ENVIRONMENTAL RISK ASSESSMENT OF METALS CONTAMINATED SOILS AT SILVERMINES ABANDONED MINE SITE, CO TIPPERARY, IRELAND

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Abstract. A centuries long history of mining and mineral processing has resulted in elevated Cd, Pb and Zn soil concentrations in the vicinity of the Silvermines abandoned mine site (AMS), Co. Tipperary, Ireland. A process for preliminary evaluation of environmental risk was developed and implemented. Potential pathways of metal compound transport and deposition were mapped and used to optimise the subsequent site investigation. Elevated soil metals are shown to be predominantly in areas where metal deposition in soil is associated with water related pathways (surface runoff, seasonal groundwater seepage and floodplains). Extensive areas of soil in the surrounding district are classified as contaminated on the basis of Cd, Pb and Zn concentrations, both total and potential bioavailable (EDTA-extractable). The most affected areas, with metal concentrations in soil comparable with that within the AMS, were floodplains located 2–3 km downstream from the site. Assessment of the sequential effects on grass and grazing animals indicates that Pb poses the greatest risk due to its high toxicity and high concentrations in soil (more than 10 000 mg kg^{-1}). Within floodplain areas grazing cattle may intake a lethal dose of Pb. On the basis of the investigation an approach to risk assessment was developed which allowed quantified assessment of the risks related to individual metals, areas of contamination and contamination targets.

Key words: metal contamination, pollution pathways, risk assessment, soil

1. Introduction

Soil contamination by metals represents one of the major environmental impacts from Abandoned Mine Sites (AMSs) (Thornton, 1993). Not only is soil commonly contaminated within the boundaries of AMSs, but also metal compounds may be delivered to soil in the vicinity of an AMS by wind (as dust particles) or by water related pathways (surface runoff, seasonal groundwater seepage, shallow groundwater table occurrence, or surface water overflow in the floodplains). The characteristics of these pathways are influenced by climatic, hydrologic and hydrogeologic conditions, which determine locations of potentially contaminated areas, where environmental risk of metal contamination in soil is high.

Within the conceptual model of the Environmental Pollution Event soil is considered as a prime recipient of pollution from AMSs, and soil in turn acts as a pathway for metal transformation to vegetation or other elements of the ecosystem.

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Metal concentration in soil in the areas of intensive mining activity may be significant, and particularly high within old mine sites. For instance, metal concentrations in soil in Shipham, Somerset, UK, were 2–360 mg kg^{-1} (Cd), 250–37 200 mg kg^{-1} (Zn) and 108–6540 mg kg^{-1} (Pb). Cd concentration reached 540 mg kg^{-1} in soil polluted by Pb–Zn mining in North Wales, UK, and up to 750 mg kg^{-1} in the vicinity of a Zn smelter in Montana USA (Alloway, 1995).

Since AMSs are also a source of environmental contamination, soil contamination by metal compounds is a common problem in regions with intensive mining activity. Both water related pathways and atmospheric fall-out might contribute to soil contamination. Mining activity in UK has contaminated about 4000 km^2 of mainly agricultural land in England and Wales (Thornton, 1995). Agricultural soils in Northeast Wales contained 920–5897 mg kg^{-1} of Pb and garden soil contained 920–5897 mg kg^{-1} of Pb. In this area about 47 km^2 of soil had Pb concentrations ranging from 1000 to more than 10 000 mg kg^{-1}.

In a review of previous research, Alloway (1995) concluded that within 1–3 km of a well-established smelter, soils were likely to contain about 1500 mg kg^{-1} Pb, an enhancement of 15 times the background level. However values may be much higher in close vicinity of the stack. For instance, in Derbyshire, UK, within 100 m from an old smelter the mean Pb soil content was 30 090 mg kg^{-1}. Anomalous Cd concentration was detected as far as 40 km from a smelting complex in South Wales, UK, and up to 10–15 km from the Avonmouth smelter, near Bristol, UK.

In comparison with smelting emission, dust generated within AMSs causes soil pollution within a shorter distance from the source. For example, in the vicinity of the Avoca AMS, Pb concentration reduced from 1000 mg kg^{-1} at the AMS to less than 150 mg kg^{-1} at 200 m distance from the AMS (Gallagher and O'Connor, 1997).

