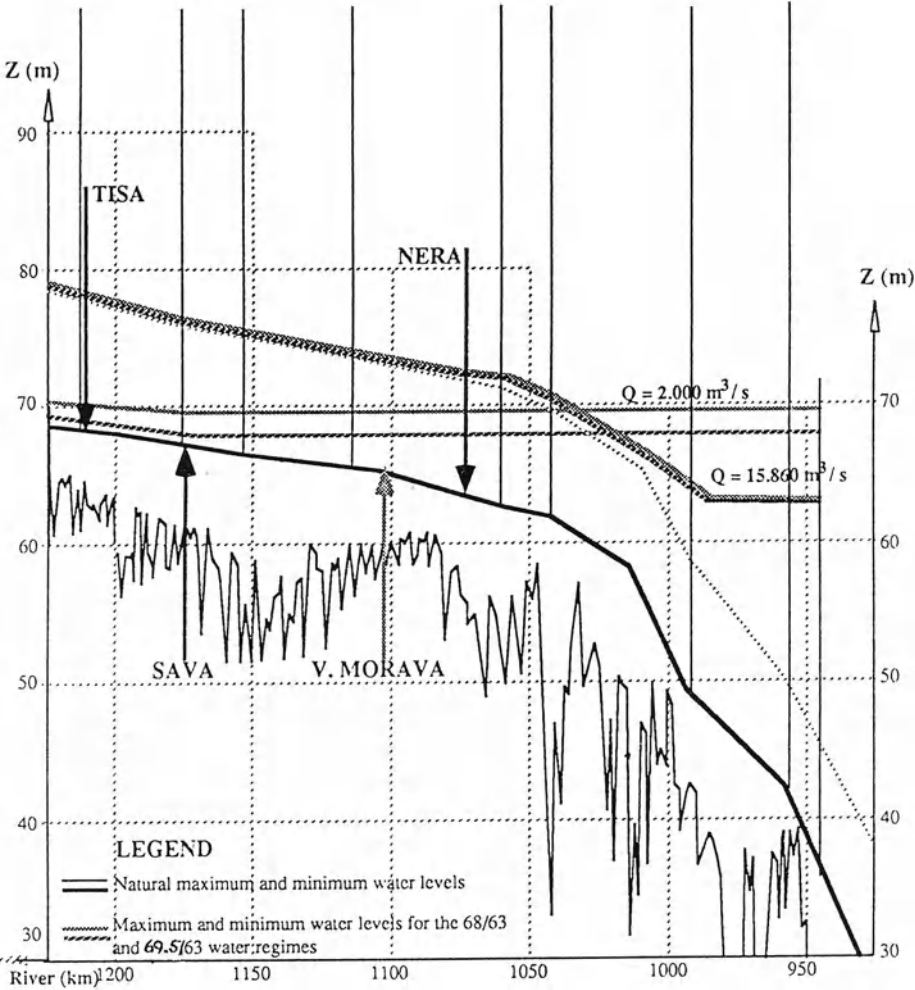


Fig. 2. Longitudinal water level profiles along the reservoir

3. Station at the outlet from the reservoir at the dam (at the overflow and the outlet from the power station).

Table 1 shows the total sediment input to the reservoir and the output of sediments from the reservoir for an 18-year period from 1971 to 1987, and the amount of sediments retained in the reservoir.

As can be seen, 80% of the sediment inflow is retained in the reservoir. This is much more than had been anticipated during the studies and design stages of the project. Analyses of the morphological changes of the river channel during the operation of the Iron Gate system have shown that the greatest part of the sediment accumulation occurred downstream of the mouth of the river Nera.

Table 1. Sediment budget for the Iron Gate reservoir, 1971–1987

Sediment inflows		Sediment outflow		Sed. accumulation	
10 ⁶ t	%	10 ⁶ t	%	10 ⁶ t	%
339.1	100	67.8	20	264.3	80

The sediment deposits in the reservoir range from a few centimeters to a few meters in the regions of the most intensive sediment deposition. The intensity of sediment accumulation and the associated morphological changes vary along the reservoir and change with time as well as across the reservoir. All this is a function of the flow regime along the reservoir and the water inflow and outflow regime which is directly controlled by the operation of the Iron Gate system (Figs. 3, 4, 5).

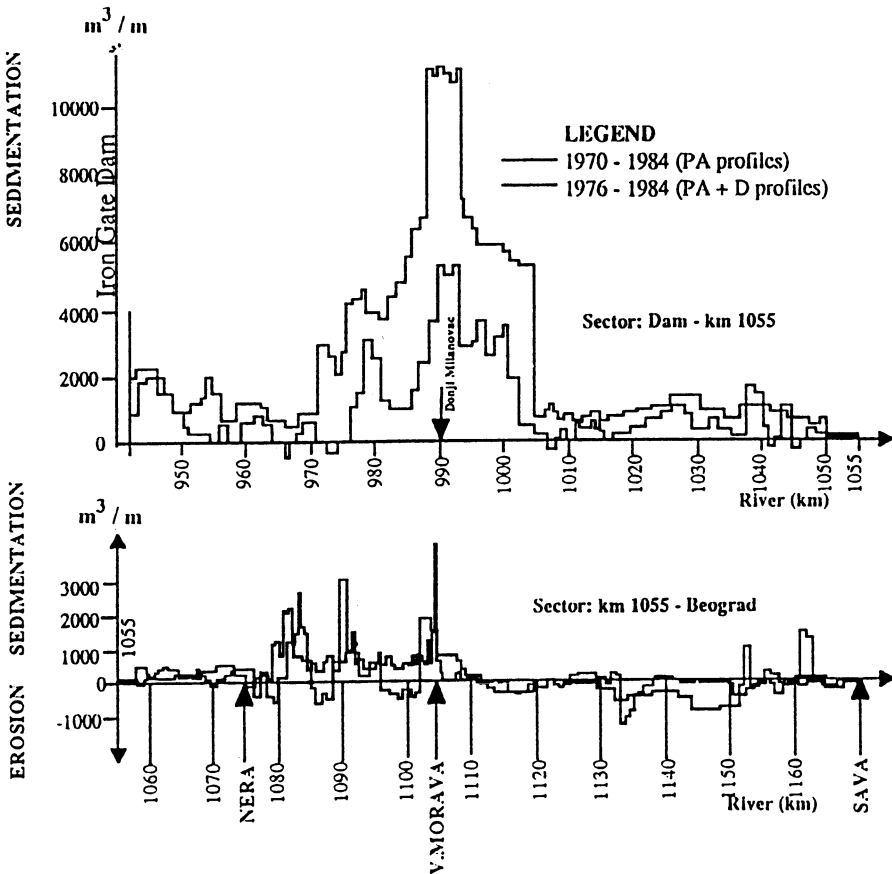


Fig. 3. Morphological changes of the Danube river channel along the Iron Gate Reservoir (data include dredging effects)

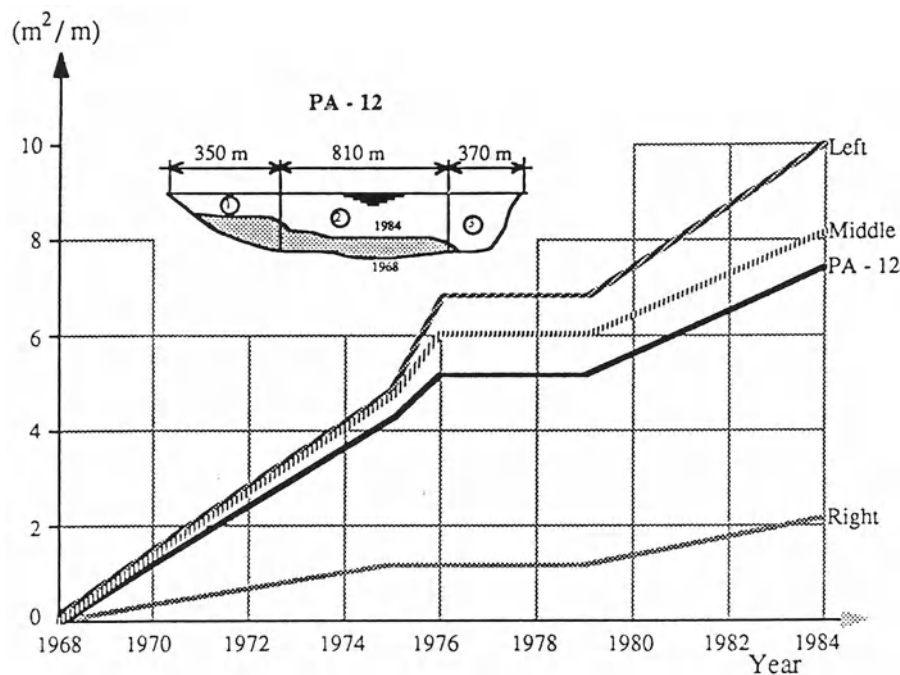


Fig. 4. Differential sediment deposition across the profile at km 995 + 100

The uneven distribution of sediment deposits at a given cross section results from the water flow regime at a given section while the amount of sediment deposition depends on the morphological changes of the river channel and the water level at the dam.

The particle size and sediment density are of special importance for the evaluation of the impact of sediment deposits upon the water quality and especially heavy metal pollution. These parameters have also been monitored over time and the results of these studies indicate that sediment deposits may be characterized by particles ranging in size up to a particle diameter of around 0.0025 mm. The sediment deposits have a relatively high content of fine particles with a diameter of around 0.01 mm. This content varies between 5 and 60% depending on the location of the observation station. The density of sediment deposits downstream of the mouth of the river Nera (km 1076 + 000) is almost always below 1 g/cm^3 .

A comparison of the changes in the density of sediment deposits and the suspended sediment particle size along the river Danube, before and after the construction of the Iron Gate reservoir shows a reduction along the reservoir downstream of the mouth of the river Morava (Fig. 6). The suspended sediment particle size after the construction of the dam is much finer. This phenomenon has not been observed downstream the river Danube section between the mouth of the

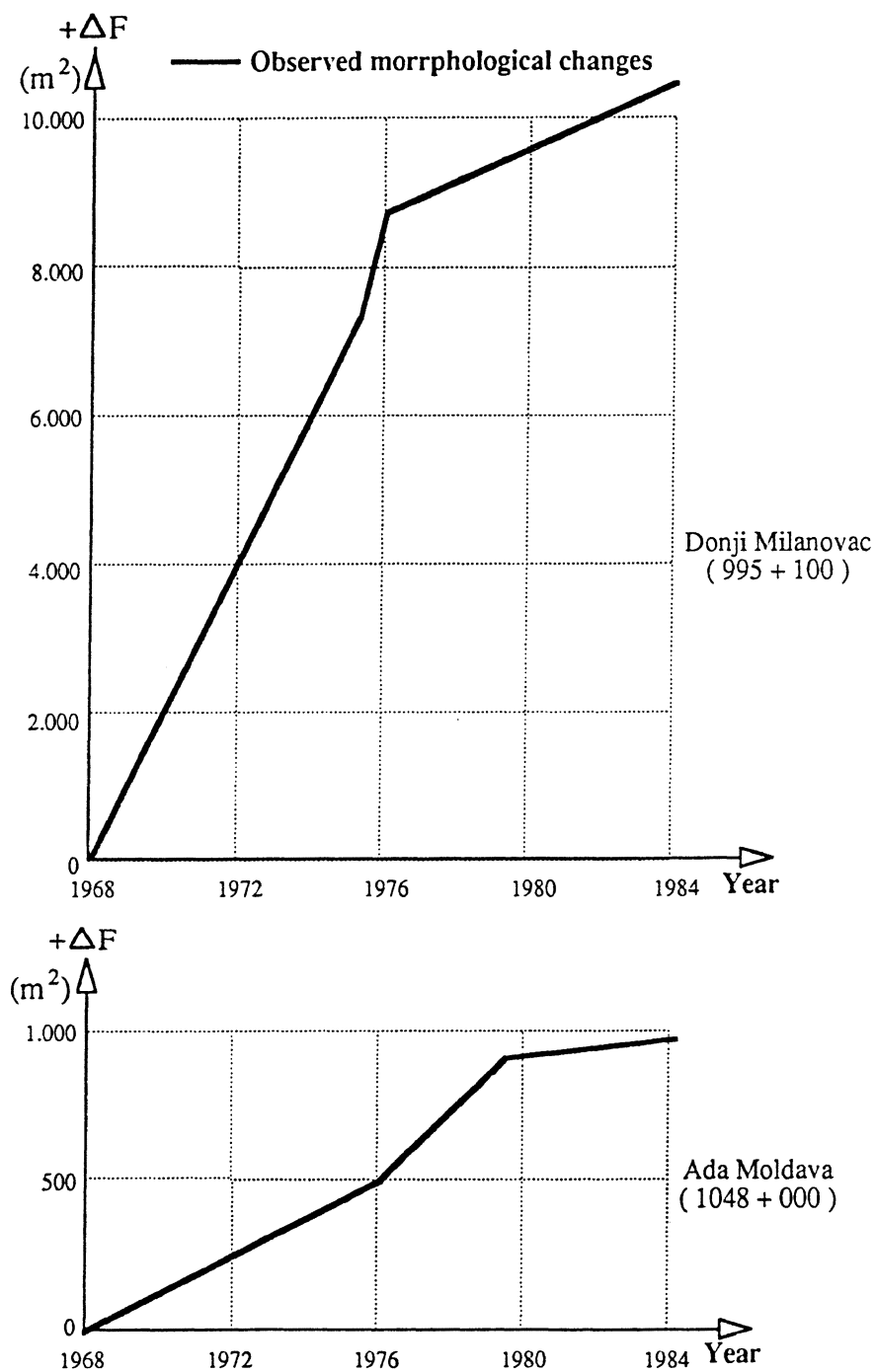


Fig. 5. Trends in the changes of the morphology of the River Danube channel downstream from the mouth of the river Nera

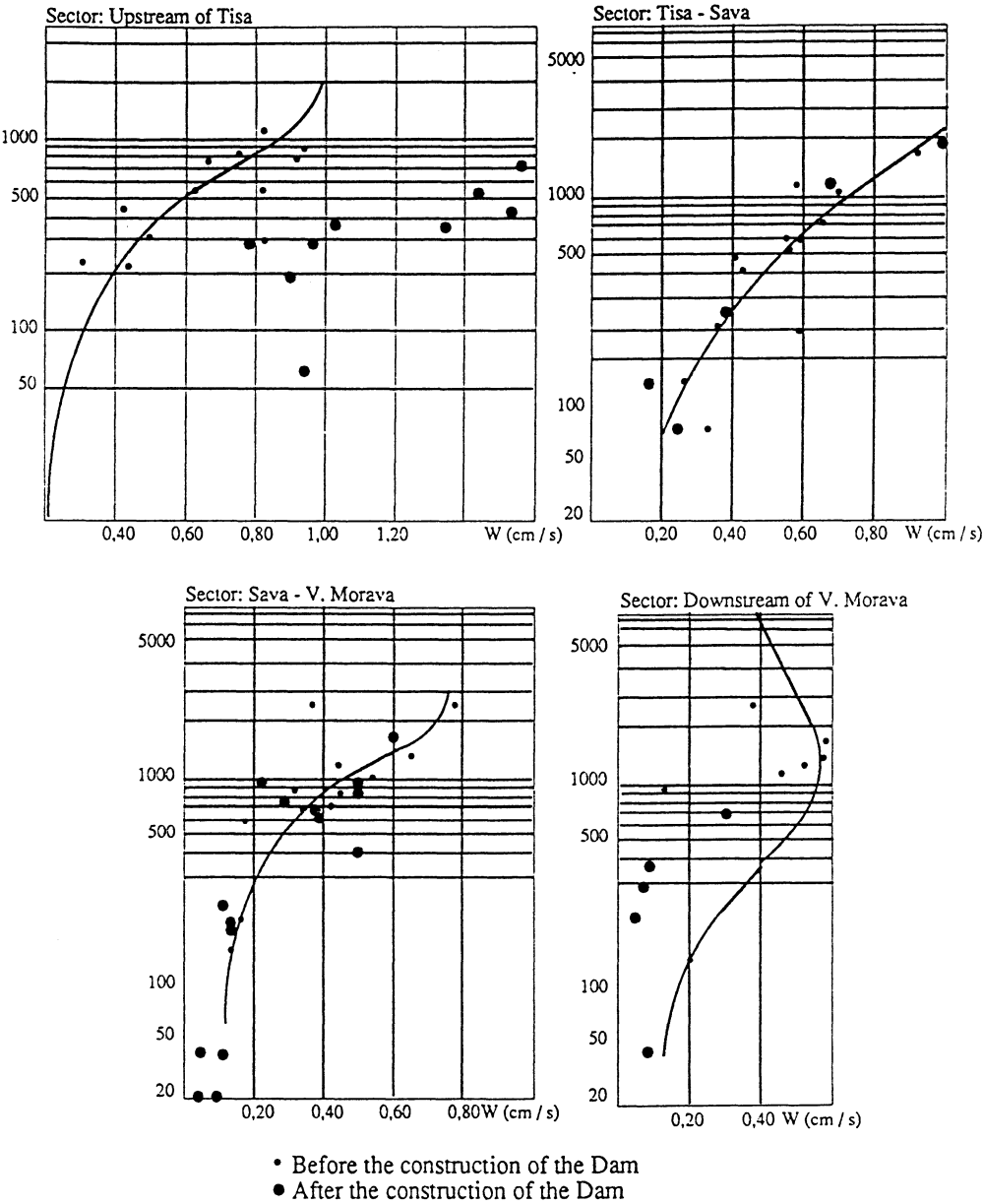


Fig. 6. Suspended sediment transport and particle size before and after the construction of Iron Gate Dam

river Morava and the mouth of the river Tisza. At the river sections above the mouth of the river Tisza, suspended sediment particle size has become coarser, which is probably the result of the reduced loading of the finer suspended sediments from the upper watershed. This reduction is probably the result of river regulation and erosion control works carried out since the construction of the Iron Gate dam.

4 Heavy Metal Budget and Water Quality

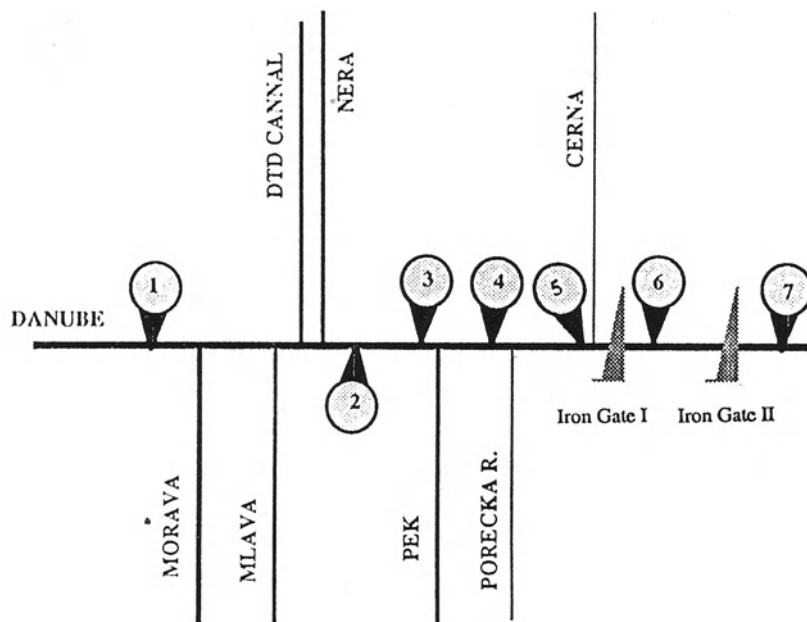
4.1 Water Quality Monitoring and Results

The water quality in the Iron Gate reservoir has been monitored for many years by different institutions and individuals. The entire data have not been analyzed so far, and some may not be very useful due to the different study methodologies employed. Since 1985 the Jaroslav Cerni Institute for the Development of Water Resources from Belgrade, under contract with the Iron Gate Power Company, has monitored the water quality in the reservoir at seven observations stations (Fig. 7) by collecting three samples per year at each station (spring, summer, and fall). The samples are collected at three points across the river at a depth of 0.5 m and are analyzed for an extensive list of water quality constituents. The data are collected for a large number of parameters: BOD₅, COD, O₂, Min. oil, NH₄, NO₂, NO₃, Ortho P, Phenols, SS, TP, Secchi disk, water temperature, As, Cd, Cu, Fe, Hg, Mn, Pb, and Zn, Atrazin, DDT(DDE + DDT), HCH, Heptahlor + Heptahlore-poksid, and Lindan. These data have kindly been made available to the authors by the Iron Gate Power Company.

All the data on the heavy metals were used to compute the overall average concentrations and the standard deviations for the 1985–1991 period. The average concentrations obtained in this way were then used to compute the average mass flow at each station using long-term average water flows at a given station.

The results of these analyses are presented in Table 2 and the respective graphs for each of the mentioned water quality constituents. Mass flow analyses and reservoir retention for each of the constituents are presented in Table 3 and the associated graphs.

By taking the long-term average concentrations (the most consistent data set available) the data variability was reduced and this enabled the input-output analyses for the selected metals. The budget computations are of a semiquantitative character since only part of the annual water quality cycle is included in the analyses. Nevertheless, the identified processes and the relative magnitudes of the mass transport may be considered typical and indicative of the situation in the real world. It is important to bear in mind the limitations of the data set when making conclusions about the results. As far as the authors of this chapter know, the analytical techniques used in the sample analyses have followed standard methods and have been executed with care. However, no formal quality control and quality



STATION IDENTIFICATION

1. Smederevo
2. Ram
3. V. Gradiste
4. D. Milanovac
5. Tekija
6. Kladovo
7. Radujevac

Monitoring by the "J.Cerni" Institute is carried out as a part of a bilateral, Yugoslav-Romanian, research and monitoring program. Samples are collected 3 times per year in the spring, summer and winter by both sides at 3 points across the river at each station.

Samples for depth profiles are not routinely collected by either side. Station 1, Smederevo is monitored by the Yugoslav side only.

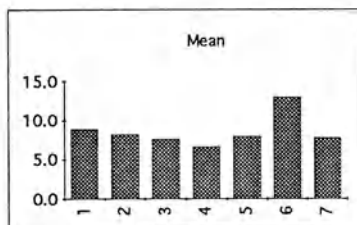
Tributaries are not monitored as a part of this program.

Occasionally specific aspects of water quality are analyzed in greater detail.

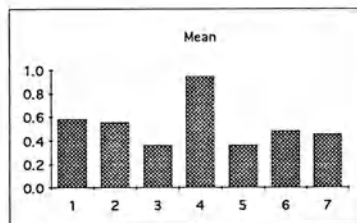
Fig. 7. WQ monitoring stations at the Iron Gate Reservoir

Table 2. Iron Gate reservoir, average metal concentrations, (three samples per year) computed using data from 1987 to 1991 as reported by the J. Cerni institute**As, $\mu\text{g/L}$**

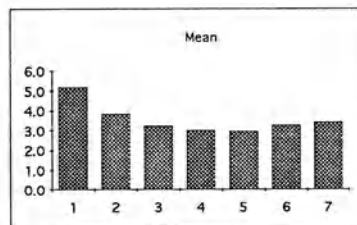
STATION	St. no.	Mean	Min.	Max.	St.Dev.	n
Smederevo	1	8.9	0.5	25.0	6.2	36
Ram	2	8.3	1.0	20.0	4.9	36
V. Gradiste	3	7.7	0.6	20.0	5.1	35
D. Milanovac	4	6.7	0.0	29.0	6.8	35
Tekija	5	7.9	0.1	26.0	5.3	32
Kladovo	6	13.0	1.0	110.0	24.3	33
Radujevac	7	7.7	1.5	20.0	3.9	35

**Cd, $\mu\text{g/L}$**

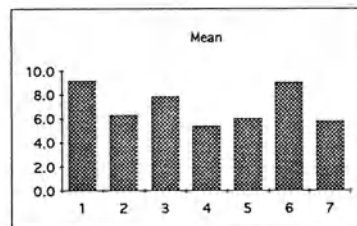
STATION	St. no.	Mean	Min.	Max.	St.Dev.	n
Smederevo	1	0.6	0.1	5.2	0.8	38
Ram	2	0.6	0.1	2.1	0.5	30
V. Gradiste	3	0.4	0.0	1.2	0.3	36
D. Milanovac	4	0.9	0.1	15.0	2.8	28
Tekija	5	0.4	0.1	1.2	0.3	28
Kladovo	6	0.5	0.1	1.9	0.4	32
Radujevac	7	0.5	0.0	2.5	0.5	30

**Cr, $\mu\text{g/L}$**

STATION	St. no.	Mean	Min.	Max.	St.Dev.	n
Smederevo	1	5.2	1.0	12.0	3.3	39
Ram	2	3.8	0.3	9.5	2.7	39
V. Gradiste	3	3.3	0.1	11.6	2.7	39
D. Milanovac	4	3.0	0.3	11.0	2.6	38
Tekija	5	3.0	0.3	10.5	2.4	39
Kladovo	6	3.3	0.3	9.0	2.6	37
Radujevac	7	3.4	0.4	11.0	2.7	39

**Cu, $\mu\text{g/L}$**

STATION	St. no.	Mean	Min.	Max.	St.Dev.	n
Smederevo	1	9.2	0.8	26.5	5.8	39
Ram	2	6.3	0.5	13.0	3.9	37
V. Gradiste	3	7.9	1.0	46.0	7.7	37
D. Milanovac	4	5.4	0.5	25.0	4.7	39
Tekija	5	6.0	0.5	21.0	5.0	33
Kladovo	6	9.0	1.0	55.0	10.8	35
Radujevac	7	5.8	1.0	21.0	5.1	36

**Fe, $\mu\text{g/L}$**

STATION	St. no.	Mean	Min.	Max.	St.Dev.	n
Smederevo	1	427.0	10.0	1460.0	345.6	39
Ram	2	363.1	40.0	940.0	285.5	39
V. Gradiste	3	363.7	40.0	780.0	224.8	38
D. Milanovac	4	262.2	10.0	900.0	225.6	37
Tekija	5	183.1	20.0	380.0	111.6	35
Kladovo	6	212.6	30.0	610.0	152.6	39
Radujevac	7	245.3	30.0	1150.0	215.6	38

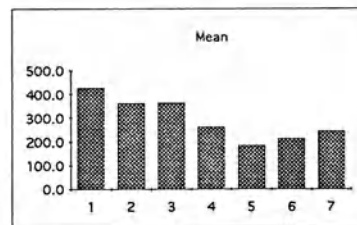
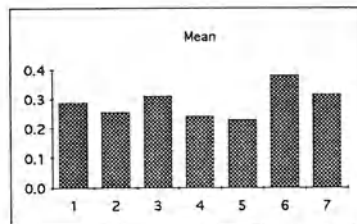
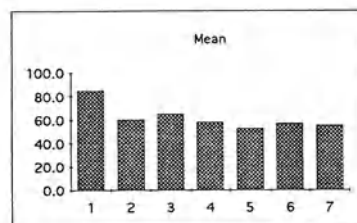


Table 2 (continued)**Hg, µg/L**

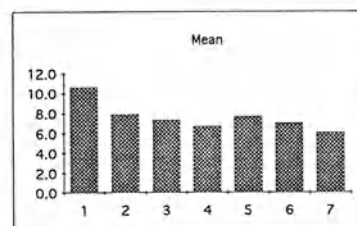
STATION	St. no.	Mean	Min.	Max.	St.Dev.	n
Smederevo	1	0.3	0.2	0.8	0.2	25
Ram	2	0.3	0.2	0.8	0.1	26
V. Gradiste	3	0.3	0.2	2.0	0.4	25
D. Milanovac	4	0.2	0.1	0.7	0.1	27
Tekija	5	0.2	0.2	0.7	0.1	28
Kladovo	6	0.4	0.2	3.5	0.6	29
Radujevac	7	0.3	0.1	1.6	0.3	30

**Mn, µg/L**

STATION	St. no.	Mean	Min.	Max.	St.Dev.	n
Smederevo	1	85.1	20.0	340.0	77.4	39
Ram	2	60.5	10.0	170.0	42.7	37
V. Gradiste	3	65.1	10.0	170.0	45.5	39
D. Milanovac	4	58.0	10.0	150.0	40.6	35
Tekija	5	52.6	10.0	130.0	34.5	34
Kladovo	6	56.8	10.0	150.0	36.9	37
Radujevac	7	55.0	10.0	130.0	36.2	38

**Pb, µg/L**

STATION	St. no.	Mean	Min.	Max.	St.Dev.	n
Smederevo	1	10.7	1.5	42.5	8.1	38
Ram	2	7.9	1.0	26.0	6.0	38
V. Gradiste	3	7.3	1.0	33.0	6.4	37
D. Milanovac	4	6.7	1.0	25.0	5.6	37
Tekija	5	7.7	0.5	80.0	12.9	37
Kladovo	6	7.0	0.5	20.0	4.9	36
Radujevac	7	6.1	0.5	29.5	5.7	34

**Zn, µg/L**

STATION	St. no.	Mean	Min.	Max.	St.Dev.	n
Smederevo	1	99.9	10.0	790.0	175.7	39
Ram	2	109.6	10.0	760.0	189.3	36
V. Gradiste	3	84.4	12.0	550.0	134.1	36
D. Milanovac	4	56.4	9.0	250.0	63.3	38
Tekija	5	71.4	13.0	520.0	125.6	40
Kladovo	6	80.1	15.0	620.0	148.5	39
Radujevac	7	96.1	10.0	820.0	187.2	40

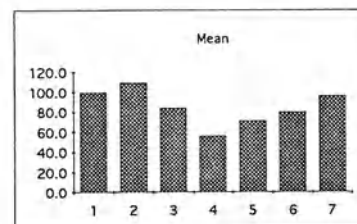
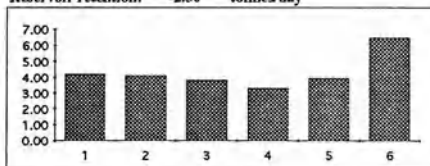


Table 3. Iron Gate reservoir, input-output analyses for selected parameters computed using data from 1987 to 1991 as reported by the J. Cerni institute

As

STATION	Stat. No.	Flow, m ³ /sec	Mass Flow, t/day
Smederevo	1	5478.0	4.20
Ram	2	5750.0	4.11
V. Gradiste	3	5760.0	3.82
D. Milanovac	4	5764.0	3.32
Tekija	5	5767.0	3.95
Kladovo	6	5795.0	6.50

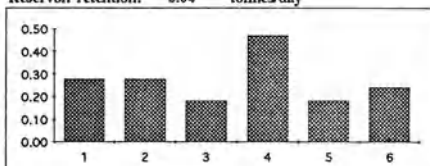
Reservoir retention: -2.30 tonnes/day



Cd

STATION	Stat. No.	Flow, m ³ /sec	Mass Flow, t/day
Smederevo	1	5478.0	0.28
Ram	2	5750.0	0.28
V. Gradiste	3	5760.0	0.18
D. Milanovac	4	5764.0	0.47
Tekija	5	5767.0	0.18
Kladovo	6	5795.0	0.24

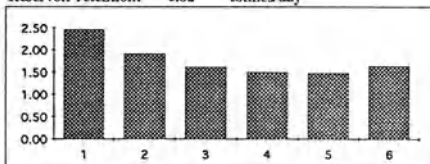
Reservoir retention: 0.04 tonnes/day



Cr

STATION	Stat. No.	Flow, m ³ /sec	Mass Flow, t/day
Smederevo	1	5478.0	2.46
Ram	2	5750.0	1.91
V. Gradiste	3	5760.0	1.62
D. Milanovac	4	5764.0	1.50
Tekija	5	5767.0	1.48
Kladovo	6	5795.0	1.64

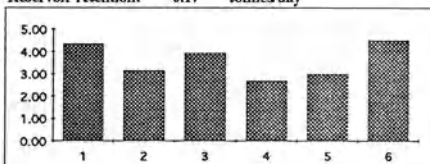
Reservoir retention: 0.82 tonnes/day



Cu

STATION	Stat. No.	Flow, m ³ /sec	Mass Flow, t/day
Smederevo	1	5478.0	4.35
Ram	2	5750.0	3.15
V. Gradiste	3	5760.0	3.93
D. Milanovac	4	5764.0	2.70
Tekija	5	5767.0	3.00
Kladovo	6	5795.0	4.52

Reservoir retention: -0.17 tonnes/day



Fe

STATION	Stat. No.	Flow, m ³ /sec	Mass Flow, t/day
Smederevo	1	5478.0	202.10
Ram	2	5750.0	180.38
V. Gradiste	3	5760.0	180.99
D. Milanovac	4	5764.0	130.56
Tekija	5	5767.0	91.25
Kladovo	6	5795.0	106.43

Reservoir retention: 95.67 tonnes/day

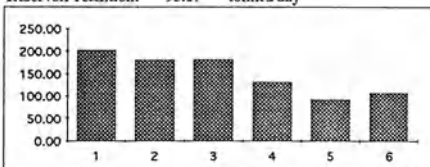
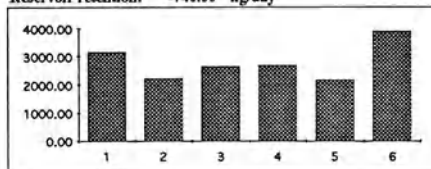


Table 3 (continued)

Atrazin

STATION	Stat. No.	Flow, m ³ /sec	Mass Flow, kg/day
Smederevo	1	5478.0	3160.00
Ram	2	5750.0	2230.00
V. Gradiste	3	5760.0	2650.00
D. Milanovac	4	5764.0	2680.00
Tekija	5	5767.0	2180.00
Kladovo	6	5795.0	3900.00

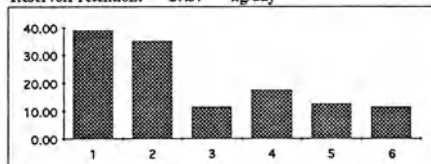
Reservoir retention: -740.00 kg/day



DDT(DDE+DDT)

STATION	Stat. No.	Flow, m ³ /sec	Mass Flow, kg/day
Smederevo	1	5478.0	38.94
Ram	2	5750.0	35.08
V. Gradiste	3	5760.0	11.37
D. Milanovac	4	5764.0	17.59
Tekija	5	5767.0	12.65
Kladovo	6	5795.0	11.37

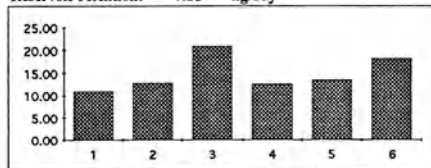
Reservoir retention: 27.57 kg/day



HCH

STATION	Stat. No.	Flow, m ³ /sec	Mass Flow, kg/day
Smederevo	1	5478.0	10.87
Ram	2	5750.0	12.75
V. Gradiste	3	5760.0	20.83
D. Milanovac	4	5764.0	12.44
Tekija	5	5767.0	13.44
Kladovo	6	5795.0	18.08

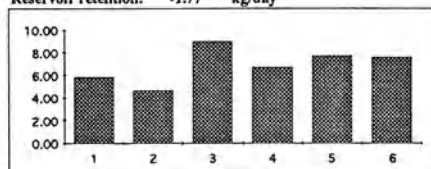
Reservoir retention: -7.21 kg/day



Heptahlor+Heptahloreposid

STATION	Stat. No.	Flow, m ³ /sec	Mass Flow, kg/day
Smederevo	1	5478.0	5.82
Ram	2	5750.0	4.64
V. Gradiste	3	5760.0	9.00
D. Milanovac	4	5764.0	6.71
Tekija	5	5767.0	7.70
Kladovo	6	5795.0	7.60

Reservoir retention: -1.77 kg/day



Lindan

STATION	Stat. No.	Flow, m ³ /sec	Mass Flow, kg/day
Smederevo	1	5478.0	13.09
Ram	2	5750.0	15.35
V. Gradiste	3	5760.0	14.73
D. Milanovac	4	5764.0	12.08
Tekija	5	5767.0	16.57
Kladovo	6	5795.0	17.27

Reservoir retention: -4.17 kg/day

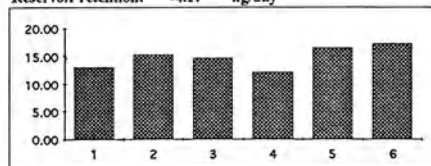
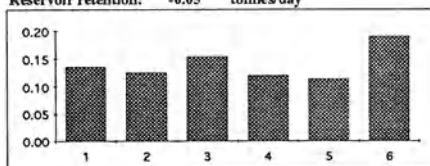


Table 3 (continued)

Hg

STATION	Stat. No.	Flow, m ³ /sec	Mass Flow, t/day
Smederevo	1	5478.0	0.14
Ram	2	5750.0	0.13
V. Gradiste	3	5760.0	0.15
D. Milanovac	4	5764.0	0.12
Tekija	5	5767.0	0.11
Kladovo	6	5795.0	0.19

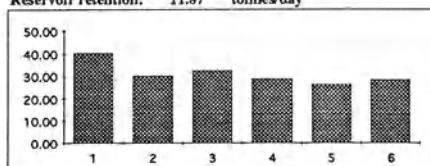
Reservoir retention: -0.05 tonnes/day



Mn

STATION	Stat. No.	Flow, m ³ /sec	Mass Flow, t/day
Smederevo	1	5478.0	40.29
Ram	2	5750.0	30.08
V. Gradiste	3	5760.0	32.41
D. Milanovac	4	5764.0	28.88
Tekija	5	5767.0	26.23
Kladovo	6	5795.0	28.42

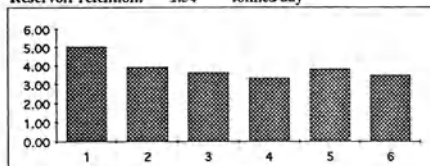
Reservoir retention: 11.87 tonnes/day



Pb

STATION	Stat. No.	Flow, m ³ /sec	Mass Flow, t/day
Smederevo	1	5478.0	5.04
Ram	2	5750.0	3.93
V. Gradiste	3	5760.0	3.64
D. Milanovac	4	5764.0	3.34
Tekija	5	5767.0	3.83
Kladovo	6	5795.0	3.50

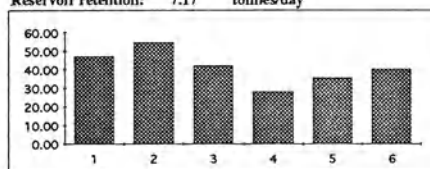
Reservoir retention: 1.54 tonnes/day



Zn

STATION	Stat. No.	Flow, m ³ /sec	Mass Flow, t/day
Smederevo	1	5478.0	47.28
Ram	2	5750.0	54.47
V. Gradiste	3	5760.0	42.02
D. Milanovac	4	5764.0	28.10
Tekija	5	5767.0	35.58
Kladovo	6	5795.0	40.11

Reservoir retention: 7.17 tonnes/day



assurance program for laboratory work has been implemented and there has been no formal interlaboratory calibration. This could represent a problem, since some of the data reported is not in line with the reported data by other institutions (State Hydrometeorological Bureau, State Public Health Institute). Having said this, it should be mentioned that the quality of this particular data set is supported by the consistent and logical interrelations between the concentrations of the constituents studies.

4.2 Heavy Metal Changes Along the Reservoir

Table 2 and enclosed figures show the average long term (1985–1991) trends of heavy metal changes along the Iron Gate reservoir. Table 4 gives the results of corresponding correlation analyses which show that the heavy metals are most closely associated with suspended sediments.

Table 4. Iron Gate reservoir water quality – correlation analyses for selected parameters. Pearson correlation matrix; each station value represents an average over a 6-year period (85–91)

	Sus.sol.	As	Cd	Cr	Cu	Fe	Hg	Mn	Pb	Zn	Atrazin	DDT	HCH	Lindan	Seki
Sus.sol.	1.00														
As	0.01	1.00													
Cd	0.09	-0.29	1.00												
Cr	0.85	0.10	0.05	1.00											
Cu	0.64	0.70	-0.30	0.56	1.00										
Fe	0.96	-0.21	0.09	0.78	0.42	1.00									
Hg	0.07	0.76	-0.35	0.06	0.65	-0.07	1.00								
Mn	0.95	0.01	0.11	0.91	0.65	0.85	0.06	1.00							
Pb	0.80	0.07	0.00	0.88	0.59	0.69	-0.17	0.88	1.00						
Zn	0.51	0.13	-0.40	0.65	0.30	0.60	0.20	0.42	0.40	1.00					
Atrazin	0.17	0.74	0.01	0.29	0.67	-0.03	0.87	0.27	0.06	0.06	1.00				
DDT	0.74	-0.11	0.27	0.88	0.23	0.76	-0.29	0.73	0.78	0.64	-0.06	1.00			
HCH	-0.20	0.25	-0.57	-0.43	0.20	-0.18	0.68	-0.30	-0.55	0.00	0.29	-0.68	1.00		
Lindan	-0.51	0.42	-0.72	-0.22	-0.01	-0.49	0.49	-0.48	-0.39	0.34	0.24	-0.36	0.49	1.00	
Seki	-0.93	0.22	-0.25	-0.69	-0.37	-0.96	0.20	-0.81	-0.69	-0.43	0.14	-0.74	0.30	0.68	1.00

Looking at the concentration changes of investigated heavy metals (with the exception of Cd), along the Iron Gate reservoir, it may be seen that water column concentrations are usually lowest near station 5 (Milanovac). This is in agreement with the observed pattern of sedimentation and sediment accumulation in the reservoir. Also, our earlier research shows that the critical oxygen concentration occurs downstream of Milanovac. Therefore, heavy metal concentrations usually increase downstream of Milanovac, indicating that desorption from the sediments may be occurring due to the anaerobic conditions which probably develop at the bottom of the reservoir.

The results show that significant amounts of some metals are retained in the reservoir. The budget computations indicate that Fe, Mn, Zn, Pb, Cr, and Cd are trapped by the reservoir (less mass flows out of the reservoir than enters it), indicating that these metals are closely related to the sediment transport mechanisms. On the other hand, there is a net release of As, Hg, and Cu from the reservoir, indicating weak bonding between these metals and the sediments but also indicating that these metals must have accumulated in the reservoir at earlier times.

Suspended solids show a very close association with Cr and Pb, which is not surprising. What is surprising is that the Cd transport does not seem to be associated with either the suspended solids transport or the Fe and Mn transport, as would be expected based on the findings of other researchers (Koelmans and Lijklema 1992; Balls 1989; Conway and Williams 1979; Davies-Colley 1984; Jenne and Zachara 1987). This is only so until one looks into the possible reasons for this. One possible and highly probable explanation of this phenomenon is the pollution from the industrial landfill located on the Romanian island downstream of the Gradiste station (river km 1005) and upstream of the D. Milanovac sampling station (river km 990). The landfill leaches "small" quantities of very fine particulates which probably carry some adsorbed Cd. Because the quantities of suspended solids are small, and particle size is fine, the changes of SS concentration in the Danube cannot be detected, while Cd analyses are very sensitive and thus the Cd is detected at Milanovac. However, additional research is necessary to truly explain the sudden increase in Cd concentration at Milanovac.

It is interesting to note the relatively close association of Atrazine with As ($r = 0.74$) and Hg ($r = 0.87$). All three of these substances show transport rates out of the reservoir that are higher than the inflow rates. The increase in the transport rates for these substances occurs at the first station below the dam and could be the result of the mode of operation of the dam and influences which sediment water interaction at the bottom of the reservoir could have upon the concentrations of these substances in the water column. Like Lindan (which also has a relatively high affinity for sediments), Cu and possibly Zn exhibit what seems to be similar behavior. The net "production" rather than the As, Cu, and Hg retention in the reservoir is indicative of pollution by these substances along the reservoir (natural availability, tributaries, direct runoff, etc.) but it has not been monitored, since the tributaries are not sampled as a part of the monitoring program.

When comparing the amount of sediments that are retained in the reservoir every year (in excess of 20 million tonnes) and the amount of metals and pesticides

which have been shown to remain in the reservoir, the content of these substances in the sediments is not alarming. However, since toxic substances can accumulate in the food chain, due attention should be devoted to the sediment quality in the Iron Gate reservoir in the future.

Since the construction of the Iron Gate Dam, the reaeration capacity of the Danube along the reservoir section has been reduced by a factor of 15 (based on the computation of the reaeration coefficient using the water surface drop in elevation prior to and after the construction of the dam and the empirical relationship developed by Parkhurst and Pomeroy 1972). Coupling this with the increased interface area between the water and the sediments, and the large amount of sediment accumulation in the reservoir and its impact on the oxygen resources of the Danube, it is not surprising that a reduction of oxygen occurs along the reservoir in low flow conditions (Perisic et al. 1990) and that in possible anaerobic conditions at the sediment-water interface, a mobilization of the metals buried in the sediments could occur. This could also be the reason for the "net production" of some metals in the Iron Gate reservoir.

5 Sources of Metal Pollution in Yugoslavia

Ambient water quality management in Yugoslavia in general, and Serbia in particular, leaves much to be desired. Water quality management is institutionally connected to all other water resources areas of activity, and this creates a conflict of interest which is reflected in the rules and regulations in existence. Even though the ambient water quality is regulated by a set of rules and regulations in Serbia and Yugoslavia, the legal acts do not reflect the real situation in the field. If regulations were adhered to, the pollution problems of the Danube and its tributaries in Yugoslavia would be reduced.

Generally speaking, all the tributaries of the Danube are polluted. According to the existing standards, the only rivers that satisfy the prescribed II class standards are the Drina upstream of Loznica, the Uvac, the Vlasina, the Moravica upstream of Ivanjica, the Danube downstream of the Iron Gate I dam, Mlava, Karas, Drim, and Ibar upstream of Studenica. The worst situation has been detected on the rivers Borska Reka, Veliki Lug, Lepenica, Timok, Begej, and Sitnica.

In 1981, 46% of the population in Central Serbia was not connected to the sewage system. Of the 54% that were connected, only 1.5% had primary wastewater treatment and only 1% secondary biological treatment. Some progress was made by 1991, and today approximately 8% of the population receives wastewater treatment of some kind. On the average, 65 to 70% of the population is connected to a sewer system, but many communities, especially in Vojvodina, still remain without this service.

The pollution from the nonpoint sources has not yet been evaluated.

Figure 7 shows the Danube river system in Yugoslavia and the routine water quality monitoring stations. The State Hydrometeorological Service monitors the

water quality at most stations once a month and the data set from 1981 to 1990 has been used in the analyses presented in this chapter. Some of the minor tributaries are monitored with a lower frequency and for shorter periods of time.

Along the international sector of the river Danube samples are taken only on the stations on Yugoslav side (close to the shore) and this shows in the results due to the localized effects of the point sources located on Yugoslav shores.

Analyses of the results collected over a 10-year period at these stations show the following:

1. The river Danube doubles its flow in Yugoslavia and some of its tributaries have a better water quality than the Danube itself. This "dilution" effect reduces the concentration of the major substances in the Danube river and is just as important as the effect of the Iron Gate reservoir.
2. The mass outflow from Serbia for all the parameters is greater than the mass inflow. From these analyses, it is obvious that the water quality control measures in Serbia will not be governed by the overall quality of the river Danube, but much more so by local critical points on the river Danube (zone of mixing and low flow conditions) and the overall quality of the tributaries, some of which are drastically polluted along parts of their watercourse.
3. The assimilative capacity of the Danube is enormous, and for classical water quality parameters, the pollution entering the Danube on Serbian territory is not of major concern. The same cannot be said for conservative and toxic and hazardous substances, and this aspect needs to be analyzed in detail once good data are collected.

19 Problems of Heavy Metal Pollution in Hungary

- "State-of-the-Art" -

E. Molnár, T. Németh And O. Pálmai*

Research Institute for Soil Science and Agricultural Chemistry of the Hungarian Academy of Sciences, Budapest and

* Experimental Station of the Soil Conservation Service
of the Ministry of Agriculture, Velence

1 Introduction

During the last 40 years the social and economic structure of Hungary has changed radically: rapid industrialization and urbanization, as well as the intensification of agricultural production were characteristic of this era. Both the sector and spatial structure of the society were transformed. Most of these rapid changes occurred without taking their environmental consequences into account. As a result, environmental pollution has become an increasingly stressing problem. The country's hazardous waste load has increased in proportion with the expansion of heavy industry. Due to economic development and urbanization Hungary's natural environment can be characterized by heavy industrialization, the growth of urban centers, the large-scale mechanization of agricultural production and the expansion of the transport and energy sectors. After the Second World War, Hungary expanded its industrial base at a rapid rate. The policy forcing industrialization (between 1950 and 1960) did not consider environmental aspects. During this period, industrial output grew 10% annually. The territorial distribution of industry was also altered. In pre-war Hungary nearly 60% of the industrial labor force was concentrated in the capital. By the end of the 1960s this rate decreased to 44%, dropping to 22% by 1986. This was due mainly to a centralized restructuring of the country's industrial and manufacturing sectors. Modern Hungary is divided into industrial regions, which were created during the restructuring of the economy from 1950 to 1970. These regional complexes have significant impacts on the quality of the environment. Hungary's most polluted regions are also the most industrialized. Polluted areas cover only one-tenth of the country, but affect 40% of the total population, because of the high population density around industrial complexes and major urban areas.