Mine waste is often classified as non-point-source pollution. For such case surface runoff becomes an important pathway of pollutant transport (Clark, 1998). In addition contaminated surface runoff may cause soil pollution downgradient from its source (Calco and Perez, 1994; Niagu *et al.*, 1998).

Another example, given by Alloway (1995), illustrated the effect of fluvial sediment re-deposition on metal content in soil. Alluvial soils in the Ystwyth river valley contained 90–29 000 mg kg^{-1} of Pb, compare with 24–56 mg kg^{-1} in neighbouring valley which was not affected by mining, alluvial soil in the Tamar valley contained Pb 60–1000 mg kg^{-1} while in upland areas above the AMS Pb concentration was 62–850 mg kg^{-1}.

The metal content of soils is of major significance to their fertility and nutrient status. Many metals, such as Zn, Cu, Se, are essential elements for normal growth of plants and living organisms, however at high concentrations, these metals become toxic. Metals, which are not known to be essential for plant growth, such as Pb or Cd, may be tolerated by the ecosystem in low concentrations, but are harmful in higher concentrations (Alloway and Ayres, 1993). Not all the metals present in soil may be biologically available. Their bioavailability is influenced by many factors, particularly pH, temperature, redox potential, cation exchange capacity of the solid phase, competition with other metal ions, ligation by anions and composition and quality of the soil solution (Merian, 1991). The rate of metal transformation from soil to vegetation depends on vegetation type and metal type (Alloway, 1995). Transfer coefficients (concentration of metal in plant relative to total concentration in the soil, which is 1–10 for Cd, 0.01–0.10 for Pb and 1–10 for Zn) are a convenient way of quantifying the relative differences in bioavailability of metals to plants. Metals may also become bioavailable through direct soil or dust digestion by organisms. For instance, the amount of soil which may be consumed by cattle may reach up to 10% by weight of total grazing intake (Thornton and Abrahams, 1983). Metal re-mobilisation in conditions similar to those in an animal stomach may reach 60–70% of total metal concentration in soil. As a result animal health may be significantly damaged, and in some cases poisoning by metal compounds may be lethal.

Environmental risk assessment of contaminated land, including AMSs, does not follow standard protocol and is usually based on different methods, borrowed from various scientific disciplines and adopting various models (Ferguson *et al.*, 1998). A simplified approach to risk assessment may be based on comparing the measured level of contamination with established guidelines or screening values. A functional approach to risk assessment of contaminated sites takes into account

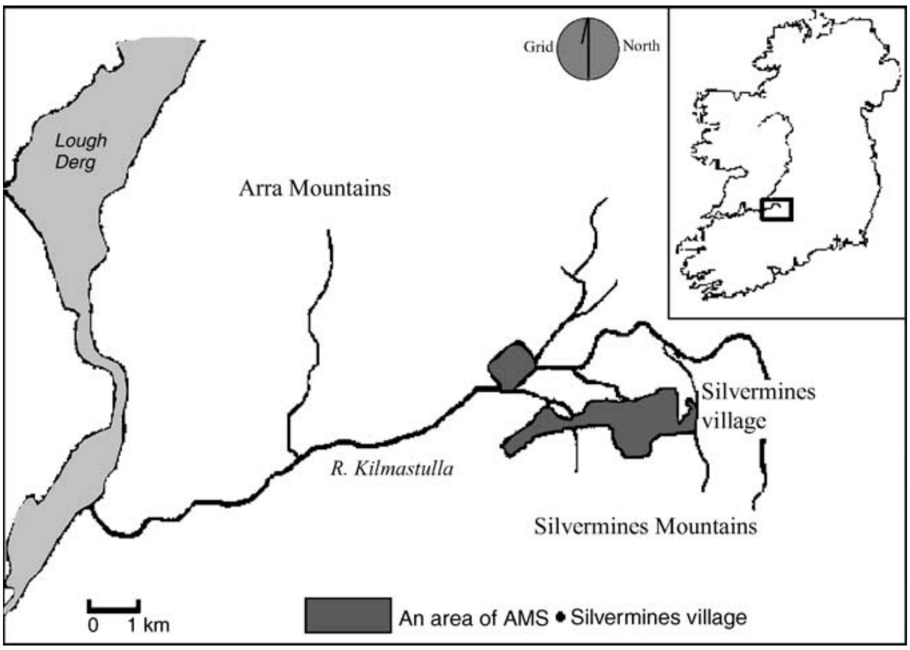

Figure 1. Location of the Silvermines AMS.

potential soil reuse, with target concentrations set for garden soil < playground soil < green field soil < industrial areas (Bieber, 1998; Marioti, 1998).