Table 1. The minimum, maximum, and average concentration values (in ppm) of some macroelements and heavy metals of 0–30 cm soil layer in different extractants

	Al-EDTA				LAK.ERV.		
	min	90%	max	aver	90%	max	aver
Ca	0.1	33.400	54.800	12.608	35.000	232.000	14.109
Mg	0.01	1.950	11.600	879	1.220	6.660	595
P	1	800	8.100	487	370	7.360	245
K	0.11	590	2.970	324	510	2.460	271
Na	1	100	3.755	61	84	4.970	50
S	1	92	1.436	46	35	768	17.9
Fe	0.5	870	5.130	465	370	3.555	209
Al	1.0	520	1.070	322	143	552	78
Mn	0.1	620	1.000	371	460	1.000	252
Zn	0.01	6.0	253	4.0	4.7	161	2.82
Cu	0.02	15.8	151	8.7	9.1	146	5.1
B	0.1	3.5	17.9	1.55	2.4	12.3	1.0
Mo	0.03	0.46	1.36	0.19	0.16	0.05	0.06
Cd	0.07	0.24	34	0.16	0.15	26.5	0.12
Co	0.04	6.4	10.8	3.7	4.1	6.4	2.1
Cr	0.3	0.38	64.5	0.19	0.06	23.3	0.03
Hg	0.1	3.7	39.7	1.4	0.69	1.34	0.3
Ni	0.02	12.2	104.7	6.4	8.0	33.7	3.0
Pb	0.1	13.1	64.5	8.9	8.4	37.4	5.3
Se	0.3	1.24	9.4	0.4	0.92	2.4	0.38

HNO ₃			CaCl ₂			(NH ₄) ₂ SO ₄		
90%	max	aver	90%	max	aver	90%	max	aver
38.500	84.000	14.056	–	–	–	5.000	7.200	3.200
2.710	4.110	1.274	360	930	199	660	1.860	325
1.220	5.680	742	8.1	178	3.6	50	1.564	24.1
620	2.270	361	185	985	105	440	1.825	256
92	4.275	58	62	3.740	40	69	4.056	43.0
29	815	13	0.5	591	2.3	–	–	–
1.590	4.420	709	0.37	4.2	0.16	1.56	15.5	0.65
2.180	4.050	1.294	0.0	3.85	0.008	6.8	54.0	3.3
308	479	200	25.5	115	7.6	33.0	115	11.0
12.5	302	7.2	0.013	2.0	0.12	0.4	65	0.38
12	190	6.7	0.21	0.6	0.08	0.64	2.6	0.31
5.8	15.3	3.0	0.37	3.9	0.21	0.46	3.5	0.25
0.22	2.3	0.11	0.217	0.39	0.087	0.42	0.98	0.17
0.26	30.8	0.19	0.013	0.219	0.0037	0.02	1.0	0.01
4.6	12.3	2.8	0.11	0.57	0.04	0.13	1.38	0.044
0.05	12.1	0.05	0.0	0.023	0.00008	0.0	4.23	0.004
1.03	2.4	0.40	0.102	0.22	0.036	0.44	1.58	0.17
10.20	61.0	5.5	0.279	1.34	0.093	0.62	3.7	0.20
9.8	66.8	5.8	0.160	0.89	0.047	0.32	2.1	0.10
1.14	13.3	0.34	0.38	1.69	0.13	0.96	3.8	0.28

2 Heavy Metals in the Environment

Most of the elements occurring on Earth can be found in the air as well as in water and in the soil. Their quantity, quality, solubility, mobility, availability for micro-organisms, plants, animals and human beings show an extremely wide spectra. Most of these elements are essential for the living organisms, but - over a certain "threshold concentration" - a great part of the same elements can be harmful, or even "toxic" for the same organisms. The occurrence of the so-called toxic heavy metals is due to various human activities (in irrigation water, organic manure, liquid manure, mineral fertilizers, amendments for soil reclamation, sewage waters, sewage sludges, solid wastes, pollution caused by transport, industry, etc.) as well.

For the evaluation of the status and regime of these elements in soil the determination of the following parameters is necessary:

- a) **"Total Content".**- the permissible total quantity of various (potentially toxic) elements, which greatly depends on the determination procedure. In Hungary the "total content" is defined as 1 M HNO₃-soluble and determined in 3-year cycles at 6000 sampling points (0-30, 30-60, 60-90 cm depths), representing 5 million hectares of arable land (Table 1). Due to the heavy metal content of the applied different amendments, fertilizers, waste materials, etc. chemical amendment may lead to the heavy metal pollution of agricultural land, as it can be seen in Table 2. The quantity and quality of wastes containing heavy metals, and their "critical load" for the country can be characterized according to

Table 2. Heavy metal content of different chemicals used in agriculture ppm/dry matter

Element	Sewage sludge	P-fertilizer	Liming powder	N-fertilizer	Organic manure
Cd	2.0–1500	0.1–140	0.04–0.1	0.05–8.5	0.3–0.8
Co	2.0–260	1.0–12	0.40–3.0	5.40–12	0.3–24
Cr	20.0–40 600	66.0–245	10.0–15.0	3.2–19	6.2–55
Hg	0.1–50	0.01–1.2	0.05	0.3–2.9	0.0–0.2
Mn	60.0–3900	40.0–2000	40.0–1200	–	30.0–550
Mo	1.0–40	0.1–60	0.1–15.0	1.0–7.0	0.05–3.0
Ni	16.0–5300	7.0–38	10.0–20.0	7.0–34	7.70–30
Pb	50.0–3000	7.0–225	20.0–1250	2.0–27	6.6–15
Sn	40.0–700	3.0–19	0.5–4.0	1.4–16	5.8
Zn	700.0–49 000	50.0–1450	10.0–450	1.0–42	15.0–250

Table 3. Quantity of wastes and by-products produced in Hungary (in millions of tons)

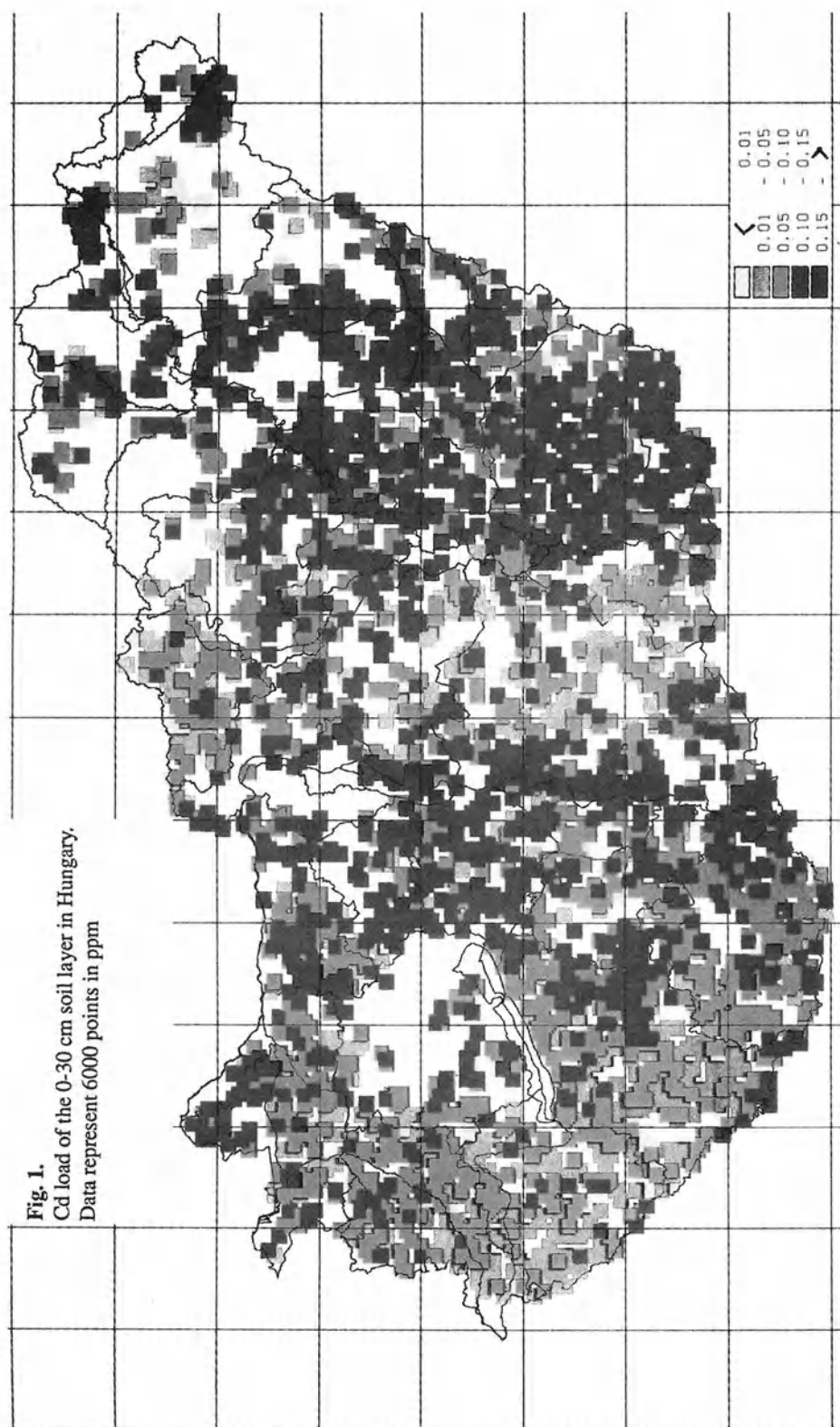
Industrial wastes	
Total	100.8
Harmful	4.9
Reused recycled	52.4
Communal wastes	
Solid	5.0
Reused recycled	0.5
Liquid	16.8
Collected	0.15
Total waste quantity	122.6

Quality of harmful wastes produced in Hungary (in tons)

Hazard Class I:	
586000	
Hazard Class II:	
1128000	
3129000 (red mud)	
Hazard Class III:	
105000	
Total:	4948000

the data in Table 3. As an example, the cadmium load of the upper 0-30 cm of Hungarian soils can be seen in Fig. 1.

- b) "Soluble Content". This value is highly solute-specific. The "soluble content" depends on the characteristics of the given compound (e.g. solubility, electronegativity, polarizability rate of oxidation, ability for complex formation) (Table 1). Non-soluble compounds are:
- immobile: they cannot be transported by the liquid flow - there is no (or limited) possibility of contaminating surface and subsurface water resources;
 - not available for plants, consequently;
 - not toxic for plants, animals and human beings.



The solubility of various heavy metals shows a great variability, depending on the influencing factors. That is the reason for the "Chemical Time Bomb" effect. This means that the concentration of various elements may exceed the permissible (tolerable) concentration in soil and may become "toxic" without any additional load of this element to the matrix.

- c) "Mobile Content". Only the mobile fraction of the various elements (compounds) are reactive and can be transported and translocated to other places (leaching, accumulation, migration), and may reach water resources and plant root surfaces.
- d) "Plant Available Content". In addition to the total, soluble and mobile content of a certain element in the soil, its availability for a certain plant depends on its selective ion uptake, which is a plant- (species, sort, variety, type) dependent characteristic. Non-available elements cannot enter the "food chain", and consequently, cannot be toxic either for animals or for humans, with the exception of the case when the potentially toxic elements are deposited and accumulated on the surface of plants.
- e) "Animal Available Content". The potentially toxic elements taken up by plants, or deposited to plant surfaces may enter the plant-eating (herbivore, vegetarian) organisms and may result in serious health problems or even death. In some cases the element is non-toxic for plant-eaters, but after a quick or slow translocation, it accumulates in their particular organs, and may cause health problems when carnivores eat that organ "poisoned" by carnivore or human-toxic elements.
- f) "Human Available Content". Human-toxic elements may enter the human organisms either directly from plant surfaces or through the food chain.

In this chapter the authors give further information on the heavy metal pollution status of the Hungarian surface- and subsurface waters and soils. Research on the prevention of harmful side-effects caused by heavy metal pollution is also presented.

3 Pollution of Waters by Heavy Metals

It is evident that industry, being the largest water consumer, is also the largest source of water pollution. Despite the fact that untreated industrial effluents discharged into Hungary's surface waters have been reduced significantly over the past two decades - due mainly to the construction of treatment plants and the reuse of waste waters - approx. 84 million m³ of untreated industrial waste water still end up in Hungary's rivers and lakes yearly. Consequently, the discharge of organic pollutants, heavy metals, oil and its derivatives, and dissolved salts has increased accordingly. Naturally, the quality of both surface- and groundwaters in Hungary is determined partly by the quantity and type of pollutants discharged.

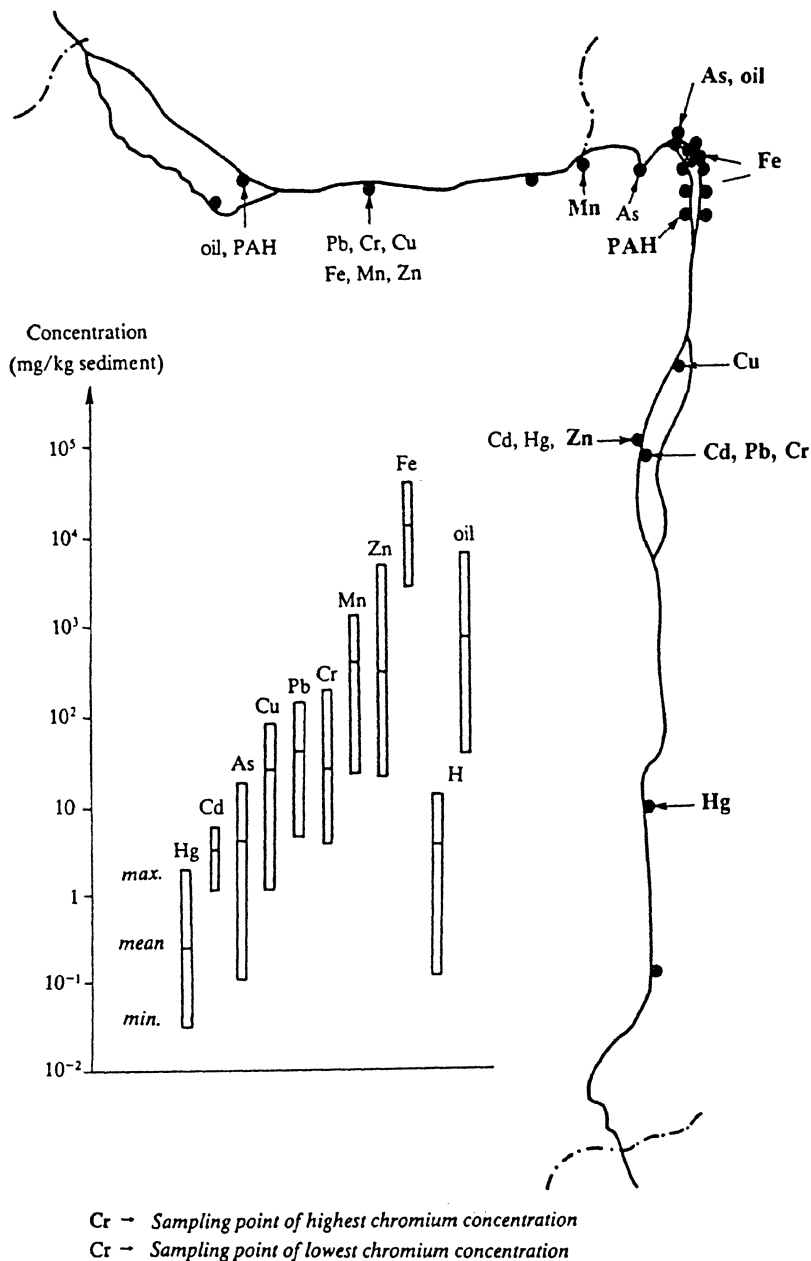


Fig. 2. Bottom sediment pollution of the Hungarian stretch of the Danube River. (László 1985)

Table 4. Heavy metals in the Danube, upstream (R. St. 1659 km) and downstream (R. St. 1631 km) of Budapest, based on the 1982–1983, records. (László 1985)

Components	Location	Minimum	Mean	Maximum
Mercury ($\mu\text{g/l}$)	Budapest upstr.	< 0.1	<u>1.0</u>	<u>4.7</u>
	Budapest downstr.	< 0.1	<u>1.2</u>	<u>18.1</u>
Lead ($\mu\text{g/l}$)	Budapest upstr.	< 0.1	2.4	11.0
	Budapest downstr.	< 1.0	4.2	<u>55.0</u>
Cadmium ($\mu\text{g/l}$)	Budapest upstr.	< 0.1	0.6	<u>29.0</u>
	Budapest downstr.	< 0.1	0.4	4.0
Iron ($\mu\text{g/l}$)	Budapest upstr.	0.23	<u>0.87</u>	<u>3.5</u>
	Budapest downstr.	< 0.05	<u>0.81</u>	<u>10.7</u>
Manganese (mg/l)	Budapest upstr.	0.04	0.07	0.28
	Budapest downstr.	< 0.02	0.08	0.50

Table 5 a. Bottom sediment analyses in the Danube. (László 1985)

Sampling site	Hg mg/kg	Pb mg/kg	Cr mg/kg	Cu mg/kg	Fe mg/kg	Mn mg/kg
R.St.1688 km	0.30	50	30	22	12000	350
R.St. 1675 km	0.39	71	38	39	22000	<u>710</u>
R.St. 1663 km	<u>3.30</u>	33	14	9	9400	320
R.St. 1635 km	0.87	<u>190</u>	<u>90</u>	<u>230</u>	<u>28000</u>	400

Table 5 b. Vertical distribution of heavy metals in the bottom sediments of the Danube, downstream from Budapest (R. St. 1629 km) (László 1985)

Depth below sediment surface (m)	Concentration of heavy metals (mg/kg)				
	Hg	Cd	Pb	Fe	Mn
1.0	0.38	1	95	6400	210
2.0	0.20	0.5	25	7600	250
3.0	0.01	1	10	5400	160
6.0	0.07	0.5	10	6000	130
8.0	0.12	0.5	10	5800	145

The importance of the Danube River as a source of bank-filtered water has prompted a study of pollution levels in the river's bottom sediments (Fig. 2). It is interesting to note that the maximum values registered for iron and zinc, i.e. exceed maximum concentrations set for soils growing food crops.

Minimum, mean and maximum values recorded for some heavy metals have been compiled in Table 4, based on samples taken upstream and downstream from Budapest. Heavy metals, bound to suspended solids, tend to accumulate in the river's bottom sediments (Table 5). The high concentrations of mercury, lead, chromium, copper, manganese, and iron downstream from Budapest are assumed to be pollution loads from wastewaters discharged from the capital. Some of the heavy metals deposited in the bottom sediments are transported further downstream by flood flows, others are remobilized into dissolved form, and still others penetrate deeper into the sediment. Table 6 demonstrates the variations in heavy

Table 6. Mode of calculation

IA is the amount of sewage sludge of effluent (t/ha) calculated from the N demand of the crop.

F is the amount of toxic metals (kg element/ha) in IA.

$$\begin{aligned}
 \text{IA} &= \frac{\begin{array}{c} \text{specific N demand} \\ \text{of the crop (kg N/t)} \end{array} \times \begin{array}{c} \text{planned yield of} \\ \text{the crop (t/ha)} \end{array}}{\begin{array}{c} \text{N content of the sewage sludge or effluent \%} \times 10 \\ \\ \text{X N utilization index} \end{array}} \\
 &\quad \times 10 \\
 \text{F} &= \frac{\text{IA (t/ha)} \times \text{element in the sludge (ppm)}}{1000}, \text{ whereby} \\
 \frac{\text{F calculated}}{\text{F allowed}} &= \frac{\text{number of the years till the next}}{\text{permissible application of the sludge}} \\
 \text{F allowed} &= \text{maximum permissible addition of the element} \\
 &\quad \text{(kg/ha/year, see Table 1)}
 \end{aligned}$$

If the amount of any element in the soils reaches 80% of the maximum permissible amount (first column), any further addition in the form of sewage sludges of irrigation water is allowed only according to more strict regulations

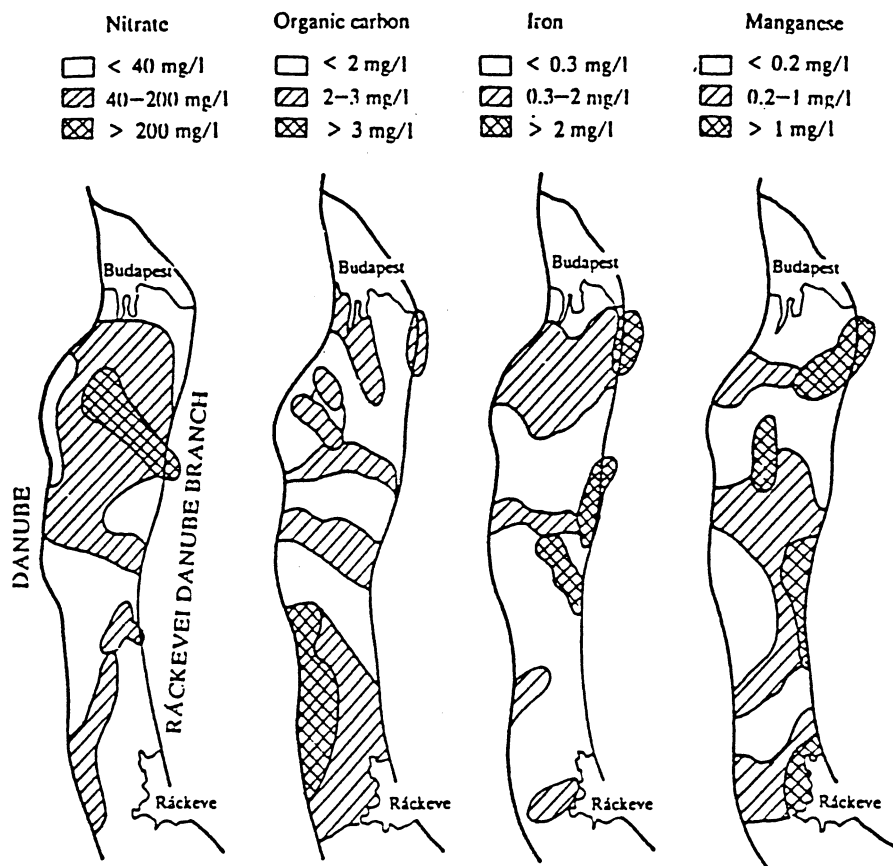


Fig. 3. Groundwater pollution on Csepel Island (László 1985)

metal content - mercury, cadmium, lead, iron, and manganese - along vertical profiles of the bottom sediment downstream from Budapest.

Bank-filtered groundwater is the main source of water supply for the communities situated along the Danube River. The quality of bank-filtered water is dependent upon the quality of Danube water. The level of groundwater pollution is illustrated in Fig. 3 for Csepel Island. From this map, it is evident that:

- the groundwater is highly polluted under a major part of the island for each of the four components considered (nitrate, organic carbon, iron and manganese), and
- nitrate pollution is reaching dangerously high levels. On over half of the island, nitrate levels are 40 mg/l, while 5% of the area has nitrate values reaching 200 mg/l. The standard for nitrate in drinking water is set at 20 mg/l, with tolerable values not exceeding 40 mg/l.

In the last decades a set of monitoring observation wells were established along the Danube riverbed for the control of water quality and prediction of pollution.

4 Pollution of Soils by Heavy Metals

Soil is a chemically and biologically complex porous medium consisting of weathered mineral fragments, organic matter, microorganisms, water, and air. The fate of organic chemicals and inorganic components in soils has been extensively studied. For the purpose of describing the behavior of various components in soils, the physical features of the soil frequently are divided into four compartments: atmospheric, aqueous, solid and biotic. The physical, chemical and biological processes that partition a constituent in the soil among these four compartments are fundamental with respect to land application of wastes. Land treatment is an engineered delivery of wastes to a designated site with prescribed objectives.

The mechanisms responsible for immobilizing and attenuating anthropogenic elements in soils are essentially the same as those in the other segments of the environment. Reaction kinetics determining mass transfer, however, may be different from those in the aqueous or the atmospheric media. Experience indicates that rate constants for the transport process in the soil are influenced by both soil properties and the nature of the chemical component.

A porous medium, like soil, is capable of trapping particles while permitting the solution to pass through. Depending on the particle sizes and the solids suspended, the water may be deposited at the soil water interface or incorporated into the soil matrix upon the water's contact with soil. Even particles with sizes considerably smaller than the soil pores can be effectively retained. These components are immobile unless they are chemically or biologically altered and enter the aqueous phase. Solute movement in soil is governed to a great extent by the movement of water. Reactions with soil, however, retard the movements of solutes. Ideally, water leaving a land treatment zone is free of undesirable constituents. In land treatment, it is essential to match the reaction rates with the hydraulic loading to ensure favorable results.

The main properties determining the mobility of waste components are:

- cation exchange;
- precipitation and adsorption;
- volatilization;
- degradation of compounds;
- bio-absorption.

All of these mechanisms have a very important role in the regulation of transport processes in different pathways, as shown in Fig. 4.

To state that a soil is contaminated with heavy metals, some reference is needed, such as the so-called "background concentration" of heavy metals in a given soil or soil region. Nowadays, it is very difficult to find territories where anthropogenic effects or other pollution sources are excluded. A joint research group of Austria and Hungary proposed the study of the so-called "Iron Curtain" between the two countries. From a pedological-agricultural point of view and compared to the adjacent Austrian and Hungarian border areas, this area was used

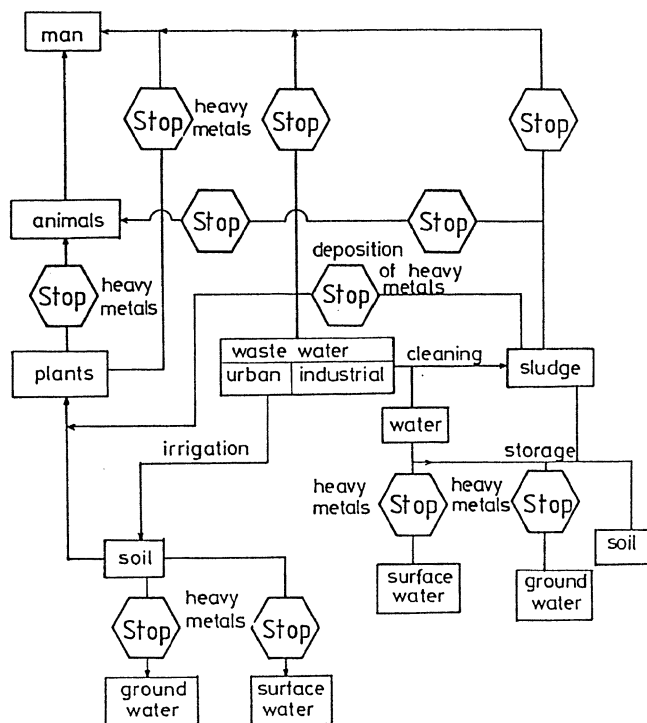


Fig. 4. Relationship between sewage sludge, waste water application, and environment, and the effects to be eliminated

as green or black fallow for about 44 years without relevant anthropogenic influence. This means that the soils of this area were predominantly influenced through natural pedological factors (climate, vegetation, water, relief, parent material, biota) and can be used as references (= undisturbed) for the adjacent sites. The aim of this research program is to determine the "up-to-date" heavy metal levels - among other soil parameters - to serve as a reference basis for the further evaluation of heavy metal concentrations measured in other parts of the two countries. The program was planned to start in January, 1993.

Over the past 10 years, due to the increasing canalization, intensive industrial development, and introduction of new technologies in animal husbandry (liquid manuring) the amount of wastewater and sewage sludge has nearly trebled. Currently, in Hungary the most rational and economic decontamination and deposition of these materials are their use on agricultural fields, utilizing the elements suitable for fertilization without harmful secondary effects on the environment (drinking water, soil, plants, humans, etc.).

In 1984 an integrated research program was initiated by the Ministry of Agriculture and Food, the National Water Authority and the Ministry of Health to study the physical, chemical, agrochemical and microbial soil factors which can be

influenced by waste water and sludge application, focusing on urban wastes, sewage sludges, wastes of the food processing industries and liquid manure.

As a result of the study a 3-step system was compiled to limit the application of waste water and sludge on agricultural fields. The limiting factors are as follows:

- the amount of water (or the water content of the sludge);
- the N content of the waste water or sludge;
- the concentration of any toxic element exceeding the critical values.

The recommendations and the mode of the necessary calculations are given in Table 6.

In Tables 7 and 8 some further information can be found concerning the regulation (now an accepted prescription for all authorities) of the disposal of sewage sludge and waste waters as an irrigation source on agricultural fields.

The limiting conditions for each soil factor related to the application of waste waters and sewage sludge on a given agricultural field have been defined as well (Tables 9 and 10).

A permanent monitoring is necessary to control the load effect caused by waste water and sewage sludge application. The recommended frequency of such monitoring is given in Table 11.

One of the relevant questions to be further examined is the mobility of the most dangerous heavy metals along the soil profile. Research is focused on Zn, Pb, Cr and Cd, which can be present in the soil as well as in sewage sludges and waste waters in relatively high amounts, and are very harmful for human beings (Cd, Cr, Pb). They especially become dangerous for the environment when these elements enter the liquid phase of the soil, because they are more easily available for plants and with the movement of the soil solution they can be leached into the groundwater from the soil.

A possibility to measure and quantify the real hazard of heavy metal mobility is to ensure a near-natural environment under laboratory conditions with the help of physically and chemically controlled undisturbed soil monoliths, and test plants grown and monitored on them. A joint U.S. - Hungarian (USDA Riverside, California and RISSAC) research project started in 1991 with the main objectives:

- a) to characterize the plant-availability of selected toxic elements by quantifying their release into the soil solution of undisturbed soils;
- b) to quantify the transport and distribution of these elements in parts of plants as a function of different element loadings and soil moisture contents/soil water pressure;
- c) to identify stress situations in plants using a quadrupole mass spectrometer (QMS);
- d) to develop, on the basis of these experiments, a theoretical model which predicts the transport and fate of the investigated elements in the undisturbed soil profiles, and the uptake of elements by plant roots.

Table 7. Permissible admission of heavy metals in the form of sewage sludges (if the pH of the soil is under 6.5, only half of these amounts is permitted)

Element	Permissible admission total (kg/ha) ^a yearly (kg/ha) absorption capacity of the soil 25–35 mg Eq/100 g		Addition (ppm years) ^b absorption capacity of soil (mg Eq/100 g soil)		
			5–15	15–25	25–35
As	6	0.3	0.03	0.05	0.10
Cd	0.4	0.02	1.5×10^{-3}	1.5×10^{-3}	1.5×10^{-3}
Cr	200	10	0.83	1.65	3.3
Cu	200	10	0.83	1.65	3.3
Hg	2	0.1	8×10^{-3}	1.5×10^{-2}	1.5×10^{-2}
Mn	400	20	1.66	3.32	6.65
Ni	40	2	0.16	0.33	0.66
Pb	400	20	1.66	3.32	6.65
Zn	400	20	1.66	3.32	6.65

^a For 20 years.^b Basis of calculation: addition of the metals to 20 cm deep layer of 10^3 m^2 soil ($3\text{--}10^6 \text{ kg}$).**Table 8.** Maximum permissible amount of irrigation water using sewage effluents for irrigation (mm/year)

	Absorption capacity of the soil (mg Eq/100 g)		
	5–15	15–25	25–35
As	38	75	150
Cd	100	100	100
Cr	500	1000	+
Cu	125	250	500
Hg	250	500	+
Mn	100	200	400
Ni	50	100	200
Pb	500	1000	+
Zn	100	200	400

Table 9. Limit values of soil parameters interdicting or conditionally permitting watering with or deposition of waste waters

Parameter	Limit values interdicting the use of waste waters	Limit values conditionally permitting the use of waste waters
a	b	c
Relief, slope	Slope > 5% – depending on the way of watering	
Thickness of surface soil	< 35 cm (solid rock, gravel, etc.)	
pH _{H₂O}	< 5.6	5.6–6.4 and 6.4–6.8 resp., complementary maintaining liming
CaCO ₃ content		> 0–5%, complementary liming is needed
Type of soil texture	Coarse sand ($K_A < 25$) heavy soils, marshland, peaty soils, „kotu“	Clay ($K_A = 50–60$)
Soil water management properties, pF-curve	$V_{KSZ} < 15\%$ DV = 5–10% sand peaty soils, surface soil	$V_{KSZ} = 42–50\%$ DV = 10–15% heavy clay, and „kotu“, shallow layer
		$V_{KSZ} = 35–42\%$ DV = 12–17%
Hydraulic conductivity	$K > 1000$ cm/day, $K-10^{-1}$ cm/day and peaty soils, „kotu“, rendzina 9th category of stratification code T-value < 5 mEq/100 g T-value > 45 mEq/100 g	$K = 1-10^{-1}$ cm/day 8th category of stratification code T-value: 35–45 mEq/100 g
Depth of soil water table	Mean depth < 1.5 m	Mean depth 1.5–2 m
Water type according to anions and cations	Na, HCO ₃	Ca–Na, Mg–Na

Table 9 (continued)

Parameter	Limit values interdicting the use of waste waters	Limit values conditionally permitting the use of waste waters
a	b	c
Na % in soil water	> 40%	30–40%
Danger of water lodging	1st and 0th categories of the category system	6th, 7th, 8th, and 9th categories, and a part of the 1st and 5th categories of the category system
Type of water regime	7th, 8th, and 10th categories of the category system	2nd (pseudogley) and a part of the 5th categories of the category system
Particle size distribution	Fraction < 0.02 mm; <15%, and > 80% clay %	Fraction < 0.02 mm: 70–80%
Infiltration rate	> 500 mm/h, and < 50 mm/h, resp. 50–70 mm/h	
Toxic heavy metals	If the concentration of any toxic element is more than given in Table 1	
Mean salt content of soil water	> 1 g/l /1000 ppm	

On the basis of the 3-year experiment the redistribution of the test elements in the soil matrix will be followed and relationships between the toxic heavy metal content of soil solution fractions available for plant uptake, the metal content of the main plant parts, and selected markers of plant stress will be established.

Modern Hungary was divided into industrial regions, created during the restructuring of the economy. One of the "hot spots" (extremely overloaded areas) in the Danube catchment area is the Sajó Valley, north-eastern Hungary, an industrialized region. A case study was carried out to characterize the pollution status of soils, the natural vegetation, cultivated crops as well as groundwater in the region. The description of the degree of contamination, the mapping of the hot spot will

Table 10. Limit values of soil parameters interdicting or conditionally permitting the deposition of sewage sludges

Parameter	Limit values interdicting the use of sewage sludge	Limit values conditionally permitting the use of sewage sludge
a	b	c
Relief, slope	Liquid sewage sludge, slope > 6% dry sewage sludge, slope > 12%	
Thickness of surface soil	< 15 cm (solid rock, gravel, etc)	
pH _{H₂O}	< 5.6	5.6–6.8 + complementary (maintaining)/liming needed
CaCO ₃		0–5% + complementary liming needed
Type of soil texture	Heavy clay, K _A > 60, skeletal soils	Clay K _A = 50–60, complementary soil melioration
Particle size distribution	Fraction < 0.02 mm: > 80%	Fraction > 0.02 mm = 70–80%
Soil water management properties, PF curve	V _{KSZ} = 42–50%; DV = 10–15% shallow surface soil layer	V _{KSZ} = 35–42%; DV = 12–17%
Hydraulic conductivity, K	K < 10 cm/day	K = 1–10 cm/day + soil melioration
Stratification	9th category of stratification code	5th and 8th categories of stratification code
Absorption conditions	T-value > 45 mEq/100g	T-value = 35–45 mEq/100g
Danger of water lodging	1st and 0 codes of the category system	6th, 7th, 8th, and 9th codes of the category system
Toxic heavy metal	If the concentration of any toxic element reaches the given limits (see heavy content of sludges)	

Table 11. Frequency of monitoring of soil parameters by sludge deposition

	For design and control	First year of deposition	Monitoring (permanent)
Ground-water	Four times a year (each season) before deposition	Once a season	Once a season (for a few parameters)
Drainage water (if any)	–	Once in the vegetation period	Once in the vegetation period
		Three times in the vegetation period	Three times in the vegetation period
Soil	– physical – water management – chemical – nutrient status – redox status	Control of – salt balance – pH – organic matter – macro- and micro nutrients – water balance Two times a year	Every 3 years Control – water- and salt balance – organic matter – macro- and micro nutrients

serve as an example, which we hope to continue in the program "Long-Term Environmental Risks for Soils, Groundwater and Sediments in the Danube Catchment Area".

From the results obtained the following conclusions can be drawn:

- Both groundwater and river water are polluted mainly by the by-products (stored wet ash, washing water of the plant, chemical deposits originating from different part procedures) of the power plant.
- The main problem is the high Na-content and electrical conductivity (total salt content) of the different solutions leaving the factories (pH = 9; EC = 800-2700 μ S).
- It also can be stated that a considerable increase in Pb, As, Cr and Hg concentration was registered jointly with a certain decrease of Mn, Cu, Ni and Zn during the hydrological cycle in surface- as well as in subsurface waters.
- It is interesting to note that i.e. Hg-concentration decreases in the flow direction of groundwater [data of the observation wells: 4.0 μ g/l (150 m), 2.0 μ g/l (800 m) - 0.5 μ g/l (1350 m)] which indicates a very complicated flow phenomenon.

- From the complex study (air pollution, hazardous waste evaluation, water pollution, etc.) it is obvious that the main sources of toxic elements' load are the different by-products of the electric power plants. The wet ash and dust contains As, Al, Ni, Cu in nearly full concentration in comparison to the permissible amount. On the contrary, Hg and Cd, as well as Ni and Cr most probably originate from the metallurgy in the region.
- With the increase of acidic character of the media, As and Al concentration may become the most important problem in the future. Zn concentration is also over the limit value in certain cases.
- A considerable proportion of the native vegetation has degraded or disappeared as a consequence of environmental pollution and improper agricultural land use.
- Although the matrix (soil and groundwater) is rather polluted with different heavy metals, the plant uptake is non-significant. This might be due to the fact that plants are selecting according to their needs during the nutrient uptake, taking the nutrient level ratios into consideration.

5 What Is to Be Done?

Research results show that in many cases non-rural wastes are contaminated with some toxic elements, first of all with heavy metals, which can spoil the mentioned beneficial effects and may exclude or limit their utilization.

According to the concept, an optimum regulation should be extended to two main areas of protection:

1. Strict source control on the site of heavy metal emission.
2. Regulation of the use of sewage sludge: acceptable quality specifications for their utilization on agricultural land.

Both areas of regulation can be divided into two lines. In the case of source control, full attention must be paid to the following steps of primary source control:

- source survey to determine the real and exact source of heavy metals. (This is important not only from the viewpoint of sewage sludge land application, but also for environment protection in general.)
- source selection,
- retention and/or separation of heavy metals at the place of their origin,
- when and where it is possible, to change technologies and apply so-called wasteless or minimum waste technologies.

Secondary source control should be established:

- to avoid too high quantities of heavy metals from getting into communal sewages and sewage sludges, and
- to avoid their spreading in the environment.

These aims can be achieved by specifying and controlling:

- permissible concentrations of heavy metals in industrial effluents before they reach the sewage system, and
- permissible concentration of heavy metals in sewage sludges (originating from sewage treatment plants) from the land application point of view.

Further regulation should be introduced in two main directions as well:

- to avoid harmful accumulation of heavy metals in the soils, surface- and sub-surface waters and
- to avoid harmful contamination of heavy metals in food and fodder plants and generally in the food chain.

For a better and more specified regulation further investigations are necessary, and the results and experiences gained so far in other countries should also be taken into consideration. In Hungary the following research work should be carried out or continued:

- investigations on long-term effects of sewage sludge land application on different former experimental sites;
- laboratory and special model investigations on the effects of heavy metals on soils;
- research on combined and synergetic effects of heavy metals (e.g. As-Pb, Cd-Pb) on soils and plants,
- determination of limit values for heavy metals in food and fodder,
- standardization of sampling, sample preparation, and analytical methods for heavy metals from the points of view of land application, soil contamination and soil/water pollution control.

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20 Heavy Metal Pollution in Kosovo

Luan Shllaku and Lars Landner

Dardania, SV 3/1 Lam c1/4, 380 00 Pristina, Yugoslavia

1 Introduction

In Kosovo large-scale exploitation of mineral resources has a long history, and has strongly expanded in this century. It has furthermore triggered a rapid expansion of the various downstream industrial activities, such as energy generation, ore smelting, metal refining, chemical industry and manufacturing of finished products.

Most of this mining and industrial development took place without installation of adequate environmental protection equipment and without proper siting of the industrial plants, which has resulted in serious environmental degradation and impacts on the health status in local populations.

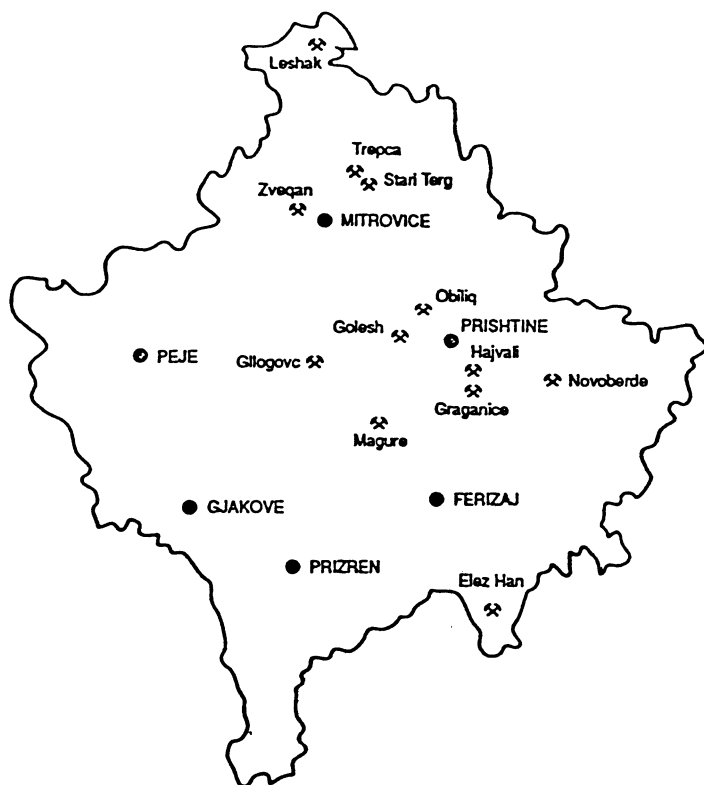


Fig. 1 Map of Kosovo, showing the major cities and sites where large scale mineral exploitation is carried out

The economic development of Kosovo has resulted in a very strong concentration of the population of the already densely populated province to the main axis between the two cities of Ferizaj, in the south, and Mitrovice, in the north, following the valley of Sitnice and with the capital, Pristine, in the middle (Fig. 1).

2 Main Sources of Pollution

The town Mitrovica and the surrounding region has been exposed for a very long time to heavy air pollution, the river Sitnice and Iber to considerable water pollution and the degradation of landscapes and ecosystems has taken important dimensions.

Only 30 kilometres south of Mitrovice is located another industrial complex with large-scale exploitation of lignite and the big lignite fuelled thermopower plants, coal gasification plant and fertiliser production.

Other smaller scale exploitation activities in Kosovo are in progress in Glogovc (ferro-nickel production) and in Elez Han (cement plant).

In the Mitrovice region, in addition to the large lead and zinc mines Stari Trg and Prvi Tunel, with the flotation plants, the following main industrial units are located in the northern outskirts of the town Zveqan and inside the southern part of the urbanised area, on the left bank of Sitnice-Iber river system:

Location	Production unit	Products	Tonnes/year
Zveqan	Lead smelter ^a	Raw lead	100,000
	Lead refinery	Refined lead	80,000
	Steam power plant	Steam, electr.	
South Mitrovic	Zinc electrol.plant	Eletrolyt.zinc	50,000
	Sulphuric acid pl.	Sulphuric acid	80,000
	Fertiliser plant	NPK, superphos.	50,000
	Battery plant	Lead accumulat.	30,000

^a The lead smelter is equipped with the 300 m stack.

All industrial activities in the Obiliq area are based on the exploitation of the lignite giving rise to the huge amounts of solid mining wastes, in addition to the large ash deponies from the thermo power plants. All installations are located on the right bank of river Sitnice, about 5 kilometres from the Kosova capital Pristine.

The annual production of ferro-nickel in Glogovc, in the middle of the 1980s was about 15,000 tones. Cement production in Elez Han was about 240,000 tonnes/year.

Production unit	Products	Actual production
Open cast mines	Lignite	10,000,000 t/y
Thermo power, Kosovo A (4 units)	Electricity	790 MWe
Kosovo B (2 units)	Electricity	678 MWe
Lignite drying plant	Dry lignite	1,200,000 t/y
Gasification plant	Burning gas	120,000,000 m ³ N/y
Nitrogen fertiliser plant	Calcium ammonium nitrate	100,000 t/y
Steam power plant	Steam	1,200,000 t/y

3 Emissions to the Atmosphere

In Table 1 are given the results of emissions to the atmosphere from the various activities in Kosova. These results are reached by using the methodology CORINAIR, which has been developed for the overall CORINE program, run by the Commission of European Communities. In this inventory two different categories of sources are specified: the diffuse, mobile and stationary sources of less importance constitute the "Area Sources" while the most important stationary sources constitute "Point Sources". Five different types of pollutants are included, SO₂, NO_x, VOC, dust and air-borne lead [2].

The major point sources are the following: The smelting and refining of lead in Mitrovica (Trepca), the sulphuric acid plant, the electrical power plants and the nitric acid plant.

Table 1. Emissions to the atmosphere from various activities in Kosova, in 1988, expressed in tonnes per year. AS = Area Sources; PS=Point Source

Groups of activities	SO ₂		NO _x		VOC		Dust		Pb	
	AS	PS	AS	PS	AS	PS	AS	PS	AS	PS
Energy generation	638	47306	187	16464	667	2164	78620			
Combustion in industry	11644		1897		475					
Industrial production	301	43310	735	468	481		48	672		1228
Solvent evaporation					821					
Road transport	1066		5036		3285		29			
Nature					10747					
Total	13.649	90.616	7.855	16.932	16.476	2.164	48	79.292	29	1.228
Grand total	104.265		24.787		18.640		79.340		1.257	

Below are given more details on lead emission from the smelting and refining plants in Mitrovica. The quantity of 1,230 tonnes of lead emitted in the year 1988 is almost the total of lead emission in Kosovo. Only 15 tonnes are emitted from the road traffic. This figure includes the fugitive and diffuse emission estimates as well. By using US emission factors A.P.42 for the primary lead smelting processes without control we come to the figure of 792 tonnes of lead emitted per year.

Even if this value is in order of magnitude and if some activities are more or less included in the point source of emission of lead, it is interesting to compare the total diffuse and fugitive emissions to the total point source emissions.

The other part (438 t) is emitted from the stack, which is 300 meters high.

Consequently it can be observed that the diffuse and fugitive emissions at relatively low level are more important or, at least, as important as the point source emissions.

If we compare the emission of lead from the Trepca plant with the emissions coming from the smelting and refining plants in Germany for instance, the emission factor taken from several plants in Germany was 0.65 kg/t Pb produced. Accounting for the nominal production in Trepca, which is 100,000 t/y this factor is 12.3 kg/t Pb which is 18 times higher than the German factor.

In addition to lead emission from the Trepca plant, the quantity of 60 tonnes/year of zinc from the main stack is emitted as well as 2 t/y of cadmium and 6 t/y of mercury (this figure is the theoretical maximum).

4 Emissions to Water

There is a general shortage of water in Kosovo, which has been severely aggravated during the last decades. First, the geographic situation of Kosovo, in the headwaters of three major river systems, Sitnica-Iber-Morava-Danube, Bistrica-Drini i Bardhe and Lepenc-Vardar means that the natural water supply is limited. The rapid increase of open-cast mining has resulted in lowering of the ground water table and the increased water consumption by industries and urban centres has created a critical situation in most parts of Kosovo.

This general water shortage tends to become an obstacle to both social and industrial development.

Since it has not been possible to obtain reliable data on the amounts of pollutants being discharged by industrial effluents or municipal sewage into the rivers in Kosovo, we had to rely upon rough estimates, based on a few random samples of effluent and river waters.

Such rough estimates have given the following orders of magnitude regarding the water pollutants discharged from Trepca industries in Mitrovica during the period 1985-88:

Lead	150 tonnes/year
Zinc	300-900 tonnes/year
Fluorides	900 tonnes/year

In a general sense, it can be concluded that the units causing most water pollution problems are the two open-cast mines as well as the gasification plant. In second place comes the lignite drying plant.

5 Solid Waste Deposits - Emissions to Soils

The problem of industrial solid waste in Kosovo is very great. The total area covered by industrial waste dumps and transformed due to open cast mining extends over 10.000 hectares (see below):

Mines and tailings dams at Trepca (Mitrovice area)	2,700 ha
Waste deposit, battery factory	215 ha
Waste deposit, superphosphate factory	320 ha
Mines and tailing dams, Kishnice and Ajvali	1,200 ha
Mines and waste deposit, ferro-nickel, Glogovc	1,700 ha
Open-cast mines and deposits, EE Kosovo, Obiliq	4,000 ha
Total:	10,135 ha

So far no rehabilitation or revegetation of the waste dumps has been carried out. Therefore there is no real protection against wind transport of waste material to surrounding land, which strongly interferes with e.g. agricultural activities.

It has been estimated that up to 1,000 hectares of productive land are lost annually.

The deposits of sulfidic ore tailings in the Mitrovice region are located in the very vicinity of the populated areas in the city, both on the northern and southern edge, which results in considerable dusting and heavy metal pollution in the city area.

6 Environmental Quality

6.1 Air Quality Results

In the past measurements of heavy metals in the atmosphere of Mitrovice were made by means of STAPLEX system [1], operated for 10 minutes, on each sampling occasion. Some of the readings were extremely high, e.g. 25 ug/m³ for lead,

2.5 $\mu\text{g}/\text{m}^3$ for zinc and 0.015 $\mu\text{g}/\text{m}^3$ for cadmium. However, these results cannot be considered as representative of the actual concentration of heavy metals in the air. Nevertheless, the great amount of STAPLEX data from the period 1986-1988 may indicate the general level of air pollution:

	Pb ($\mu\text{g}/\text{m}^3$)	Zn ($\mu\text{g}/\text{m}^3$)
1986: average Oct-Dec	7.3	6.6
1987: average Oct-Dec	1.8	0.47
1988: average Jan-Mar	1.0	0.39
1988: average Apr-Jun	2.3	1.7

More representative data on heavy metals in air were collected in 1989 at one sampling site, using a PPA-60 device. The lead concentration data are shown in Fig. 2 in a log-log form.