As a part of wider investigation of the area, which also included analysis of natural water quality and fluvial sediment contamination, soil contamination by Cd, Pb and Zn in the vicinity of Silvermines AMS (Co. Tipperary, Ireland) (Figure 1) was investigated, so as to allow assessment of biological availability of these metals and relevant environmental risk within a framework of preliminary site investigation. From the previous studies it was known that soil within an AMS is usually heavily contaminated. For instance Steinborn and Breen (1999) reported Pb = 1830–25 500 $mg\,kg^{-1}$ in soil at the Shallee mine site, and Pb = 16 000–50 000 $mg\,kg^{-1}$ was detected at the Silvermines village, South Ballygown site (Aslibekian and Moles, 2000). However metal concentrations in soil in the area surrounding the AMS were largely unknown.

Therefore, the main objectives of the research were to identify the extent of soil contamination by Cd, Pb and Zn in the vicinity of the old mine sites in the Silvermines area, and to assess a potential environmental risk caused by soil contamination. The study was carried out as a preliminary stage of site investigation, during which the areas of soil contamination were delimited and initially characterised, aiming to develop a basis for a detailed site investigation.

2. Silvermines AMS – case study

The mining history of the site goes back for centuries. However, most intensive mining activity was related to the 19th and particularly 20th centuries. As a result of mining activity, intensive underground working, open pits, spoil heaps, tailing ponds, and other undefined mine waste are sporadically located along the northern slope of the Silvermines mountain range and the R. Kilmastulla river valley, stretching from the west to the east for about 5 km, occupying an area of about 2.7 km^2.

In the Silvermines area, Zn–Pb–Ba mineralisation occurs within basal Carboniferous (Courceyan) transgressive siliciclastics and in the overlying carbonate sedimentary rocks. The base-metal ore contained galena, sphalerite, pyrite, barite and siderite. Pb-rich ore is more common in western areas of the mineralisation, while Zn prevails in eastern zones of the mineralisation.

Basing of the geological map of the area (Archer *et al.*, 1996), the geological formations in the Silvermines region may be grouped into two categories with respect to their buffering capacity: (i) Carboniferous Formations, mainly limestones – formations providing ‘infinite’ buffering capacity; and (ii) Devonian, mainly sandstones, and to a lesser extent Silurian Formations, mainly slates – formations providing limited buffering capacity (Figure 2). As a result in the western areas of the mined region (Shallee) the buffering capacity of the environment is lower, resulting in lower pH in soil and in natural water. Here Pb ore was mainly hosted by Old Red Sandstones and the acidity of mine water and

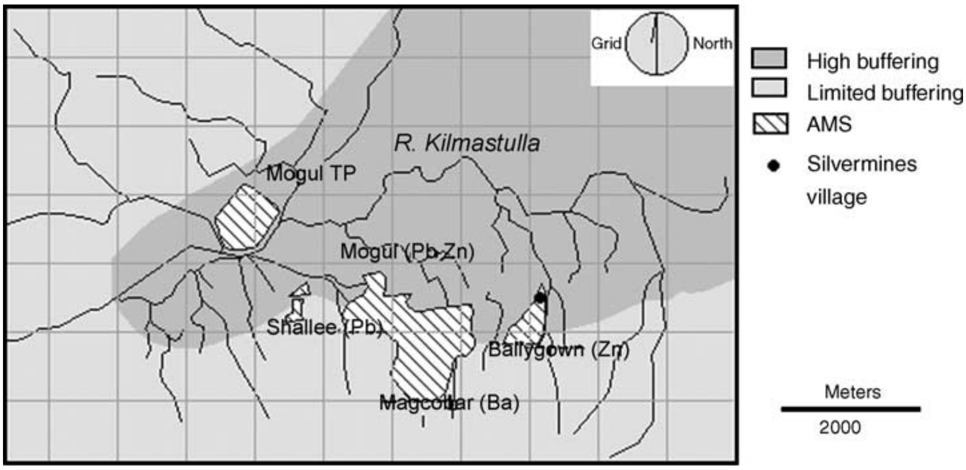

Figure 2. Buffering capacity of the geoenvironment in the Silvermines area.

seepage from tailing ponds is higher. Due to the mineral composition of mined ore, in the Shallee area Pb is likely to dominate as a pollutant, while in the area of the Silvermines village Zn is expected to be in high concentrations in mine drainage and soil.