- According to Fig. 2, two distributions may be distinguished. The first one with the median value of 2 $\mu\text{g}/\text{m}^3$ of lead, and the second one with a median value of about 15 $\mu\text{g}/\text{m}^3$. If these two models of distribution could be confirmed, a logical interpretation could be the following:
- the first distribution reflects the "normal" lead pollution of the town, due to traffic and resuspended lead-bearing particles. In this case, the town should be up-wind of the Zveqan lead smelter.
- the second distribution (high values) could represent the lead concentrations in the urban air when the wind is blowing from the Zveqan lead smelter.

The atmospheric lead concentrations in central Mitrovica exceeded the maximum allowable concentration (MAC) value on a daily basis (0.7 $\mu\text{g}/\text{m}^3$) during 62-87% of the time, depending on the month of the year. In January 1989, the MAC value was exceeded by a factor of 37, on an average. On one particular day, the MAC value was exceeded by a factor of 132.

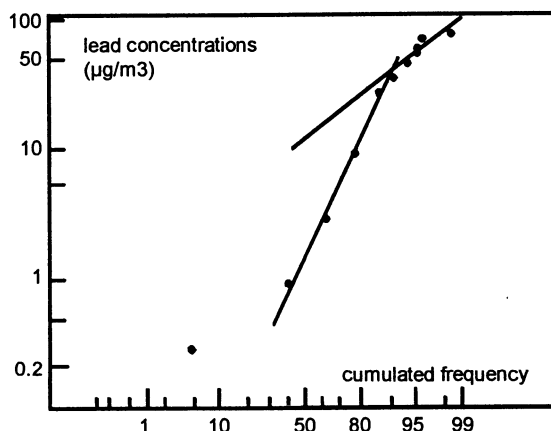


Fig. 2. Cumulative distribution of atmospheric lead concentration at the sampling site "Fakultet" in the centre of Mitrovica

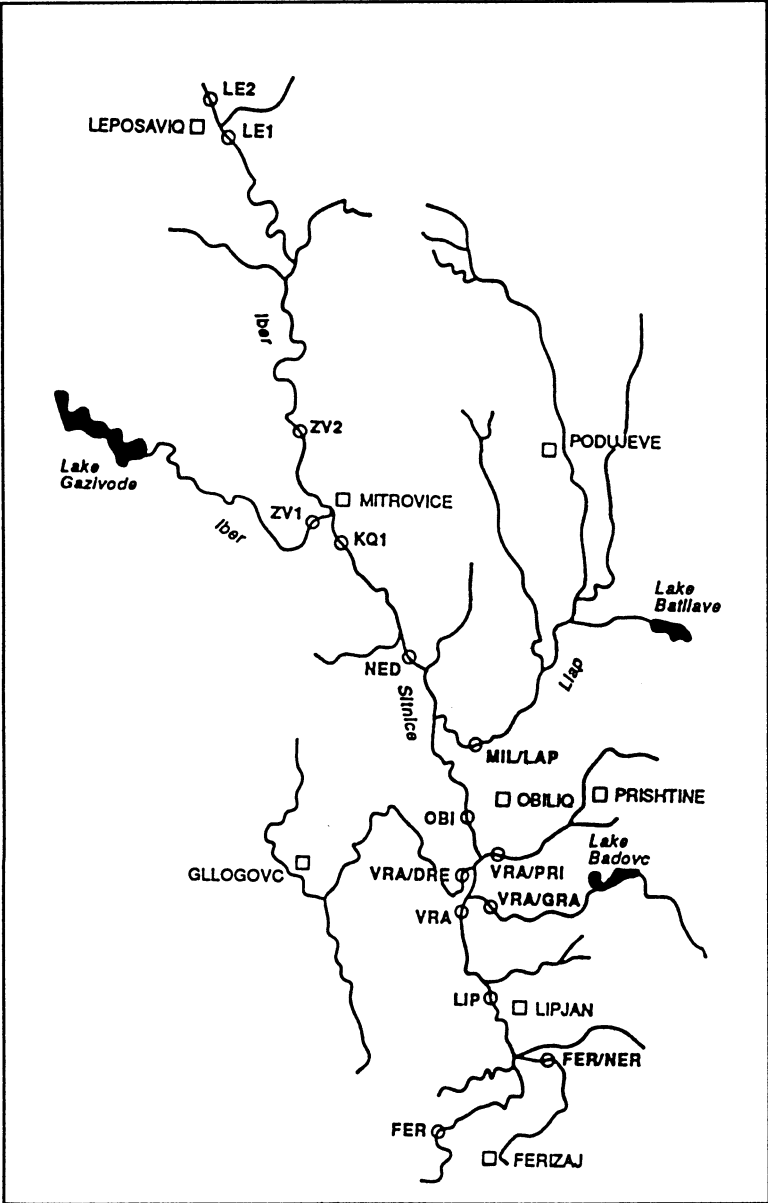


Fig. 3. Sampling sites (in bold letters) in the rivers of Kosovo. Towns are indicated in capitals and names of rivers and lakes in italics

However, the MAC value of 0.7 ug/m^3 , which was the local MAC value at the time, is somewhat lower than the standard recommended by WHO for industrial areas and MAC value used in several European countries for industrial areas, which is 2 ug/m^3 .

6.2 Water Quality Results

The most comprehensive sampling campaigns in the rivers for monitoring of physical/chemical water quality were carried out during the period May 1987 to April 1988. This sampling covered the Sitnice-Iber river system from Ferizaj to Leposaviq including the main tributaries (Fig. 3). The simultaneous measurement of water flow at the sampling points allowed calculation of the transport of various pollutants in kg/h [4].

Pollution of the river water with heavy metals, such as lead and zinc, was most pronounced in the Mitrovice area. Especially the transport of lead showed a considerable increase between the sampling points Kcic and Zvecan, except for the period March-April 1988 (Fig. 4). The amount of lead being transported in river Iber in January-February 1988 was about 1.4 t/day.

In addition to the Mitrovice area, the Obiliq section of the river Sitnice was also exposed to considerable pollution with zinc. A large fraction of the zinc transported through the Obiliq section of the river Sitnice originated from the two

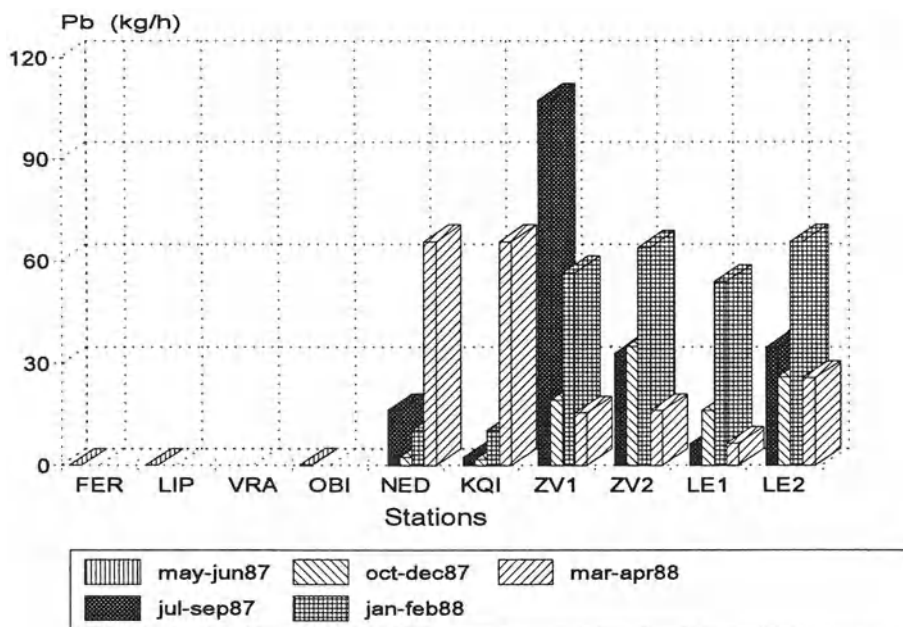


Fig. 4. Transport of lead (kg/h) in the Sitnice-Iber from Ferizaj to Leposaviq. Measuring period May 1987-April 1988

tributaries Graçanike and Prishtevke. The total transport of zinc in the river Iber varied between 1 and 25 t/day, depending on the hydrological regime.

The hot spot of pollution with iron and manganese seems to be the Obiliq area, rather than the Mitrovica area. The transport of iron and manganese through the section Obiliq-Nedakovic was in the range 2-5 t/day during some periods.

6.3 Soil Contamination

Soil contamination with heavy metals is quite widespread in Kosovo.

Samples of arable soil have been taken from several different regions of Kosovo, and the concentrations of heavy metals found are summarised below:

	Total (mg/kg D.M. ^a)	Soluble (mg/kg D.M.*)
Lead	44 - 340	4 - 6
Zinc	100 - 800	5 - 100
Cadmium	0.7 - 2.2	
Copper	36 - 85	2 - 14

^a D.M. = Dry matter

The above levels, representing "natural" soils, used for the cultivation of various crops, are very much exceeded in soils in the surroundings of Mitrovica.

In the vicinity of the Trepça industrial complex in Mitrovica, the soil concentration of soluble lead was found to be 57-720 mg/kg, which may be compared to the level, normally considered acceptable for most crops, which is 20 mg/kg of soluble lead.

The levels of soil contamination in the same region were 100-3,500 mg/kg as soluble zinc. Limit values for soluble zinc are in the range of 250-400 mg/kg.

The metal contents of the different categories of industrial solid waste are, of course, very variable, from extremely high values in mine tailings (up to 68,000 mg/kg of lead), the high concentrations in solid waste from the zinc refinery: Pb-76,000 mg/kg, Cd-9 mg/kg and Cu-600 mg/kg, to the relatively low metal contents in fly ash from the power plants in Obiliq: Pb-36 mg/kg, Zn-56 mg/kg, Cu-45 mg/kg and Ni-190 mg/kg.

6.4 Contamination of Agricultural Crops

Sampling of agricultural crops and vegetables was carried out in the Mitrovica region, in order to make an assessment of the degree of contamination, and consequently, the possible human exposure through food.

The concentrations of lead and cadmium in spinach in 1989 are presented in Fig. 5. The values, given in mg/kg dry material, show a very high increase over the background values for uncontaminated spinach, which should be in the following ranges: Pb--1-5 mg/kg, Zn--30-50 mg/kg, Cd--0.2-0.5 mg/kg, and Cu--2-5 mg/kg.

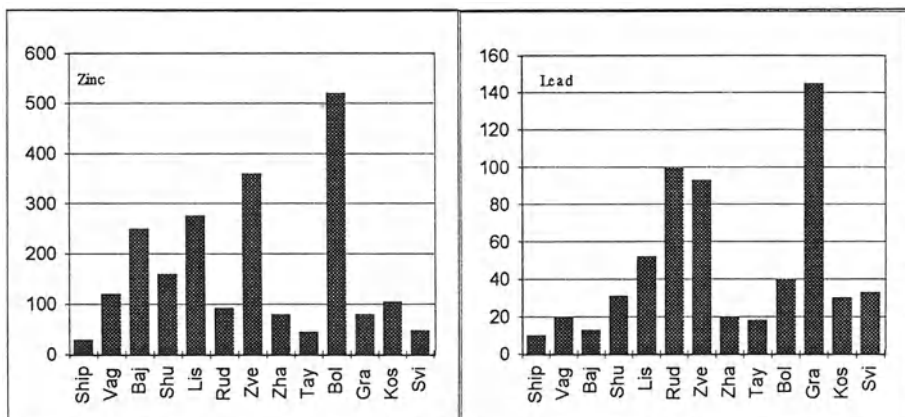


Fig. 5. Lead and zinc contamination of spinach (ug/g dry matter) from various sampling sites in the Mitrovice area. Sampling made in 1989

If using the higher background values, it can be noted that, in the Mitrovice region, the concentrations of heavy metal in spinach are increased in the most contaminated areas by the following factors: for Pb—20-30 times, for Zn—up to 10 times, for Cd—up to 20 times, and for Cu—up to 5 times.

The concentrations of lead in potatoes from the Mitrovice region are increased by up to 30 times in the most contaminated sites, and cadmium is increased by about 6 times. Also the contamination of wheat with lead is quite conspicuous, showing a steep gradient from 1 mg/kg to 21 mg/kg at the most contaminated site.

It may be interesting to use the data on heavy metal concentrations in locally produced food in calculations of the approximate intake of these metals by the local population. These intakes can then be compared with the recommendations on the maximum tolerable intake of metals, issued by WHO/FAO expert committees.

Starting with lead, the maximum weekly intake of this metal has been set at 3 mg for adults (WHO/FAO) or 0.7 mg (EEC). If it is assumed that the local population in Mitrovice eat 0.2 kg of vegetables like spinach, 1.5 kg of potatoes and about 1 kg of wheat (fresh weight) every week, the following intakes of lead can be estimated at the most polluted sites: from vegetables—about 2 mg, from potatoes—about 5 mg, and from wheat—about 4 mg, which makes a total intake of lead of about 10 mg/week.

(It should be noted that the lead concentrations above were given on a dry weight basis and therefore, they have been transformed to a fresh weight basis before calculating the intakes).

It may be concluded that persons eating locally produced food from the most contaminated areas of the Mitrovice region will have a lead intake through this food, which is more than 3 times higher than the recommended maximum weekly intake (based on the WHO/FAO recommendation) and about 15 times higher than the maximum intake recommended in the EEC countries.

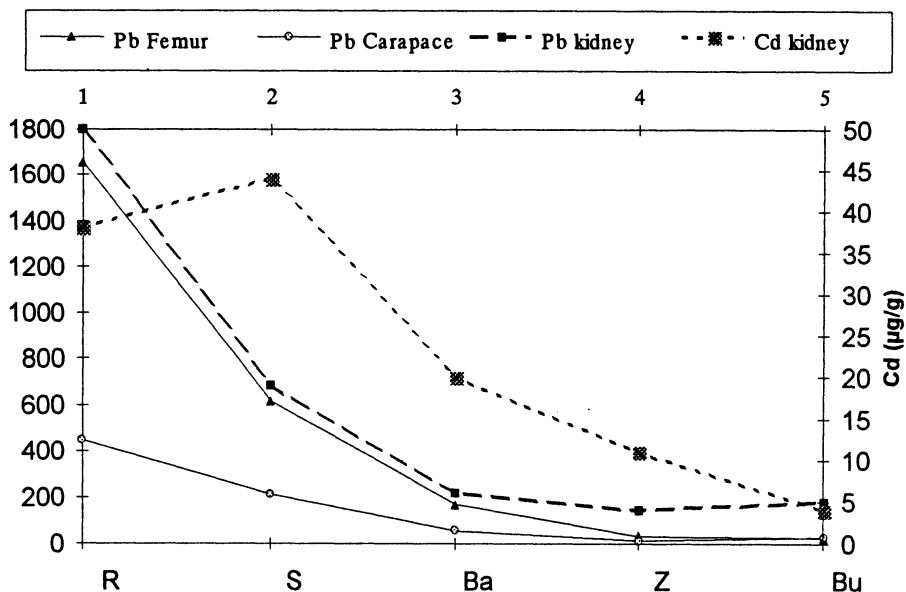


Fig. 6. Lead and cadmium contamination of tortoises. The curves show the lead content of femur and carapace (left hand scale) and the lead and cadmium content of the kidneys (right hand scale)

6.5 Contamination of Land Animals

The most comprehensive study, carried out with the aim of estimating the body burdens of heavy metals in natural populations of terrestrial animals in the Mitrovica region, used tortoises (*Testudo hermanni* Gmel.) as test animals. Five specimens were caught at each of five localities at increasing distance (0.5, 3, 11, 15, and 50 km) from the lead smelter at the metallurgical complex of Trepca. Analyses of lead, zinc, cadmium and copper were made in three different tissues, carapace, femur and kidney.

Figure 6 shows the results regarding lead content in all three tissues and the cadmium content in kidney. Variations of cadmium in carapace and femur and of zinc and copper in all tissues were relatively small, and did not indicate any great impact of the source of emission on the body burden of the tortoises [6].

In a separate, but similar sampling campaign, where the metal content of the carapace of the tortoises was determined, it turned out that the lead concentrations were increased between 10 and 40 times (compared to control animals) in the pollution gradient. Again, the increase of zinc, cadmium and copper were only small.

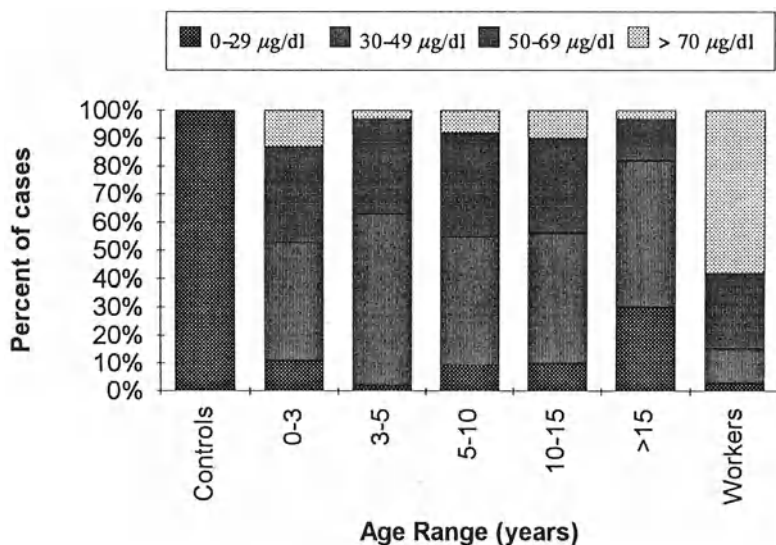


Fig. 7. Incidence of elevated blood lead concentrations in human population from the city of Mitrovica. Controls represent children from Pristina

6.6 Lead Concentrations in Human Blood

Concentrations of lead in blood samples from people living in Mitrovica have been monitored for many years [7]. In a study made in 1978-79, very much increased blood lead values were found in all age groups of the population. The highest values, excluding the workers employed in the lead smelter, were found in children in the age group of 1-3 years, see Fig. 7.

In subjects examined during 1980, blood lead concentrations of 50-69 $\mu\text{g/dl}$ were found in 35% of the children, and in 12%, the lead level was 70 $\mu\text{g/dl}$ or more. In the centre of Mitrovica, average concentrations of aerosol lead between 5 and 50 $\mu\text{g/m}^3$ have been reported for the period 1974-1986, with the maximum value (50 $\mu\text{g/m}^3$) recorded for 1979/80.

About 60,000 inhabitants living in the town area are exposed to these very high lead concentrations in the air. Out of this number, 21,000 are under 15 years of age. On the basis of blood lead findings, the estimate was made that in about 9,000 children in Mitrovica, the blood lead concentrations may be above 40 $\mu\text{g/dl}$, and in many of them even above 70 $\mu\text{g/dl}$.

It may be pertinent to compare the blood lead levels of inhabitants in Mitrovica with those in some other parts of the world. As seen in Fig. 7, about 70% of the population older than 15 years have blood lead concentrations higher than 30 $\mu\text{g/dl}$, and among children, this fraction is even higher. In several cities in central Europe, the average blood lead concentration at the beginning of the 1980s, was 14 $\mu\text{g/dl}$, in Stockholm (1985) it was 5-6 $\mu\text{g/dl}$, and in a Swedish town with a large steel plant, it was about 3 $\mu\text{g/dl}$.

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NOTE: These Sector Reports could be made available, upon request, from WHO, Regional Office for Europe, Copenhagen.

21 Heavy Metal Pollution in Romania

Corneliu Rauta, Radu Lacatusu and S. Carstea

Research Institute of Soil Science and Agrochemistry, Bucharest
Romania

1 Introduction

Romania, a country of about 23 million people, has a total area of 23.750 million hectares, of which 63.62% is agricultural land and 27.68% forest. The agricultural area includes 66.9% arable lands, 29.13% pastures and meadows, 1.77% vineyards and 2.2% orchards.

In the last three decades, Romania has had an accelerated rate of industrialisation. Thus, from 1960 to 1990, the industrial output increased almost 13 times and the installed capacity for industrial use from 3,263 thousand kW (1960) to 37,357 thousand kW (1990). The output of non-ferrous metallurgical industry (including mining of non-ferrous ores) increased about 15 times and the installed capacity increased from 87 thousand kW (1960) to 1,870 thousand kW (1990). At the same time, the installed capacity for chemical industry increased from 265 thousand kW (1960) to 4,032 thousand kW (1990) with an output increase of more than 70 times. Also, during this period, the average number of employees in industry increased from 1,255.2 thousand (1960) to 3,861.6 thousand (1990), of which from 33.7 thousand to 92 thousand in non-ferrous metallurgy (including mining of non-ferrous ores), and from 53.1 thousand to 274.5 thousand in chemical industry. The consumption of domestic coal also had a high increase from 8,163 thousand tons (1960) to 66,462 thousand tons (1989).

Annually, about 138 million tons of polluting substances are emitted into the atmosphere, including, among others, significant amounts of particulates and compounds of non-ferrous metals with very noxious effects on the environment.

The causes of the high amounts of these emissions are first of all due to the inadequate management, old technologies and installations, as well as to the lack of less or non-polluting technologies.

Unfortunately, these accelerated developments intensified and caused new phenomena of industrial pollution, one of the most important being soil pollution with heavy metals.

2 Main Sources of Soil Pollution with Heavy Metals in Romania

The most important industrial emissions polluting soils with heavy metals in Romania result from activities in the fields of mining and processing non-ferrous

ores, producing aluminium, fertilisers, cement, etc., as well as power plants using coal.

The largest areas of soils polluted with heavy metals are around the factories processing the non-ferrous ores in the towns of Baia Mare, Zlatna and Copsa Mica, as well as around the chemical factories producing sulphuric acid within the plants producing fertilisers, located at Valea Calugareasca, Turnu Magurele and Navodari. The emissions from these activities are characterised by a high or very high content of heavy metals. Also, around the power plants using coal, the soils are being continuously loaded with heavy metals. All these emissions of heavy metals are associated with emissions of SO_2 , NO_x and CO_2 which generate acid rains. Reaching the soil, these acidified rains intensify the dangerous impact of soil pollution with heavy metals, by increasing the solubility of toxic metals.

Another source of pollution, especially with lead, is represented by the emissions of car engines, which pollute soils on a strip of 20-30 m wide along both sides of some highways.



Fig. 1. Distribution of major industrial pollution sources with heavy metals of soils in Romania

Figure 1 presents the distribution of the major sources of pollution with heavy metals in Romania, as well as the main elements accumulating, at a polluting level, in soils within the areas affected by the emissions from the respective factories.

The areas of soils polluted with heavy metals around the above mentioned factories and plants vary depending on the intensity and duration of emissions, and the climatic and geomorphologic conditions. For instance, in one of the most polluted areas, Copsa Mica, the soils affected by pollution stretch over an area of 180,760 hectares, of which 149,475 hectares are agricultural land and 31,285 hectares forest. The soils severely polluted with heavy metals, where at least the content of one element exceeds the maximum allowable limit in soil, stretch over a total area of 211,875 hectares, of which 18,630 hectares are agricultural land and 3,245 hectares forest. This large area of polluted soils is determined by both the long period of emissions (more than 50 years) and their long transport by the prevailing east winds along the Tirnava Mare valley.

Around the factories producing sulphuric acid, the areas affected by the emissions with heavy metals are smaller, up to 3,000 hectares, with severely polluted soils over an area up to 1,000 hectares.

Table 1. Variation ranges and average values of total content (ppm) of heavy metals in A horizon of soils within the areas severally influenced by polluting effect of heavy metals^a as compared with the maximum allowable limits (MAL)

Element	Area					MAL ^b
	Baia Mare	Zlatna	Copsa Mica	Valea Calugareasca	Turnu Magurele	
Lead						
Range	25-1083**)	22-2248	106-3550	55-88	26- 500	100
Average	210***)	324	1062	73	108	
Cadmium						
Range	0.7-115	1.0-6.2	0.5-31.5	0.6-3.1	1.8-3.9	3
Average	7.2	1.4	6.0	2.1	2.9	
Copper						
Range	40-1189	33-951	29-805	68-750	28-1050	100
Average	204	182	149	416	230	
Zinc						
Range	58-1378	56-396	101-2010	35-1125	38-600	300
Average	341	159	717	572	206	

^a After Rauta et al., 1988; Ciobanu et al., 1990; Lacatusu et al., 1991 a and b, 1992.

^b After Kloke, 1980.

3 Loading Levels of Soils with Heavy Metals

The soils around the factories processing non-ferrous metals and those producing sulphuric acid present a large range of heavy metal contents (Table 1), the size of intervals being directly proportional with the aggressiveness of polluting factors.

The average values of contents exceed the maximum allowable limits up to 10.6 (Pb), 2.4 (Cd, Zn) and 4.2 (Cu) times. The maximum contents were recorded at Baia Mare (Cd), Copsa Mica (Pb, Zn) and Valea Calugareasca (Cu).

The specific character of some polluting elements for certain areas is due to the nature of processed ores, concentration of noxious elements and disposal of residual materials. Thus, the high content of copper in soils in the south-southwestern part of the Sulphuric Acid Factory at Valea Calugareasca is due both to the ore processing emissions and blowing out of the unprotected heaps of pyrite ashes.

The average values of heavy metal contents emphasise: (a) the soils in the Baia Mare and Copsa Mica areas are heavily loaded with all four discussed heavy metals; (b) the soils in the Zlatna area are heavily loaded with lead and copper and slightly loaded with cadmium and zinc; (c) the soils in the Valea Calugareasca area are heavily loaded with zinc and copper, and medium loaded with lead and cadmium; and (d) the soils in the Turnu Magurele area (around the Pyrite Ash Processing Factory) are heavily loaded with copper and lead, and medium loaded with cadmium and zinc. Also, very high concentrations of copper, lead and zinc were detected in soils, on smaller areas, around some non-ferrous metallurgical factories located east of Bucharest (Table 2). In this case, contents higher than maximum allowable limits were detected only up to 200 m far from the sources, 1.9 (Cu), 9.8 (Pb), and 1.7 (Zn) times higher, respectively.

The depth of migration in soil of heavy metals deposited by industrial emissions varies: shallow (up to 15 cm) in forest soils and deeper (up to 30-40 cm or more) in arable soils. In the latter, the deeper movement of elements is favoured by soil tillage, while in the former the litter has a role in the storage of heavy metals. Thus, in the arable soils in the southwest-south part of the Valea Calugareasca Fertiliser Factory, the heavy metals penetrated down to 60 cm (Fig. 2). We have to

Table 2. Ranges of contents (ppm) of Cu, Pb and Zn in soils around some non-ferrous metallurgical factories located in the eastern part of Bucharest (after Rauta et al., 1980)

Element	Area up to 200 m far	Area from 200 m to 700 m far	Area beyond 700 m	Natural content of soil
Cu	60 - 188	31 - 55	24 - 45	20
Pb	93 - 975	50 - 160	33 - 112	12
Zn	140 - 500	90 - 355	70 - 150	50 - 70

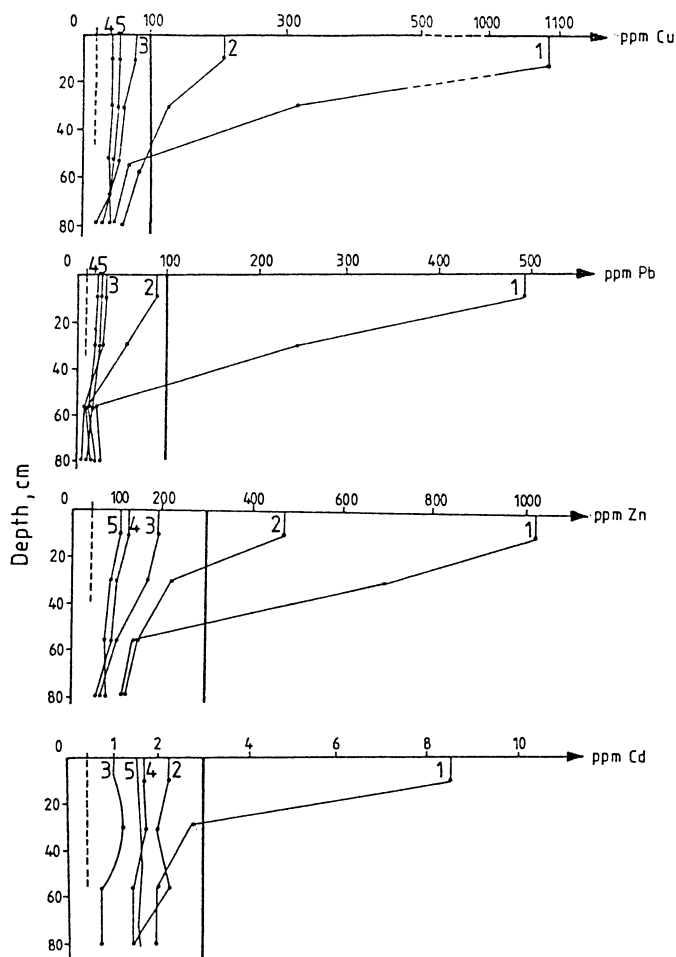


Fig. 2. Distribution of contents of heavy metals in soil profiles located at 100 m (1), 500 m (2), 1000 m (3), 1500 m (4) and 2000 m (5). South of the Fertiliser Factory at Valea Calugareasca (general average content ----, maximum allowable limit ____)

outline the fact that the analysed soil profiles are located on the direction of pyrite ash blowing out.

The soils around the major power plants using coal have contents of heavy metals higher than the normal values recorded in normal soils, but less than the maximum allowable limits (Table 3). The average values of contents in the investigated soils lie, without exception, in the first half of the interval: Normal content - maximum allowable limit. This means that, after the graduation proposed by Lacatusu et al. (1992), the soils around the investigated power plants have a reduced load of heavy metals.

The soils contiguous with routes of high traffic in Bucharest, and the Bucharest-Ploiesti and Bucharest-Pitesti highways have various contents of lead (Fig. 3).

Table 3. Statistical parameters of total content of heavy metals in soils (A horizon) within the areas influenced by the power plants at Mintia, Paroseni, Rogojelu, Turceni and Doicesti (analytical data after Rauta et al., 1990; Lacatusu et al., 1990), as compared with the values of normal content (NC) in soils (after Fiedler and Rosler, 1988)

Element	$X_{\min}$	$X_{\max}$	X	σ	VC^a %	NC
ppm						
Pb	17.0	100.0	27.4	8.5	31	15
Cd	1.0	4.0	1.6	0.8	50	1
Cu	11.3	81.0	30.3	10.3	34	20
Zn	44.6	245.0	80.1	24.0	30	50

^a Variation coefficient

Thus, the urban soils in Bucharest have, in the first centimetres of soil surface, Pb contents higher than the maximum allowable limit, while the soils outside the city have a medium load; the values of contents lie within the right half of normal content - maximum allowable limit interval.

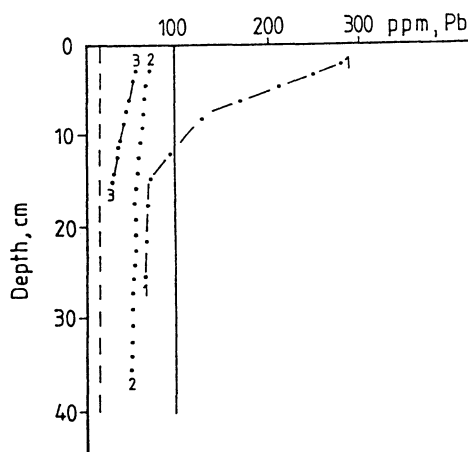


Fig. 3. Distribution of Pb content in soils along the Kiselelt-Bucharest highway (1) and the Bucharest-Ploiesti highway at Otopeni (2) and Km 19 (3) as compared with the maximum allowable limits (—) and normal content in soils (----) (adapted after Rauta et al., 1980; Rauta and Carstea, 1983)

4 Mobility of Heavy Metals in Soils Under the Edaphic Conditions in Romania

The global loading with heavy metals is only one of the factors outlining the phenomenon of soil pollution with such elements. The determination of soil deterioration degree by pollution with heavy metals has also to take into account the other physical and chemical properties of soils, particularly, the reaction (pH), redox potential, texture and organic matter content.

On the whole, the soils in the areas influenced by the emissions from the above mentioned industrial factories have a high degree of deterioration caused by native slight-moderate acid reaction, low content of organic matter, medium or coarse texture. The association of these unsuitable properties with the acidifying impact of the precipitation carrying heavy metals enhances the capacity of soils to increase the solubility of these elements, sometimes up to the noxious levels. These dangerous effects are also associated with the moderate sorption and storage capacity of these soils for heavy metals (Florea et al., 1991).

However, some parts of these areas make an exception, such as: Alluvial Gleyed Soils and Gleyic Soils around the Fertiliser Factory at Turnu Magurele, and Alluvial Soils in the bottom lands of the Tirnava Mare (Copsa Mica), Sasar (Baia Mare) and Ampoi (Zlatna) rivers. Particularly, the reaction and redox potential of soils decrease the solubility of the heavy metals, although these soils accumulated significant amounts of these elements. These soils represents 10-20% of the total area of soils polluted with heavy metals.

Table 4. Content (ppm) of heavy metals, soluble forms in EDTA-CH₃COONH₄ at pH 7.0, in A horizon of soils within the areas influenced by the emissions from the Pyrite Ash Processing Factory (PAPP) at Turnu Magurele and the Sulphuric Acid Factory (SAF) at Valea Calugareasca, as compared with the maximum allowable limits (MAL) (after Lacatusu et al., 1991)

Element	PAPP area		SAF area	MAL ^a
	up to 200 m	beyond 200 m		
Copper				
Range	7 - 127	4 - 32	20 - 305	18
Average	43	16	167	
Lead				
Range	4 - 25	3 - 7	5 - 11	8
Average	14	5	7	
Zinc				
Range	10 - 72	2 - 14	24 - 163	43
Average	37	11	106	

^a After Lacatusu et al., 1987.

The mobility of heavy metals in soil, that is their entering the soil solution, reaches values close to or higher than the maximum allowable limits. Table 4 presents analytical data concerning the content of soluble forms of the heavy metals in soils within the areas influenced by the emissions from the Pyrite Ash Processing Factory at Turnu Magurele and Sulphuric Acid Factory at Valea Calugareasca.

It is to be mentioned the significant exceeding of the maximum allowable limits by the average content of copper up to 2.4 times in the case of soils from Turnu Magureale, and up to 9.3 times in the case of soils from Valea Calugareasca. The maximum allowable limit for lead was exceeded only in the case of soils from Turnu Magurele (1.75 times), and the maximum allowable limit for zinc was exceeded only in the case of soils from Valea Calugareasca (2.33 times).

5 Consequences of Soil Pollution with Heavy Metals

Besides the alterations caused to soil due to loading with heavy metals and the changing balances between different phases and chemical component elements, the pollution with heavy metals has an inhibiting effect on microbiological activity. Thus, the polluted soils with heavy metals in the Zlatna area, as compared with the non-polluted or slightly polluted soils in the same area, are characterised by a decrease in the number of bacteria (particularly nitrification ones) and the index value of colonisation with actinomycetes, and by an increase in the index value of colonisation with micromycetes particularly the cellulolytic ones (Table 5). Generally, a decrease in dehydrogenasic activity occurs.

Unlike the other components of the environment, soil has the capacity to store chemical elements, heavy metals included. At the same time, it has the capability

Table 5. Influence of heavy metal pollution degree on the microbiological activity in the Zlatna soils (after Ciobanu et al., 1990)

Pollution degree	Horizon	Depth cm	Microflora		Actinomycetes (Colonisation index)
			Bacteria (Mil/l g soil)	Micromycetes (Colonisation index/soil granule)	
Slight	Aom	0 - 7	382.0	985	1.05
	Ao	7 - 31	182.3	610	0.50
Moderate	Aom	0- 20	104.4	1075	0.50
	Ao	20 - 35	141.9	1400	0.30
Severe	Aot	0- 20	104.1	1690	0.00
	Ao	2 - 17	3.1	1220	0.00

to directly release in solution the stored elements as they are taken up by plants, or a certain part migrates towards the ground waters. When the soils are heavily loaded with heavy metals and soil physico-chemical properties favour a high mobility of heavy metals, excessive transfer of heavy metals from soil into plants and waters takes place and from these to animals and human beings with high content levels of heavy metals, sometimes noxious for consumers.

The negative changes induced in plants (decrease of vegetal mass, chlorosis, burns, accumulation of heavy metals in fruit and edible organs) grown on soils polluted with heavy metals were detected both directly in the field on the occasion of field research and in pot experiments with soils from the polluted areas or with soils experimentally polluted with heavy metals (Rauta and Carstea, 1983; Rauta et al., 1988 and 1989; Mihailescu et al., 1990).

Due to the heavy loading with copper of soils around the factories at Turnu Magurele and Valea Calugareasca and due to the transferring of copper in fodder crops, some cases of cupric intoxication of sheep were recorded (Lacatusu et al., 1987).

Within the area influenced by the emissions from the Copsa Mica Factory, some cases of saturnism with horses and human beings were recorded (Lacatusu et al., 1991). Similar phenomena were recorded in the Baia Mare area, too.

6 Vulnerability of Romanian Soils to Heavy Metal Pollution

As already mentioned, the intensity of polluting effect of heavy metals on soils largely depends on soil physico-chemical properties. Therefore, at the same level of loading with heavy metals, the soils respond differently, depending on their properties. Thus, each kind of soils is characterised by a specific vulnerability to pollution with heavy metals. Fig. 4 presents a map of the Romanian soils classified according to their vulnerability to pollution with heavy metals. For this classification the following features were mainly taken into account: sorption capacity, storage capacity and buffering capacity.

According to these considerations, the most vulnerable soils to heavy metals pollution are represented by the following soil categories (Rauta, 1991):

- Sandy soils mostly non-calcareous and with a low organic matter content;
- Acid soils with a very high organic matter content, coarse texture and with shallow to medium profile;
- Acid to neutral soils, medium textured and with low organic matter content (mostly with low permeability); and
- Acid to neutral soils, medium textured with medium to deep profile and medium organic matter content.



LEGEND

		Level of vulnerability to heavy metals	
1	Calcareous alluvial soils	L - M	
2	Smectitic - clayey soils, with high organic matter content and shallow ground - water	M	
3	Smectitic - clayey mostly calcareous soils, with shallow ground - water	M	
4	Sandy soils non-calcareous and with low organic matter content	H	
5	Acid allophane-rich soils with very high organic matter content	M	
6	Smectitic - clayey and neutral - alkaline soils	M	
7	Alcaline soils, fine textured and with shallow ground - water	L - M	
8	Calcareous soils, medium textured and with low organic matter content	L - M	
9	Calcareous soils, medium textured and with medium organic matter content	L - M	
10	Slightly acid to neutral soils, medium textured and with medium organic matter content	M	
11	Slightly acid to neutral soils, with coarse to fine texture and low to high organic matter content	M	
12	Acid to neutral soils, medium textured with medium to deep profile, and medium organic matter content	M - H	
13	Acid soils with very high organic matter content, coarse textured and with shallow to medium profile	M - H	
14	Acid to neutral soils, medium textured and with low organic matter content (mostly with low permeability) .	M - H	

Fig. 4. Map of Romania showing categories of soils grouped according to relevant characteristics determining their vulnerability to heavy metal pollution. (Explanation of symbols: L = low or absent; M = medium; H = high)

These soils cover the largest part of Romania and are ranked in the class of medium-high vulnerability to heavy metal pollution, excepting a small area of soils characterised by a high vulnerability to such a pollution.

7 Conclusions and Summary

Although the investigations on heavy metal pollution in Romania are really at their beginning, their results, however, represent a real alarming signal. Far from covering all the aspects of this problem, these investigations have contributed to identify the main "hot spots" - affected areas, main pollution sources, damages caused to soils, plants, animals, people. Thus, main areas where the contents of one or more heavy metals in soil exceed the maximum allowable limits are known, as well as cases of soil microbiological activity inhibition, vegetal mass decrease, plant chlorosis and burns, sheep cupric and horse lead intoxication, and human health deterioration. All these emphasise the severity of the problem Romania is facing at present. To obtain the best results, a special research approach is imperative. Under the conditions of a high quality international assistance, besides a complete understanding of the heavy metal pollution in Romania and a severe control of heavy metal pollution sources, a special research strategy and engineering have to be undertaken with the purpose of reaching the ecological reconstruction of polluted soil with heavy metals in complete harmony with the ecological balance.

Soil pollution with heavy metals in Romania is mainly due to the activities concerning the non-ferrous ore metallurgy and sulphuric acid production. For instance, around the most important factory for processing the non-ferrous ores, Copsa Mica, the area with soils affected by heavy metal pollution stretches up to about 180,000 hectares, while around a factory for sulphuric acid such an area is less than 1,000 ha.

The polluted soils present, on an average, heavy metal contents up to 10.6 (Pb), 2.4 (Cd and Zn) and 4.2 (Cu) times higher than the maximum allowable limits in soil (Pb-10 ppm, Cd-3 ppm, Zn-300 ppm and Cu-100 ppm).

A significant accumulation of Pb was recorded in soils along the roads with intensive traffic, exceeding the maximum allowable limit only in some urban areas (e.g. Bucharest).

Increasing contents, without exceeding the maximum allowable limits, were detected in soils around the power plants which use coal.

Particular physico-chemical features (pH 5.8, organic matter content 2%, light texture) specific for the most soils (about 80%) within the polluted areas, favour the solubility of heavy metals and their uptake by plants. Due to these circumstances, the investigation of polluted soils emphasises: inhibition of soil microbiological activity, decrease of vegetal mass, chloroses and burns of plants, some

cases of sheep cupric intoxication and horse saturnism, as well as the health deterioration of one part of the population.

Taking into account some specific soil features, a map showing the vulnerability of the Romanian soils to heavy metals pollution is presented.

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22 Exposure of the Population of Novi Sad and the Surrounding Areas to Lead

N. Roncevic¹, J. Siriski², D. Darmati³, M. Dordevic, M. Kristoforovic-Ilic²,
L. Vajagic², M. Vojinovic-Miloradov⁴, S. Pakov⁵

¹ Medical School, University of Novi Sad

² Public Health Institute, Novi Sad

³ Public Health Institute of Serbia, Belgrade

⁴ Faculty of Natural Sciences, University of Novi Sad

⁵ Veterinary Institute, Novi Sad

1 Introduction

There are numerous examples of environmental pollution caused by lead with lead concentrations showing an ever increasing trend (Bellinger et al. 1987; Committee Environmental Hazards 1987). Once lead enters the human body, its effects are toxic and it causes numerous hematologic and neuropsychologic disorders. Children are especially vulnerable, with lead sometimes causing irreversible disorders even in asymptomatic children. This is why studies are being conducted in many countries to find out to what extent children are exposed to lead. This is done by determining the concentration of lead in the blood and protoporphyrin in erythrocytes. Such studies have not been conducted in the Novi Sad region in the province of Vojvodina. Consequently, this chapter is an attempt to determine the possible exposure of the population, especially children, to lead concentrations in Novi Sad and the surrounding villages by determining the lead concentration in the air, potable water, and in the blood from the umbilical cord.

2 Material and Methods

In order to determine the concentration of floating particles of lead in the air in Novi Sad, 144 samples of air were collected between April 1989 and March 1990. The sampling was done once a month and the samples were collected at the 12 busiest intersections in town.

Four samples were also collected in July and August 1990 in the centers of the villages surrounding Novi Sad. The samples were collected on glass fiber filters using a pump with a capacity of 140 l/h. The collected samples were then digested in nitric acid. The lead concentration was determined using the flame atomic absorption spectrophotometry method (AAS; Stankovic et al. 1984).

The water quality and health safety of potable water was analyzed in 25 settlements in Vojvodina. Ten of the settlements with a population of over 230 000 have a central water supply system and use treated water. Fifteen of the settlements are villages with a population of around 35 000 people, where raw water or only chlorinated water is used. The water quality was also tested for 43 subartesian wells. According to the existing regulations and standards for potable water, the maximum allowed concentration of lead (MAC) in potable water equals 0.05 mg/l (Drinking Water Standard).

Fifty-eight children born at the Novi Sad Clinic for Gynecology and Obstetrics between August 1989 and June 1990 were tested to determine the lead concentration in their umbilical cord blood. A more or less equal number of mothers of these children were from Novi Sad (27) or the surrounding villages (29), while residence records could not be found for two of the mothers. The blood samples from the umbilical cord were taken at the time of delivery. The lead was determined from heparinized full blood, digested in nitric acid, while the fats were extracted using diethylether. The lead concentrations were recorded on the AAS (Stankovic et al. 1984).

The statistical analysis used the central tendency methods (arithmetic mean – $\bar{x}$ and standard deviation – SD) and the method for determining the level of statistical importance (Student's t-test).

3 Results

The lead concentration in 144 samples of air collected in the town of Novi Sad ranged from 0.0 to 7.7 $\mu\text{g}/\text{m}^3$. The mean value equaled $\bar{x} = 1.0 \mu\text{g}/\text{m}^3$, which is 43% higher than the maximum allowed concentration (MAC) for an inhabited area (MAC = 0.7 $\mu\text{g}/\text{m}^3$). Concentrations higher than the maximum allowed were recorded in 69 samples, i.e., 48% of the total number of measured samples. The highest concentrations (7.7 $\mu\text{g}/\text{m}^3$) exceeded the maximum allowed concentration 11-fold. In 8 of the samples taken in the vicinity of Novi Sad the lead concentration ranged between 0.0 and 0.4 $\mu\text{g}/\text{m}^3$ and were all within the set limits. The mean value amounted to $\bar{x} = 0.15 \mu\text{g}/\text{m}^3$.

From the above settlements, 277 samples of potable water were tested to determine the residue lead. The detected lead residue did not exceed the MAC concentrations listed in the regulations (Drinking Water Standard; Vajagic et al. 1992).

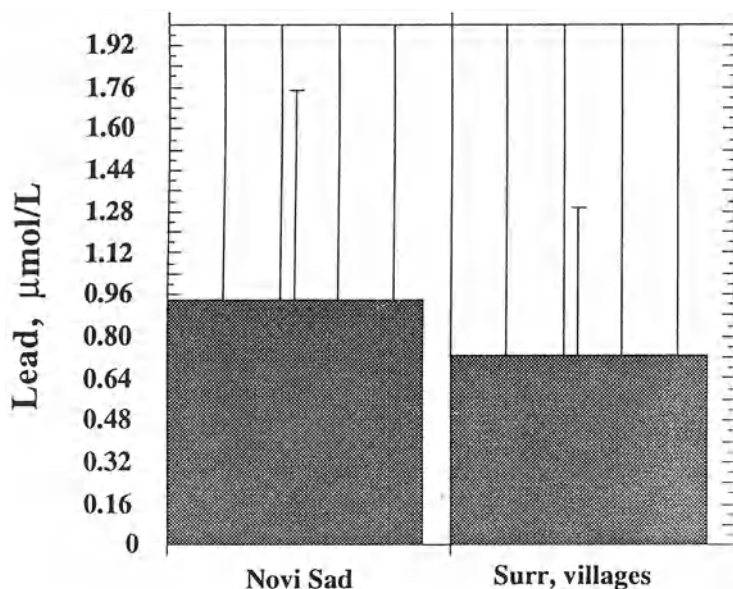


Fig. 1. Percentage distribution of the Pb concentrations found in the umbilical cord of the tested groups

The lead concentrations in umbilical cord blood were analyzed in 58 samples. The highest concentration of $7.20 \mu\text{mol/l}$ was not considered in the statistical analysis because we could not exclude the possibility of the sample being contaminated. The other concentrations ranged between 0.00 and $2.88 \mu\text{mol/l}$. The average value equaled $\bar{x} = 0.836 \mu\text{mol/l}$. Figure 1 shows the average lead concentrations in umbilical cord blood of children from the town of Novi Sad and the surrounding villages. Although there is a difference in the average values of the two groups, it is not statistically significant ($t = 1.08$; $p > 0.1$). The percentage distribution of lead concentrations in the umbilical cord blood of the tested samples shows that the concentration was lower than $1.21 \mu\text{mol/l}$ in 44 samples (77%). This is considered as the upper allowed limit for lead found in blood (8), while the concentration exceeded this value in 13 samples (22.8%).

4 Discussion and Conclusions

The increased lead concentrations in the air in the town of Novi Sad indicate that there is a significant amount of pollution. Such high concentrations could be due to the use of oil derivatives which contain lead and to the considerable traffic. The lead concentrations in all the air samples taken in the surrounding villages were within the allowed limits, although no premature conclusions should be drawn because of the small number of samples.

The quality control and health safety analyses of the potable water in the above settlements showed no deviation in the lead residue.

Until recently, a lead concentration of $1.45 \mu\text{mol/l}$ in the blood was considered acceptable. However, in 1978, the American Health Control Center recommended that concentrations above $1.21 \mu\text{mol/l}$ should be considered as increased. Today, many authors believe that lead concentrations in the blood exceeding $0.48 \mu\text{mol/l}$ can cause undesirable effects in the human body, especially in children.

According to a report published by the American Health Control Center, in 1976 the lead concentration recorded in the blood of the general population in the USA was $0.71 \mu\text{mol/l}$. In 1980, this concentration was reduced to 0.44 , which was largely attributed to the use of unleaded gasoline. In this chapter the mean value for the entire group equalled $0.836 \mu\text{mol/l}$. The lead concentration in the umbilical cord blood in 24 samples (42.2%) was below $0.48 \mu\text{mol/l}$, in 20 samples (35.1%) it ranged between 0.48 and $1.21 \mu\text{mol/l}$, while it was higher than $1.21 \mu\text{mol/l}$ (increased value) in 13 samples (22.8%). This means that the lead concentration in the blood of every fifth baby born in Novi Sad is such that it could adversely effect his/her physical and psychological development (USDH 1985).