Geological setting also influences soil type and three main soil series are represented (Finch and Gardiner, 1993).

(a) Elton series occur on limestone formations and are found on slopes <5°. This soil is mainly well-drained and of loam to clay-loam texture. Topsoil pH is 6.0–7.3, which increases with depth. It has a wide use range, and it is highly suitable for tillage and grass production over a long season.

(b) Borrisoleigh series are associated with the slopes ranging between 5° and 30°. The pH is normally acid (4.3–4.6), increasing with depth (5.7–6.0). The texture of the topsoil is a clay loam to silty clay loam. Use of this soil is limited by topography and high runoff. Where the slope is favourable it gives a good grass yield and is suitable for tillage. Due to its acidity the Borrisoleigh soil series is the most sensitive to metal contamination.

(c) Feale series are formed from alluvium on river floodplains. The surface horizon is plastic and sticky and has a loam to clay-loam texture. Topsoil pH is 5.3–5.8. This series supports only grazing, being unsuitable for tillage due to heavy texture, poor drainage, high water table and high risk of flooding.

A number of farms and Silvermines village are located close to the AMS. Most of the terrain is grassland with some forestry to the south of the village, upslope from the mined area. Grassland is mainly used for grazing, and only a few fields are tilled.

A number of environmental incidents related to the Silvermines AMS have occurred during mining and after closure. The Mogul mining company was fined for polluting a stream near the mines (1976); a major spill of tailings into the R. Kilmastulla affected 15% of the Limerick City drinking water supply (1980); dust blow from the tailing pond affected an area of more than 2 km^2 (1985). The cattle deaths by Pb poisoning have been reported previously (O'Sullivan, 1999).

3. Research method

A generic approach to site investigation was developed to assess the environmental risk associated with AMSs. Contamination pathways were considered a key-issue in determining the preliminary soil sampling programme, which is designed to optimise site survey by minimising the cost of investigations. The following potential contamination hot spots were preliminary mapped, using GIS methodology (Figure 3) (Aslibekian and Moles, 2001):

(a) The area downwind of the AMS (to the east) relative to prevailing wind direction (westerly), where soil may become contaminated due to dust emission and re-deposition;
(b) The area affected by contaminated overland runoff from the mine sites, where metal compound in dissolved and particulate forms compounds may be re-deposited downslope from the mine site;
(c) The area where groundwater contaminated by old mine sites may form shallow water table or seepage zones downgradient from the mine sites; in such zones metal in dissolved forms may be delivered to soil;
(d) Floodplains of the R. Kilmastulla downstream from the mined area, where contaminated fluvial sediments (Aslibekian and Moles, 2001) may be distributed over soil.

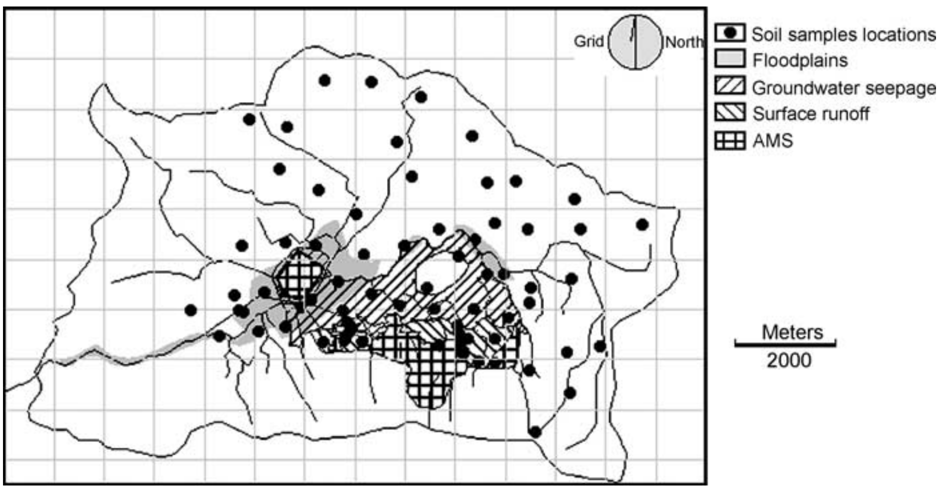

Figure 3. Contaminated areas in the vicinity of the Silvermines AMS and soil sampling sites.