This chapter shows the difference between the mean values and the lead concentrations found in the umbilical cord blood of babies born in Novi Sad and the surrounding villages, although this difference is insignificant from the statistical point of view ($p > 0.1$). Eight of the mothers whose babies were found to have lead concentrations higher than $1.21 \mu\text{mol/l}$ in their umbilical cord blood were from Novi Sad while four were from the surrounding villages. It would be reasonable to expect a greater difference in the lead concentrations found in the blood samples because of the considerable difference in lead concentrations in the air in Novi Sad and those in the surrounding villages. The small difference in the lead concentrations in the umbilical cord blood of the newborns whose mothers were from Novi Sad and the surrounding villages leads to the conclusions that besides air, there are other important ways in which lead enters the human body.

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23 Some Aspects on Metal Pollution in Eastern/Central Europe: Former Eastern Germany

Rudolf Reuther

Environmental Research Group (MFG), Kandelstraße 30, D-7835 Teningen,
Germany

1 The Sociopolitical Framework

For more than 40 years, the "iron curtain", cutting the political and social life of Eastern and Western Europe into two. In fact, the harsh and strictly maintained mutual isolation of socialistic countries in the East from Western capitalistic societies also separated the natural environment in Europe.

In the same way as social and cultural progress and exchange between East and West was rather limited and people could hardly move or travel between one and the other side, floral and faunal species and populations, and thus ecosystems, developed more or less separately, under different regional, external conditions, implied by two opposing socio-economic systems.

Not only historical human settlements and relations, but also natural habitats and climatically evolved boundaries established during the evolution of this part of the world, became overlapped and cut up by an arbitrarily drawn and rigorously maintained new borderline extending from the Mediterranean Sea to the Arctic north. The true ecological impact of this artificial cut is still far from being understood.

During these decades, a differing view of life developed with regard to "how we can learn to evaluate and appreciate nature as invaluable in itself". However, the competition of ideologies between East and West, aimed at the demonstration of which political system might prove best, both with regard to human and social rights as well as economic welfare, and resulting in an enormous armament race to intimidate the other side, were one major reason to consider wealth and abundance as nothing more than a means to serve these idle and short-sighted ambitions.

In the early 1970s, in the Western part of Europe, and in particular in those democracies which had already reached a high degree of economic stability, pluralism and welfare, the understanding grew that the higher living standard was being produced by an exploitation of nature that did not "cover real costs". Public environmental concern, paired with new scientific evidences, soon gave rise to an enhanced general awareness of man's responsibility to protect and conserve nature against his own activities.

At the same time, the socialistic countries in the East submitted their economies almost completely to planning targets, set up by an anthropocentric ideology, which does not take into account individual needs and limitations or their strong

interdependence with environmental health. Air, water and soil compartments seemed to be ranked under the absolute definitions and valuations given by the planning economy and put forward by the 'sphinx' of full employment and resource-intensive production.

A country's natural resources have to serve the goals formulated, regardless of the final price in natural and human consequences.

Finally, these two different ways of valuation resulted in a differing response to man's impact on nature (e.g. by industrial and/or infrastructural production or consumption): in the West it was soon recognised that human health and prosperity not only depends on economic growth, but is equally related to long-term environmental stability, safety and regeneration.

The East, however, was faced with fixed and short-term production quota, set up primarily to ensure and save the autarky and survival of the political system, thereby accepting isolation, harm and loss of life quality as necessary evils.

These different economic developments led to differing environmental strategies in Europe: while in Western countries environmental aspects and considerations became more and more integrated in the legislative, executive and jurisdiction, as well as in the planning and implementation of environmentally relevant processes. In the Eastern communities, the realisation of an effective environmental control and improvement failed due to the lack of executive power of responsibilities to transfer the existing law and as a consequence of neglecting those benefits, which may result from the application of emission-poor and highly preventive technologies.

The present precarious conditions, after the rapid collapse of the political and economic system within the former socialistic countries, are by and large the outcome of the decade-long degradation of the self-regulating capacity of human and environmental resources in those Eastern states, leaving a ruined economy behind.

In the following, I will try to give a short description and preliminary estimate of some major critical fields of environmentally relevant legislative activities, the problems we are faced with, and the need for action arising from it with regard to metallic pollutants. Due to the great uncertainty, scarcity or even lack of data on heavy metal (HM) pollution aspects from East European countries, I will focus on the pollution situation found in the former GDR ('German Democratic Republic') where relevant and reliable information is now becoming available, which, of course, may not always be representative for other East European countries.

2 The Situation Afterwards

In 1990, German reunification made it possible to transfer and apply West German environmental legislation to the five newly founded East German federal states. Concerning emission control, hazard and toxicity assessment and the disposal of HM-containing material, all the standards, classification and technical regulatory framework, set by West German laws, together with the corresponding guidelines

of EC-directives, came into effect according to the agreement of the German 'Environmental Union' (1,2).

However, the whole size, type and intensity of the overall pollution by health and ecologically hazardous substances, in particular by toxic HMs, originating from former GDR state-owned enterprises, became only gradually evident and has still to be evaluated. Due to the lack of available, highly sensitive analytical equipment to trace pollution, the careless and irregular attention and action of official controlling authorities and the measures taken, as well as the not seldom competing interests between central governmental boards and provincial departments, the amount and quality of collected data before 1989 are insufficient to obtain a reliable quantitative estimate of the actual degree and extent of contamination by HMs (and other toxic components).

In order to assess both the short- and medium-term need of action to further protect those environmental compartments, which are still unaffected, and to prevent a worsening of already impacted ecosystems, main areas with a high population and industrial density were identified and selected by the German Government for first stock-taking investigations. In addition, those regions with a significant preload of or susceptibility for HMs (and micro-organic pollutants) were included into these preparatory surveys in order to obtain necessary background data on naturally critical and vulnerable sites (a great deal of the data used here is derived from ref. 3 and 4).

Parallel to these primary investments, efforts were made to collect data for the main sources and pathways of HM discharges into air, water, soil and food-stuff, listed from previous recordings with the objective of knowing where necessary and immediate action and countermeasures have to be taken first, to reduce or stop emissions.

Early successive measurements (fingerprinting) initiated by the German Environmental Protection Board (Umweltbundesamt), with regard to the HM contamination of surface water, soils and sediment, confirmed the presumed scope and potential of pollution. In many cases, the concentration values found exceeded by far the quality standards and criteria established or recommended by German and international legislation. As one consequence, whole facilities and production lines had to be closed, in order to avoid a direct threat to local people and ecosystems.

Due to initial improvements in key production, handling and control technology and practices, infrastructural changes and the enforcement of public awareness and private responsibilities, by the strengthening of both executive and educational instruments and institutions in favour of a better integration of environmental aspects, the existing stress at highly critical sites could be mitigated and further severe effects averted. The higher level of information, and thus participation, may enhance the willingness of the public to cooperate with the responsible administration to protect the environment, despite obvious socio-economic constraints and obstacles at the beginning. The German government plans high quality changes by the year 2000 for all people and the environment in the former GDR, reaching at least the Western level.

3 Problem Areas and Characteristics in East Germany

As the major emission source for HMs, the energy and (brown coal) mining sector have been identified. Representative data gathering by comprehensive environmental monitoring programs and networks is now underway (see 3 and 4). According to studies initiated by the German EPA, the main ecological "trouble spots" are centred around the extended areas of

- Leipzig, Bitterfeld, Halle, Merseburg
- Mansfeld (metal mining and processing)
- Niederlausitz (energy centre of the former GDR), and
- Rostock

3.1 Air pollution

Power plants of the energy and chemical industry as well as brown-coal mining operations represent the major sources of air pollution. With a total of 5.2 mio. t/a of SO₂, the new federal states in the East show still the highest emission rate of this gaseous, acidifying pollutant, per unit area, in Europe.

The energy-producing sector, with an annual atmospheric output of 4.2 mio. t/a of SO₂ (1989), 1.1 mio. t/a of dust and 0.3 mio. t/a of NO_x, proves to be the dominant air polluter. It is estimated that the SO₂-load in Eastern Germany exceeds the one in the Western part by a factor of 11.5 (!), and 8.5 times the respective value for atmospheric dust. In Table 1, a comparison is given for top-SO₂ levels from selected, highly populated and industrialised sites in West and East Germany.

According to references given in (4), the main sources for atmospheric dust deposition, beside energy production and mining, are the following:

Table 1. Air SO₂-concentrations at selected sites in West and East Germany (after ref.1)

SO ₂ -load (ug/m ³)	
West Germany	
◦ Ruhr area	17
◦ Munich	32
East Germany	
◦ Merseburg	270 - 380
◦ Leipzig	160 - 310
◦ Erfurt	210 - 330
◦ Berlin	90 - 125

- cement factory (Deuna)
- steel mill (Henningsdorf, City of Brandenburg, Riese and 'Maxhütte' Unterwelkenborn)
- copper smelter (Ilseburg; shut-down), smelter and rolling mill (Hettstedt), lead-colour factory (Ohrdruf) and accumulator plant (Zwickau).

Inorganic dust particles derived from industrial production processes usually contain oxides, sulphates and carbonate of Al, Fe, K, Si and Mg. Their critical burden, however, originates from their association with trace amounts of toxic HMs, like Cd, Pb, Ni, Hg, Be and As, besides an undefined number of persistent organic compounds (like PCDDs and PCDFs).

It was demonstrated, that only about 10% of all energy power plants meet the air quality standards set up by the German technical regulatory work ('TA Luft') for air pollution control, thereby exceeding established limit values up to a factor of 100 (!).

3.2 Water Pollution

Again, a complete picture of past and present environmental stress on aquatic systems is still unavailable. One reason for this obvious information deficit may be partly the lack of interest of the former responsible GDR water administration to spread data on water quality or to create a higher public awareness. Another excuse may be the shortage of adequate and sufficient analytical capacities (personal skill and instrumental equipment) to cope with the growing control demand. For a systematic registration of water-threatening substances, like HMs, both the analytical resources and validated water quality criteria were highly missing.

Although there seems no acute threat to the drinking water supply in Eastern Germany, the distribution network is in bad condition and the chlorine disinfection is often insufficient. Still today, about 10 mio. people in the former GDR receive qualitatively affected drinking water (> 70% produced by ground water). It is supposed that about 9.6 mio. people are supplied with (HM-) contaminated drinking water, and about 1.4 mio. people depend on water for their living with an elevated nitrate load (> 50 mg/l) (1).

Another amazing result of first surveys on the state of surface waters is the fact that only 3% of all running water and about 1% of stagnant water could be classified as ecologically safe.

Alarming are also the results from a recently conducted groundwater (pilot) investigation, which showed that from 230 control stations only 11 (!) were in accordance with the determinations given by the German legislation ('Trinkwasserverordnung'). With regard to HMs, 24 of 214 measurements pass the respective standard for cadmium, and 16 of 218 measurements the value established for lead (in addition, 9 of 61 controls exceed the corresponding limit for chlorinated hydrocarbons (4) (see also Table 2).

Only about 58% of the East German population (with a total of ca. 17 mio. people) are connected to public waste water (ca. 1.2 bio m³/a) treatment plants

Table 2. Data on groundwater contamination in the new federal states (4)

	number of controls	exceeding the limit	in %
manganese	188	133	71
iron	200	135	68
aluminium	113	51	45
phenolic compounds	162	67	41
ammonium	203	72	36

(about 89% of 61 mio. people in West Germany), and just 10% (!) of the about 4 bio. m³/a discharged industrial waste effluents are rather insufficiently treated. Moreover, two thirds of the waste water from municipalities is directly released, without any previous treatment, into rivers.

It is often found that the combined effect of insufficient water treatment and high geogenic and/or anthropogenic load particularly result in abnormally high arsenic and aluminium concentrations in the raw water.

As an example with regard to the HM input into surface waters at Boizenburg (SE of Hamburg), which represents in total about 75% of the pollutant discharge into surface water from the former GDR, the annual load is listed in Table 3. For the River Oder, no data on HM pollution is available yet.

Main sources of metal input to natural waters are again the energy producing and mining industry, in addition to smelting and metallurgical operations (iron and non-ferrous metal processing), the pulp and paper production as well as petrochemical manufacturing.

Severe groundwater contamination arises often from the fact that in previous times filter ashes from coal burning containing significant amounts of HMs, like Pb, Cd, Cu, As, Cr, Ni, Zn, Hg, were deposited in residual holes left open by mining operations without any precautions. When groundwater levels rose, water could intrude the deposit and easily dissolve part of the HMs (in particular relevant for the Niederlausitz area). Besides this, the leaching of sulphur-rich (FeS₂) old mine waste deposits has led, together with the documented high SO₂-emissions, to considerable water acidification.

Table 3. Annual load of metallic pollutants to the River Elbe from the former GDR (1)

mercury:	23 t/a	copper: 380 t/a
cadmium:	13 t/a	nickel: 270 t/a
lead:	120 t/a	zinc: 2.800 t/a
chromium:	280 t/a	

3.3 Soil Pollution

As already indicated for air and water, the whole extent to which the soil environment is affected today by HMs is unknown. What makes it again difficult is that there are not only point-sources but also from transboundary atmospheric transport and deposition.

Soils close to metal smelter and processing plants were particularly exposed, as emission control was inefficient or completely lacking in the former GDR. Soils, vegetation, fruits and fodder taken close to Pb-smelting and processing operations showed all increased concentrations resulting in blood Pb-concentrations of up to 80 µg/100 ml (maximum tolerable value at 20 µg/100 ml). In particular the non/ferrous metallurgical production at Freiberg, Eisleben, Helbra and Ilsenburg (Mansfeld area) showed a high HM-emission resulting in the contamination of soil and food beyond the regulatory standards. A first examination of the blood Pb-concentration in local populations indicated a high intake of this toxic HM, with values above 30 µg/100 ml. At the moment, there is no overview study available on the HM-load of natural crops growing on soils from these areas (1).

To what extent the intensive exploration and mining activities for uranium, within an estimated area of 1.500 km², has affected the soil system is likewise not yet known.

Highly critical attention must be given in the future to the broad application of HM-enriched sewage sludge from water treatments on agricultural fields as a soil amelioration, a common but uncontrolled practice in the former GDR. About 65% of the 1.1 mio. t of sludge (West Germany: ca 5 mio. t/a) annually produced by the 1.100 public treatment plants was used in agriculture. Additionally it is known that soil improvement measures were also carried out by spreading HM-enriched power plant filter ashes on agricultural land. Another more speculated anthropogenic source of HMs in soils may have been the high utilisation of mineral (phosphorus) fertilisers (especially cadmium) and of pesticides (with regard to arsenic and mercury). The total amount of applied pesticides is estimated at 28.500 t/a, which doubles the annual amount used in Western Germany (1).

3.4 Forest Disease

Forest disease and decline phenomena in East European countries seem generally more developed than in the Western part of the continent, as can be seen from Table 4 (the latter with regard to the situation in Germany). Among other factors (e.g. climate, parasites), air pollution with acidifying (SO₂, NO_x) and oxidising (e.g. O₃) substances as well as with HMs has been shown to contribute to the observed growth reduction. From the 1991 survey follows that about 36% of East German forests are evidently damaged (damage classes 2-4), which is double that found in the Western part of the country (4).

Table 4. Damage (class 2-4) of coniferous trees in some European countries (4)

country	- % of damaged forest area -
Spain	3.0
France	6.6
Austria	8.3
Greece	10.0
Belgium	10.7
Italy	12.8
West Germany	15.0
East Germany	31.5
Sweden	16.1
Norway	17.1
Finland	18.0
Netherlands	21.4
Hungary	23.3
Portugal	25.7
Slovenia	34.6
Bulgaria	37.4
Poland	40.7
Great Britain	45.0
CSFR	50.3
Byelorussia	57.0

3.5 Waste Disposal and Old Deposits

There is no complete registration or update of the amount and type of industrial, household and other waste material produced in the former GDR. For 1988, it was estimated that the amount of all wastes amounted to 91.3 mio. tons. In 1989, ca 55 mio. tons of industrial wastes were deposited. Waste disposal occurred at about 13.000 sites, with only 4 places, however, designed for special waste products ('Sondermülldeponien').

As in all other East European countries, the increased installation of cleaning steps for process air and water in the future may probably escalate the total amount of waste produced (as is currently the case in West European countries), if no emission-poor production alternatives are found.

To date, 260 open-cast holes left by the mining industry and representing a total volume of estimated 3 km³ were used as disposal sites and for the uncontrolled deposition of hazardous wastes and residues from both the chemical industry (e.g. at Buna, Leuna) and petrochemistry in the former GDR.

The deposition of Pb-contaminated tailings from the Mansfeld metal-mining area may serve as an example to demonstrate the carelessness employed in waste disposal: Before Second World War, this type of mine sludge was simply stored in unsheltered basins without any environmental safety. After the storage capacity

was exhausted, the tailings were just thrown onto neighbouring meadows without further attention.

In the same area, copper mining and smelting has left behind a total of about 953 potentially hazardous old waste deposits. Altogether, it is suspected that there are about 50.000 sites of previously contaminated soil, surface and groundwater on the territory of the former GDR, of which about 27.877 suspicious areas of old wastes could be identified, but without any data about their hazard potential (4).

From an early check of 55 waste incinerators (installed inside the production facility), only 3 of them were equipped with an emission control. As yet no estimates exist about the amount and type of wastes which are produced and stored inside the plant (1).

It is known that the former NVA military forces and the Soviet army together used an area which amounts to about 10% of the size former GDR. However, neither the number nor the hazard potential of armament waste disposal sites are known today.

3.6 Criteria

Isotopically stable HMs are all basic chemical elements and hence not degradable. In order to be able to know the level of concentration or dose, which may be considered as "safe", with regard to human and ecological integrity, a variety of effect-related test procedures has been developed by e.g. West European countries (2). Resulting maximum tolerable concentrations were consequently applied as quality criteria or standards, in order to safeguard and audit environmentally relevant projects with regard to possible hazardous substances.

As common practise in most West European countries, toxicity values (e.g. LC_{50} or ADI values) gained from short-term and single-species laboratory assays, in combination with field observations are directly equated with lowest adverse effect concentrations. Unfortunately these guidelines or limits still do not take into account or underestimate the influence of important environmental parameters, such as water hardness, temperature or salinity. Quality objectives based on these limits have to be looked at carefully, as they will always neglect the complex interactions and multi-component dynamics of nature. Here, competition and interferences are often the driving force responsible for our measured observation. For this reason, other contamination factors, like the ratio between the target element/compound and another component concentration relevant for its final behaviour (e.g. Hg/C_{org} or Pb/Fe) seem more powerful in prediction and risk assessment.

Some approaches designed to define acceptable HM levels in the environment refer to the natural, pre-industrial load prevailing in pristine systems. However, there is no clear definition yet and a controversial discussion of which background data is the starting point for setting quality criteria. It is always legitimate to ask, what kind of effects and risks we are willing to accept for a certain area or locality, but not for another one, and vice versa.

The stringent demands of controlling laws in Western countries, on the effective realisation of quality criteria, are faced with the fact that they should have a wide application, but at the same time an eye for detail. The message and information we can get from them should cope with a special pollution situation, yet without losing its standard characteristic. For this reason, one may conclude that standard values should be referred to regional air, water and soil quality and may vary according to the location.

With regard to the vast dimensions and severity of metal pollution incidents in today's rapidly changing Eastern Europe, and the tremendous need of both immediate and long-term action, we may suggest defining quality criteria more closely in relation to the real impact (impact criteria) for a particular area or ecosystem. The use of a definition as supposed by Swedish scientists may be simple but also helpful in the sense, that a quality criterion may be best expressed by the size of a deviation at a certain concentration or dose (mean values) from the normal situation (natural preload), which finally determines the risk of negative effects (5).

Limit values (monthly average values) and environmental standards (annual means) do exist, e.g. for HMs in water, in EC-directives; whereas cadmium and mercury are specified in List I (very toxic), other HMs, like copper and zinc, could become adapted according to the special demands of a country's quality objectives (6, 7, 8).

For comparison, the quality criteria for HMs in drinking water for Sweden and Germany are depicted in Table 5 (9, 10). There are no equivalent lists of valid environmental quality standards for HMs in any of the East European countries known to the author.

Table 5. Limit values for HMs in drinking water (in mg/l) exemplified for Sweden and Germany (after 9 and 10)

heavy metal	Sweden	Germany
arsenic		0.01
lead	0.05	0.04
cadmium	0.005	0.005
chromium	0.05	0.05
nickel		0.05
mercury	0.001	0.001
antimony		0.01
selenium		0.01
copper	0.05	3.0 ^a
zinc	1.0	5.0 ^a
iron	0.1	0.2
manganese	0.05	0.05

^a approximate values

3.7 Priorities and the Need for Action

The envisaged change in East Europe, including the new countries emerging from the former USSR, from planning to market economy will not only result in changes in socio-economic conditions, but will also cause a fundamental cut in the countries' environmental abundance. A general common ground for all is, that environmental monitoring and pollution control by official sides was both inadequate and poor, despite an existing, well-motivated legislative. As also mentioned earlier, necessary analytical capacities were missing, which in turn made it almost impossible to detect or foresee any threat to human and environmental health or to control the efficacy of alternatives to the taken measures.

For this reason, it is highly recommended to build up the personal and technical resources organised and co-ordinated under the guidance of a national controlling board (EPA), in order to meet the present development and challenges in the future. Moreover, there is an urgent need to establish observation, monitoring and control networks (early-warning system) on a regional and local scale in order to identify recent trends, to work out guidelines and to introduce proper remedial measures where necessary, in time. For taking the right measures, it is crucial to know what are the causes and effects of any activity, and where they will occur, in advance!.

In this context, international co-operation between East and West as well as bi- and multilateral assistance programs for the necessary financial and technical equipment are greatly needed.

As an example, within the Helsinki Convention (1974), the international agreement between the Baltic Sea countries on the protection of the marine environment encouraged and stimulated measures to reduce the pollutant discharges already within the catchment area, i.e. primarily at the sources.

Recently (1991), a European questionnaire was started under the auspices of Germany to establish national emission rates of HMs, like As, Pb, Cr, Cu, Ni and Zn, with the final aim to identify priority areas and the type of countermeasures.

The execution of an investment program for emission reduction should address the following aspects:

- air pollution control
- water protection
- waste water treatment
- drinking water supply
- soil fertility rehabilitation
- solid waste disposal

Within the German investment program "Aufschwung Ost", the Federal Government made about 800 mio. DM available to start up priority projects in the Eastern part designed to avert direct harm from undesired developments in the past.

3.7.1 Atmospheric Pollution

Concerning the reduction of the enormous HM load in the atmosphere of East European countries, pollution control programs should be built upon a preventive strategy including the following steps (4):

- application of emission-poor processes and procedures
- substitution/reduction of environmentally adverse resources and products
- use of effective waste gas cleaning techniques
- development and use of technology/methods to avoid, reduce or reuse residuals
- rational use of energy

In a first exemplary attempt to counteract transboundary and long-range air emissions (acid rain) on an international scale, a task force was formed, in 1991, between Poland, the former CSFR and Germany to cooperate within a 'Rehabilitation and Developing Plan', designed for the so-called "Black Triangle".

The sudden opening of the scientific landscape in the East part of the European continent has encouraged the United Nations Economic Commission for Europe to prepare a situation report and update of the HM emission, under the leadership of the former CSFR, emphasising the realisation of

- i establishment of emission factors
- ii emission estimates for selected HMs
- iii technology to reduce emissions
- iv decrees and instruction for limiting emission

The following examples of production reduction or shut-down in the former GDR have already led to a decline of air emissions (1):

- the shut-down of 8 carbide furnaces of the chemical production at Buna, of a chlor-alkaline plant and a quicklime factory should reduce annual dust emissions by 36.000 tons and the annual mercury use by 146 tons
- shut-down, displacement and sanitation of the production of ferrosilicate at Hirschfelde. Lippendorf and Lauchhammer, and of the noble-steel mill at Freital together, with shut-downs and production restrictions of the copper and silver smelting activity at Ilseburg and Hettstedt (Mansfeld area) should decrease the annual emission of HM-enriched dusts by 20.000 tons and of SO₂ by 30.000 tons

3.7.2 Water Quality

Of course, all these remedial measures will also cause a marked weakening of the actual pressure imposed by HM pollution on aquatic systems. Both a carefully planned production stop where environmentally absolute necessary, as well as a reduction of those activities which work no longer under costs including ecological goods and values, will further decrease the input of industrial wastes to air and water.

In fact, the immediate slowdown of several production lines with a high contamination potential in the former GDR, since 1990 (including 39 production plants at Bitterfeld/Wolfen and the manufacture of viscose at Pirna) has already resulted in significant alleviations of the environmental quality of surface waters. For instance, it is expected that the input of degradable organic substances and of mercury into the catchment area of the River Elbe may decrease by 19% (106.000 t) and 4% (1 t), respectively, in comparison with the 1989 level (1).

Due to the implementation of production changes it is estimated that total discharges for mercury and lead to the River Elbe (at Schnackenburg) from the new federal states may decrease, between 1989 and 1991, from 12 to 6.5 t/a and from 110 to 73 t/a, respectively (4).

The safe protection of groundwater resources require preventive means, like

- establishment of nation-wide observation networks ('Grundwassermeßstellen')
- compliance with preventive monitoring
- identification and installation of groundwater protection areas

In order to safeguard the handling of water-hazardous substances during production, transport, storage, turnover and use or consumption, a list should be prepared (like the German 'list of water-threatening substances' with about 714 single components and compounds registered, "Katalog wassergefährdende Stoffe"), in order to identify the hazard properties and potential of those substances, which have to be controlled due to their ecological relevance and amount of production in the respective country.