For comparison a traditional soil survey approach was also adopted and samples were collected on a grid basis with a frequency of one sample per km^2, where access to sites permitted. Since the mountain slopes above the AMS are not involved in any human activities, soil was not sampled to the north from the mine sites.

During 1998–1999 both soil and grass samples were collected in the vicinity of the Silvermines AMS and tested in the laboratories at the University of Limerick. Overall more than 70 samples were collected from an area of about 50 km^2, including 43 samples collected on a grid-based sampling programme and 28 samples collected within the preliminary delimited hot spots with additional 10% duplicate sampling (Table I). Each soil sample comprised 25 sub-samples, taken by an auger at intersecting points of a 5×5 m grid, from a depth of 0–10 cm. In the laboratory, air-dried samples were passed through a 2 mm sieve, and then ground to a fine powder. Using standard techniques, samples were tested for pH, loss-on-ignition (LOI) and moisture content (Rowell, 1994).

Soils were analysed for Cd, Pb and Zn, which were considered to be the most likely pollutants generated by Pb–Zn–Ba ore residuals, which were mined in the area (Smith *et al.*, 1994).

Total and potentially bioavailable metal concentrations in soil were determined. For the total metal concentration samples were digested by concentrated nitric acid (5 ml conc. HNO_3, 0.500 ($\pm$0.001) g, boiled until liquid volume halved, filtered and diluted to 25 ml). Potentially bioavailable metals were extracted by 0.05 mol L^{-1} EDTA at pH $= 7.0$, as is common practice in agricultural soil analysis (Fleming and Parle, 1974). Metal concentrations in filtrates were measured by Atomic Absorption Spectrometer (AAS). Accuracy of the results was controlled by the use of reference materials (GBW07404 Soil and GBW07405 Soil from LGC' Office of Reference Material), duplicate sample collection and duplicate soil extraction.

Metal concentrations in soil were compared with trigger values for total metal concentrations and guideline values for EDTA-extractable metal concentrations (see Table I). The trigger values are available from the 'Dutch list' (Ferguson *et al.*, 1998), which is widely used in many European countries for assessment of soil quality. Classification of soil contamination based on EDTA soil extraction was developed by Fleming and Parle (1974) and used for assessment of agricultural soil contamination in Ireland.

Bioavailability of soil metals was also assessed by measuring the metal concentration in grass samples collected from the same sampling locations as for soil within the delimited hot spots. In the laboratory, samples were washed and roots were separated from leaves. Oven-dried samples (105 °C) of 0.500 ($\pm$0.001) g were digested with concentrated nitric acid. Metal concentrations were again determined using AAS. Accuracy of the results was controlled by the use of duplicate sample collection and duplicate digestions.

Cd and Pb concentrations in grass were classified as excessive at levels greater than background values for unpolluted herbage in Irish environmental conditions (see Table III) (Minorco Lisheen EIS, 1995). As Zn is included in a group of

TABLE I

Metal concentration in soil (mg kg^{-1}) (mean values (underlined) and range are given)

	Uncontaminated area	Flood plains	Groundwater seasonal seepage	Surface runoff (Magcobar)	Surface runoff (Shallee)	Trigger guidance values
Cd						
Total	2.1 (0.4–3.2)	3.6 (1.3–9.13)	1.26 (0.85–2.05)	1.14 (0.65–1.60)	1.19 (0.95–1.50)	12[a]
EDTA	0.3 (0.1–0.6)	2.39 (0.75–4.85)	0.94 (0.64–1.55)	0.88 (0.56–1.26)	0.91 (0.85–1.13)	0.8[b]
Pb						
Total	154 (16–360)	4835 (606–10256)	1129 (225–2500)	985 (781–1270)	1678 (1066–2051)	530[a]
EDTA	4 (2–9)	1761 (320–3820)	597 (128–1220)	219 (138–382)	1000 (760–1400)	25[b]
Zn						
Total	131 (28–395)	8924 (50–35109)	930 (300–1700)	3639 (424–14428)	500 (400–600)	720[a]
EDTA	5 (2–22)	628 (70–1696)	121 (24–336)	116 (50–279)	67 (30–100)	20[c]
pH	5.1–7.0	5.7 (4.8–6.4)	5.6 (5.4–6.2)	5.7 (4.6–6.4)	4.8 (4.2–5.2)	
LOI	5.2–35.0	10.7 (8.1–14.4)	13.1 (8.5–18.4)	8.7 (7.6–12.3)	9.7 (8.2–14.8)	
Air-dry moisture	1.9–9.0	4.8 (3.5–9.0)	4.3 (2.8–5.6)	2.4 (1.9–3.0)	2.9 (2.0–3.5)	
Sample, *n*	33	11	11	8	8	
Area, km^2	>30	3.5	2.0	2.5	2.5	

[a] Ferguson *et al*. (1998).
[b] Fleming and Parle (1974).
[c] Indicates moderate level of contamination.

essential metals, the excess of the requirement limit for animal consumption was taken as the risk assessment criteria.

4. Metal content in soil

The soil test results are given in Table I. The average air-dry soil moisture content was found to be 3.1% with a minimum of 1.9% and a maximum of 9.0%, with most samples in the range of $M = 1.9$–4.0%. Average LOI was 11.7% with a minimum of 5.2% and a maximum of 35.0%, but most samples were in the range of 7.4–12.2%. Soil pH ranges from 4.2 to 7.0 with a mean of 5.5, which falls within the normal range for Irish soil pH (4.0–8.5).

Only 10 soil samples (22%) collected on a grid-based soil sampling programme contained metal concentrations, indicating soil pollution by Cd, Pb and/or Zn on the basis of total and EDTA-extractable concentrations. However analysis of all samples collected within preliminary delimited hotspots indicated soil contamination.

4.1. GENERAL CHARACTERISTICS OF SOIL METAL CONTENT

Total Pb and Zn concentration in soil (Figure 4) decreases with distance from AMSs, with concentrations greater than trigger values within about 400 m of mine

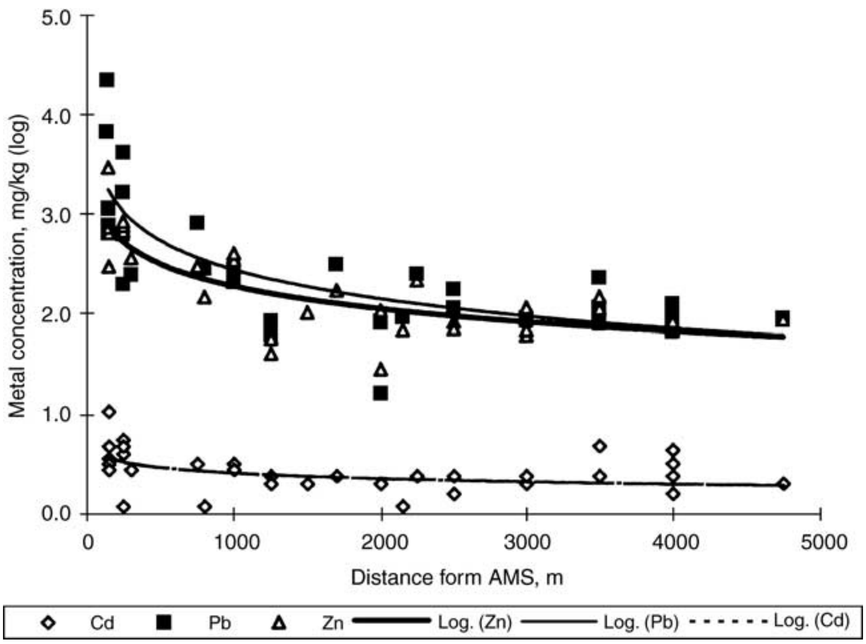

Figure 4. Changes in Pb and Zn concentrations with distance from the AMS.