3.7.3 Waste Disposal

As outlined previously, the careless dumping of partly hazardous waste material, but also routine waste disposal practises in the former GDR (and most probably in other East European countries) was in many cases the main reason for heavy groundwater contamination, also with HMs. First inspections of suspected old waste sites revealed that usually no effective isolation or sealing of the deposit body against groundwater intrusion was guaranteed, for which reason many disposal sites had to be closed immediately.

With regard to future waste treatment and disposal systems, integrated waste management conceptions based on the regional characteristics of a particular area were worked out, on the behalf of the German Ministry for the Environment and the national EPA, according to the following principle: waste handling options give priority to (a) avoidance and (b) reuse, before (c) safe disposal.

The registration and upgrading of the present situation with regard to industrial wastes makes the following steps towards improvement necessary:

- inventory of the amount and type of wastes and evaluation according to well-established international criteria
- inventory of existing disposal treatment sites and also evaluation
- immediate program with recommendations for environmentally safe disposal

- prognosis of type and amount of future waste production
- approaches to avoid and reuse wastes
- long-term recommendations for organisation and structure of future waste concepts

Priorities for new R&D activities in terms of better understanding and solution of future waste generation problems and preventive strategies may include,

- procedures to reduce the amount/toxicity of wastes during raw material production
- suitable techniques to enable a 'barrier' between waste body and surrounding
- ecologically benign biotechnology for rehabilitation of old waste sites
- reduction of waste formation from products (product line analysis)
- waste-poor production lines (best available technology)
- data inquiry and collection as well as processing for proper evaluation of measures for waste management and for modelling ecological and economic effects (4)

In the forefield of necessary stringent environmental regulations, harmonisation and standardisation of test and control methodology, at the highest possible level, should be attempted, at least on a national scale, in particular in relation to internationally accepted guidelines for effect and toxicity (ecotoxicity) evaluation of pollutants, like HMs (see 2). This will become more important for the recognition of old waste deposits and their classification according to their hazard potential.

3.7.4 Environmental Impact Assessment (EIA)

The performance of project-related monitoring programs integrated into both existing, planned or designed ecologically relevant activities of the private and public sector may correct and protect future economic developments from negative and irreversible environmental effects.

The EIA instrument may serve as (1) an early warning system to detect wrong developments in time, (2) to determine the success of remedial measures and alternatives, (3) to document the state of the environment (data base), and (4) as an information source for daily practical work and discussion.

The transformation and early adoption of the EEC-guideline from June 27, 1985, concerning the introduction of Environmental Impact Assessment studies, into national law should equally help to strengthen and speed-up the shift, away from an 'end-of-the-pipe' thinking towards a production-integrated and environmentally preventive policy. There is growing evidence today that cleaning at the end of a production line will inevitably again cause wastes, which may be even more toxic than the raw material or product itself (11).

In this context, access to data and information on material and hazard properties of old and newly introduced products and substance seems decisive for the success and validity of the impact assessment process. The build-up of priority lists for hazardous substances, including HMs could be assigned according to models developed and widely used in West European countries (e.g. the EC 'Envi-

ronmental Chemicals Data Information Network'/ECDIN, the European Inventory of Existing Commercial Substances/EINECS with about 100.000 old chemical substances being on the European market, the 'International Register of Potentially Toxic Chemicals'/IRPTC of the UN Environment Program, or the German EPA 'Rapid Information System on Hazardous Substances'/GSA).

4 Conclusions

Some preliminary conclusions may be drawn from the outline given above, with regard to the prospect of future efforts to improve the situation of pollution, in particular by HMs, in the Eastern European countries.

An attempt was made to highlight those key problem areas, where priority have to be set for immediate or long-term-planned environmental policy.

The obvious lack of sufficient and reliable data on HM emission and contamination for most East European countries has made it unavoidable to relate the statements and comments to the present environmental status of the former GDR, from where a great deal of new data is now available. It is further evident that a simple transfer of the picture and observations presented here is possible to any other historical or geographical factors. Of course, there are some common features which all of these countries share and which were elaborated:

1. There should be an update and strengthening of existing executive monitoring and control instruments in order to respond adequately to the quality objectives set by national legislations.
2. The development of the analytical capacity to detect pollution sources and effects, and to follow up the cost-effect relation of remedial measures, may be a key factor to ensure environmental improvements.
3. Priority areas with a high HM (and other pollutant) contamination should be treated first in order to stop an escalation of the pollution and to encourage further action.
4. International co-operation (bilateral-multilateral) is highly recommended between East and West, both with regard to technical and financial assistance to enable a positive harmonisation and balanced development in Europe.
5. Economy is based on a sound environment, i.e. there is no economic growth without a sustainable environmental and resource management.
6. The 'polluter pays' and 'precaution' principles should become the rule and a political steering instrument to favour environmentally protective technology and the fast integration of the monetary value of environmental benefits into business thinking and planning.

As a final note, it has to be mentioned that despite the vast problems we are faced with today in all East European countries due to both widespread and local incidents of chemical (HM) pollution, there are still many surviving areas saved so far from man's activities. As an example, 10.8% of the territory of the former GDR

(ca. 0.95% in West Germany) are reserved as Natural Protection Area. This very positive heritage from previous planning economy seems rather paradoxical, but is mainly the side-effect of an irregular regional development. It is hoped, that these highly valuable areas will be strictly protected from further pollution, as they still represent almost intact natural ecosystems with a high value for rare and vulnerable species.

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24 Some Remarks on the Contamination of the Environment with Heavy Metals in a Part of Poland

J. Suschka, U. Zielonka

Institute of Industrial Ecology Katowice, ul.Kossutha 6, Poland

1 Contamination of the Atmosphere

The particulates emitted from different industrial processes, including combustion of coal, ferrous and nonferrous metallurgical processes, and cement production, contain many toxic and harmful compounds and elements. Most often, concentration is relatively low in trace quantities.

The presence of the elements in dust particulates in small concentrations does not necessarily mean that the impact on human health is negligible. Some of the trace elements are toxic or harmful themselves, others from compounds which can have an even more pronounced effect. If present in small concentrations but over a long period of time, the effect can be mutagenic or cancerogenic. The high activity and toxicity of trace elements is the result of synergetic interactions.

The dust and gaseous particulates (fly ash) from coal combustion contain principally heavy metals and their compounds. The presence of metals like As, Cd, Co, Cu, Cr, Hg, Pb, Se, Sb, V, and Zn have been confirmed.

In Table 1 the estimated amounts of heavy metals emitted from different industrial sources are given.

The quantity of heavy metals discharged to the environment in Poland, if compared to data concerning Europe, shows a high level. In many cases, the amount of heavy metals emitted in Poland is the highest, if compared with other European countries, with the exception of the former East Germany and the European part of the former Soviet Union. In the case of mercury, about 90% of the metal is emitted to the atmosphere as mercury vapors.

Other metals, like arsenic and selenium are emitted in solid and gaseous form.

In Poland the highest concentration of industry as well as population is in the Upper Silesian Region. In this region there are 14 ferrous metallurgical plants, 2 nonferrous processing plants, 2 zinc-lead ore mines, 55 hard-coal mines, and 23 thermal power and heating plants. About 50% of steel, 98% of hard coal, and 100% of lead and zinc are produced in this region. As a consequence, the Upper Silesian region is responsible for emission of the largest quantity of heavy metals in Poland.

In order to show the magnitude of the problem, in Table 2 the amount of discharged dust particulates is given in comparison to the total amount emitted in Poland.

Table 1. Emission of heavy metals in Poland and Europe. (Pacyna 1988a, b)

Element	Poland t/a	Europe t/a	Poland	x 100%
			Europe	
As	597.0	4945.0	12.07	
Be	8.2	50.0	16.40	
Cd	207.0	1 160.0	17.84	
Co	151.0	2 000.0	7.55	
Cr	1 161.0	18 900.0	6.14	
Cu	1 313.0	15 500.0	8.47	
Hg	40.0	389.8	10.26	
Mn	1 009.0	17 770.0	5.70	
Mo	97.0	850.0	11.41	
Ni	653.0	16 000.0	4.08	
Pb	4568.0	85 520.0	5.34	
Sb	43.0	380.0	11.32	
Se ^a	37.0	420.0	8.81	
V	672.0	34 500.0	1.95	
Zn	4 725.0	42 555.0	11.10	

^a In particulates only

From the data given in Table 2, it becomes evident that the Upper Silesian Region of an area comprising only 2.1% of Poland, discharges 22% of the total amount of dust. It has to be stressed again that the emitted dust particulates contain some amount of heavy metals suspected also of catalytic reactions of gaseous pollutant transformations, especially those of nitrogen oxides (Task Force 1991).

A part of the particulates remains in suspension in the atmosphere for a long period of time, and can be transported to remote regions if the diameter is sufficiently small – usually if below 7 μ m.

Table 2. Dust particles emission in tons/year. (Annual statistic 1991)

Dust particulates	Poland	Upper Silesia	Upper Silesia	x 100%
			Poland	
Total amount	1 950.0	440.7	22.6	
Power plants	1 177.8	250.5	21.3	
Cement process	419.3	78.8	18.8	
Metallurgical process	151.1	57.4	38.0	
Others	202.8	45.8	22.6	

Another part, the larger fraction, is deposited on the surface in the vicinity of the emitter. To give an example, one can mention the dust deposition rate of 26 g/m²/a in Pszczyna, Toszek, or Wielowieś in contrast to 507 g/m²/a in Chorzów. According to Polish standards, the permissible deposition level is 200 g/m²/a.

Beginning in 1990 there a standard of 100 mg Pb/m²/a was set. There are areas where the standard is exceeded many times. In the town of Bytom, the deposition of lead reached 2822 mg/m²/a, i.e., the standard value was exceeded 28 times.

Values above those given by the standards have been determined mainly in the areas close to the industrial plants, especially of the nonferrous branch. Particularly important are the Zinc Plant Miasteczko Śląskie at Tarnowskie Góry, the Mining and Processing Plant Orzel Biały at Piekary Śl., the nonferrous Metallurgical Plant Szopienice at Katowice, the Mining and Processing Plant Bolesław at Bukowno. Also in the area of Zawiercie and Trzebinia the lead deposition standards were exceeded.

Cadmium deposition in Bytom-Radzionków was 87.5 mg/m²/a, which is about nine times higher than the standard limit of 10 mg/m²/a. The distribution of cadmium in the area of the Upper Silesian Region was similar to that of lead (Sanitary Epidemiological Station 1991).

In 1990, the atmospheric air in the Upper Silesian Region, as in the previous years, was highly polluted. The standards of suspended particulates of 50 µg/m³ were constantly exceeded, and the measured concentrations were in the range of 54 to 259 µg/m³. Also in vast parts of the Upper Silesian Region, the average permissible levels of concentration of heavy metals were exceeded (Table 3).

The 24-h standards for dust, lead, cadmium, and zinc have also been exceeded, usually many times. In 1989, according to the decision of the Ministry of Environment, in the yard of the Institute of Environmental Protection at Katowice a monitoring station in accordance with the EMEP requirements was established. An example of results obtained is given in Table 4.

From the data presented in Table 4, a decrease in concentration of pollutants in the last 3 years can be seen. Probably the main reason for this decrease is the economic recession and reduction in the industrial activity. An evident exception is the concentration of mercury, which on the other hand, is also much higher than in other industrial regions of Europe.

Table 3. Results of metal concentrations measurement in ambient air

Metal	Units	Measured concentrations	Standards (av. yearly)
Lead	µg/m ³	0.1 + 3.2	0.2
Cadmium	ng/m ³	2.0 + 119.0	10.0
Zinc	µg/m ³	0.1 + 4.2	3.8

Table 4. Ambient air pollutants – concentration in mg/m^{3a}

Pollutant	1989		1990		1991	1992
	Summer	Heating	Summer	Heating	Summer	Heating
SO ₂	38 (155)	95 (345)	25 (86)	91 (400)	23 (88)	66 (371)
NO ₂	38 (90)	77 (222)	51 (137)	99 (542)	70 (254)	62 (222)
Ozone	– (–)	– (–)	52 (144)	22 (76)	80 (180)	37 (64)
Suspended particulates	– (–)	157 (656)	91 (247)	143 (735)	95 (257)	87 (391)
Sulfates	26.47 (149.55)	31.03 (35.37)	5.51 (19.01)	11.73 (31.49)	7.89 (21.97)	7.63 (33.66)
Nitrates	8.44 (21.61)	10.73 (15.10)	1.78 (6.17)	2.78 (7.63)	1.60 (5.36)	1.71 (5.570)
NH ₄ ⁺	5.25 (19.50)	7.51 (13.07)	2.22 (4.59)	4.70 (12.26)	2.26 (5.79)	2.87 (9.21)
Pb	0.70 (1.779)	0.45 (1.297)	0.67 (3.071)	0.86 (2.015)	0.18 (0.619)	0.25 (0.929)
Cd	0.042 (0.1425)	0.0245 (0.0696)	0.0461 (0.2054)	0.0488 (0.1070)	0.0063 (0.0239)	0.0064 (0.0233)
Zn	– (–)	– (–)	0.668 (1.949)	1.110 (6.321)	2.614 (20.976)	0.737 (2.282)
Ni	0.086 (0.214)	0.104 (0.422)	0.247 (0.739)	0.417 (1.58)	0.079 (0.534)	0.048 (0.270)
Mn	0.458 (1.446)	0.370 (0.947)	0.373 (3.881)	0.418 (1.558)	0.201 (1.220)	0.106 (0.449)
Fe	11.416 (37.704)	7.862 (25.145)	6.805 (28.422)	7.283 (38.148)	8.281 (64.445)	3.174 (10.441)
Hg	0.098 (0.438)	0.088 (0.216)	0.096 (0.282)	0.094 (0.156)	0.110 (0.293)	0.100 (0.185)

^a In brackets the maximum measured values are given.

2 Atmospheric Precipitation

Results of measurements of rainfall contamination at Katowice in the period 1989–1992 are presented in Table 5. It can be seen that there is no distinct tendency in ion concentration, pH, or conductivity changes. Apart from a substantial increase in acidity in the heating period of 1991/1992, pH oscillated close to neutral values. During the heating period 1989/90 pH was somewhat higher and the average value was 6.15. From the range of pH it is however evident that there are occasions of rainfall with a pH of 3.1 and 3.2. Such low values of pH were not found several years ago. In the period 1979–1983 pH changed from 4.3 to 7.6 with an average value of 5.84 (Zielonka 1986).

Obviously, the pH value of the rainwater has a pronounced effect on heavy metal wash-out from the atmospheric air. Based on statistical data evaluation, a significant correlation of metal concentration and pH was stated; Pb ($r = 0.75$), Cd ($r = 0.54$), Zn ($r = 0.54$), Cu ($r = 0.48$), Fe ($r = 0.42$), Mn ($r = 0.40$). The correlation was described by a regression equation $y = ax^b$ with negative b values.

Table 5. Rainfall contamination (mg/dm³)^a

Pollutant	1989		1990		1991		1992
	Summer	Heating	Summer	Heating	Summer	Heating	
Sulfates	18.41 (48.00)	– (50.24)	15.02 (50.64)	23.29 (52.61)	15.59 (51.26)	16.48 (59.58)	
Nitrates	21.10 (111.80)	– (–)	5.37 (17.60)	5.52 (11.97)	3.49 (8.21)	3.89 (19.78)	
NH ₄ ⁺	3.32 (8.79)	6.26	4.19 (14.90)	5.47 (13.70)	3.34 (10.50)	1.62 (2.67)	
Ca	1.85 (11.62)	4.74 (13.40)	2.63 (11.60)	7.69 (29.00)	4.61 (18.00)	4.29 (12.20)	
K	0.61 (1.93)	1.35 (4.04)	1.45 (13.30)	1.36 (2.16)	1.93 (24.00)	0.46 (1.47)	
Na	0.52 (1.54)	1.98 (9.00)	1.99 (16.00)	1.69 (3.17)	0.69 (2.51)	0.85 (2.18)	
Mg	1.02 (2.12)	2.16 (5.44)	1.76 (5.11)	1.60 (3.14)	0.77 (2.23)	1.06 (2.37)	
pH	5.85 (3.1 + 7.1)	6.15 (5.2 + 7.8)	5.66 (4.8 + 6.8)	5.47 (5.0 + 6.5)	5.48 (3.2 + 6.9)	4.34 (3.2 + 5.6)	
Conductivity (μS/cm)	108 (46 + 600)	98 (70 + 140)	82 (46 + 150)	102 (70 + 210)	87 (37 + 172)	104 (38 + 210)	

^a In parentheses the ranges or min-max values are given.

Table 6. Concentration and load of heavy metals in rainfall at Katowice. (Zielonka 1986)

Metal	Concentration Me [$\mu\text{g/l}$]		Load ($\text{mg/m}^2 \times \text{month}$)	
	Range value	Average	Range	Average value
Pb	26.0 + 766.0	173.1	2.29 + 32.34	6.59
Cd	1.6 + 34.2	10.4	0.06 + 1.21	0.42
Cu	2.5 + 109.2	25.8	0.14 + 9.13	1.15
Fe	87.0 + 3934.0	712.5	3.82 + 152.6	28.41
Mn	22.5 + 812.9	155.5	0.61 + 15.46	6.04
Ni	<1.0 + 67.0	9.7	<0.01 + 7.41	0.53
Co	<1.0 + 21.1	2.8	<0.01 + 1.20	0.12
Zn	114.0 + 2753.0	702.1	2.57 + 100.6	27.98
Mg (mg/l)	0.346 + 22.918	3.079	13.77 + 486.9	110.17
Sr	18.5 + 2096.0	167.3	0.40 + 20.54	5.32
Ca (mg/l)	3.94 + 95.71	13.83	81.0 + 1051.0	520.0
Al	69.0 + 5847.0	941.9	0.83 + 96.45	30.3

The measured values of heavy metal concentration in rainfall at Katowice in the period 1979–83 are presented in Table 6, which gives the range of measured metal concentration as well as the flux of metals reaching the ground surface. Most of the metals were present in soluble form, except for lead.

The average concentrations of metals (Pb, Cd, Mg, Fe, Mn, and Ca) within the 5-year period of monitoring were 1.26 to 5.6 times higher than in other industrial areas in Europe and USA (Zielonka 1986).

The metal deposition rate, if compared to that for cobalt, equal to $0.14 \text{ mg/m}^2 \times \text{month}$, was for: Pb – 55, Cd – 35, Cu – 9.6, Mg – 0.18, Fe – 238, Mn – 50, Ni – 44, Zn – 233, Sr – 44, Cd – 4333, and Al – 252 times higher.

The average monthly deposition rates of metals organized for the highest to the lowest values are as follows:

$\text{Ca} > \text{Mg} > \text{Al} > \text{Fe} > \text{Zn} > \text{Pb} > \text{Mn} > \text{Sr} > \text{Cu} > \text{Ni} > \text{Cd} > \text{Co}$.

The noxiousness of rainfall contamination with metals depends not only on the quantity, but also on the form in which the metals are present. The rate of dissolved or solid form was different for the different metals and also the region in which the pollutants had been washed out. Analyzing the forms in which the metals were present, it was concluded that lead had a lower rate of wash-out than cadmium, manganese, nickel, and zinc. The metals washed out by rainfall increase the contamination of the soil. A part, however, especially if there is no buffer capacity of the soil is transported by runoff and groundwater to the hydrosphere. So far there is very little information on the prevailing manner of transportation and loads of metals discharged to surface and groundwater.

3 Contamination of Surface Waters

There are two major rivers, the Vistula and the Odra, which drain to the Baltic Sea. About 95% of the territory of Poland is within the drainage basin of these two rivers.

In contrast to relatively many data about air contamination and related impact on other elements of the environment (e.g., by deposition), there is very little information about the amount of heavy metals discharged to the water bodies. There are two main reasons for the situation. Firstly, heavy metals are discharged with industrial waste water, leaching from industrial solid waste deposition, and with municipal sewage. Also the air-borne part of heavy metals, ending finally in the hydrosphere, cannot be neglected.

Secondly, measurements at selected cross sections of the rivers or at the mouth of the Odra and Vistula Rivers do not provide more general data due to varying hydraulic conditions and depositions of sediments.

Having in mind the mentioned phenomena of suspended solid deposition, measurement of heavy metals at the mouth of the main rivers to the Baltic Sea should give a lower load than expected from the summary of loads from individual discharges.

Although no detailed balance was ever made, a glance at existing data raises many doubts.

According to Heybowicz and Rybinski (1988), the Odra River discharges yearly to the Baltic Sea (in 1987), 14.6 t mercury, 28.4 t cadmium, 198 t lead, 182 t copper, and 1039 t zinc. The Vistula River discharges yearly about 66.7 t mercury, 13.5 t cadmium, 174 t copper, 173 t lead, and 1455 t of zinc.

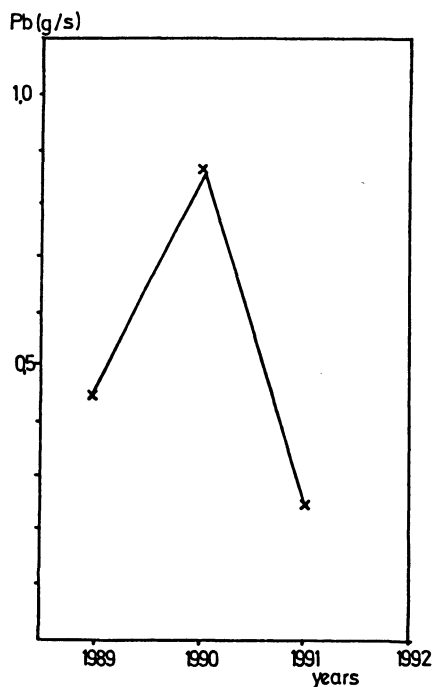
The average values are based on a limited number of measurements. What is very characteristic, as was also given by Heybowicz and Rybinski (1988), is the extremely large difference between the minimal and maximal load of heavy metals. The respective values are given in Table 7.

The waste waters discharged by industrial plants are thought to be the major source of heavy metals discharged to surface water. One of the largest single producers of heavy metals, the Mining and Processing Plant Boleslaw at Bukowno, discharges, e.g., approximately 184 kg Pb/day indirectly to the Vistula River.

At a cross section in Warsaw, the lead content of 30 $\mu\text{g/l}$ was measured on several occasions with maximum values as high as 60 $\mu\text{g/l}$. With a concentration of 30 $\mu\text{g/l}$ and an average flow of about 570 m^3/s , the calculated flux is already close to 1500 kg/day. Figure 1 gives a simplified illustration of the load of lead in the Vistula River. Even if the amount of lead discharged by other industrial plants is of the same order as that discharged from the Boleslaw plant, there will be about 1150 kg Pb/d of unknown origin. Some of the lead is, of course, introduced to the river system with municipal sewage, whose load, however, estimated from available data, seems to be much lower. Based on research, probably the process of metal resolubilization from bed sediment contributes substantially to the concentration measured in river water. One should not underestimate the contribution

Table 7. Amounts of heavy metals discharged to the Baltic Sea by the Odra and Vistula Rivers. (Heybowicz and Rybinski 1988)

Metals	Zn	Pb	Cu	Cd	Hg
Vistula					
Min (g/s)	9.58	0.54	1.61	0.054	0.104
Max (g/s)	314.60	17.71	22.0	2.248	16.942
Average (g/s)	46.14	5.50	5.52	0.428	2.116
Standard deviation (%)	114	78	70	100	142
t/a	1455	173	174	13.5	66.7
Odra					
Min (g/s)	16.73	1.85	3.93	0.432	0.0087
Max (g/s)	59.89	14.97	12.58	2.438	1.5229
Average (g/s)	32.95	6.27	5.76	0.90	0.4617
Standard deviation (%)	36	47	28	47	111
t/a	1039	198	182	28.4	14.6
Total					
t/a	2494	371	356	41.9	81.3
Average (t/d)	6.83	1.02	0.97	0.11	0.22

**Fig. 1.** Changes in the average load of lead in the period 1989–1991 in the Vistula River cross-section Bierun

of contaminated rainfall itself, and runoff from industrial and urban areas, as well as from highways. Without having sufficient data and understanding of the pathways of water contamination with heavy metals, no correct abatement strategy can be selected.

4 Conclusions

1. Ambient air in the Upper Silesia area has a very variable content of metals. In all cases the permissible standards are not met.
2. Even with the recent recession and decrease in production, which resulted in an about 50% decrease in dust pollution, the contamination with heavy metals has not changed very much.
3. The content of metals in atmospheric precipitation depends on the rate and frequency of rainfall, pH and the metal content in the air. Most of the metals are present in dissolved form, except for lead.
4. Rainfall contributes to surface water pollution with heavy metals, although it is not the major source. Most of the metals present in lotic waters originate from nonpoint sources. The surface runoff from industrial deposits and contaminated land cannot be underestimated.
5. River bed sediments can be heavily contaminated with metals, posing a threat to continuous water contamination downstream of the source of pollution for many years.

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