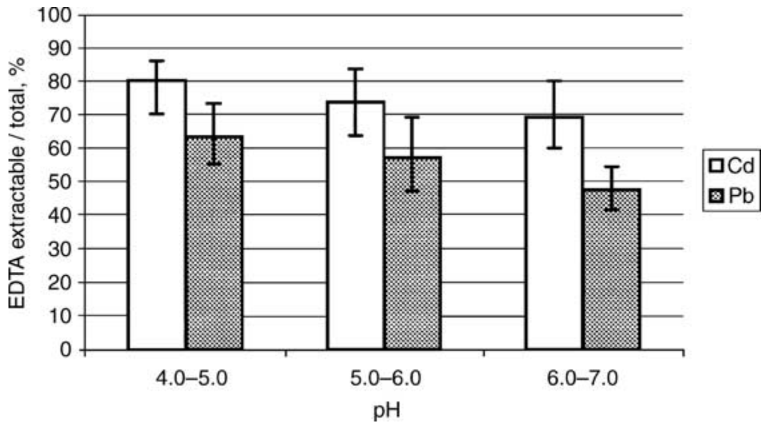

Figure 5. Effect of soil pH on the ratio between EDTA-extractable and total metal concentrations for Cd (a) and Pb (b).

sites. The average concentration of total Pb is highest within 140 m of the AMS ($Pb_{av} = 6470\,mg\,kg^{-1}$), decreasing within the 400 m zone ($Pb_{av} = 650\,mg\,kg^{-1}$), and decreasing to less than trigger values ($>530\,mg\,kg^{-1}$) further from the AMS. Total Pb $= 1590\,mg\,kg^{-1}$ was detected in garden soil in the Silvermines village, located in close proximity to the mine sites. Average total Zn concentration is highest within 140 m from the AMS ($Zn_{av} = 1040\,mg\,kg^{-1}$) and become lower than trigger values ($<720\,mg\,kg^{-1}$) further from the site. Only total Cd concentrations remain low ($<12\,mg\,kg^{-1}$) in the vicinity of the mine site.

Contrary to the trends of declining soil metal with distance from the AMS, the highest total Pb and Zn concentrations (Pb $> 10\,000\,mg\,kg^{-1}$ and Zn $> 5500\,mg\,kg^{-1}$), outside the AMS were found in two floodplain soil samples from more than 2 km away from the AMS.

Within contaminated zones there was a significant correlation between total and EDTA-extractable metal concentration in soil. The linear regression equations for a data set of 38 samples is as follows:

$$Cd_{EDTA} = 0.5376Cd_{total} + 0.3377 \quad R^2 = 0.9387;$$

$$Pb_{EDTA} = 0.4228Pb_{total} + 135.1 \quad R^2 = 0.9633$$

The ratio between EDTA-extractable/total Cd and Pb concentration tends to increase in the lower soil pH range (Figure 5), suggesting a greater bioavailability of these metals in soil with lower pH.

4.2. SOIL METAL CONTENT WITHIN DELIMITED HOT SPOTS

The soil sampling programme based on potential pollution pathways from the AMS provided decisive outcomes. It was found that excessive accumulation of metal in soil is exclusively found in areas where they are delivered by water related pathways (surface runoff, groundwater and surface water). Dust emission does not play a significant role in pollution distribution due to the prevailing wet climatic conditions. The absence of soil contamination outside of the defined water-related pollution pathways was confirmed by the grid-based soil sampling.

4.2.1. *Area affected by surface runoff (2.5 km^2)*
Comparison of metal concentrations in soil collected in the areas downslope from the Shallee mine site to the Magcobar mine site shows the effect of geological setting, soil type and ore type. At Shallee, sandstone and slate bedrock has low buffering capacity. Soil of the Borrisoleigh series developed on these clastic rocks is more acidic than in the other areas (pH = 4.8). At the Magcobar site, there are Carboniferous limestones Elton series soils with pH = 5.7.

As a result, total and EDTA-extractable Pb concentrations in soil at Shallee, where mainly Pb-ore was mined, are higher than in the area downslope from the Magcobar site, while Zn concentrations were lower at Shallee in comparison with the Magcobar site (Table I). However the proportion of EDTA-extractable metals in soil was noticeably higher at Shallee, due to higher soil acidity. EDTA-extractable Pb composed 60% of total soil Pb at Shallee compared to 22% at Magcobar (Table II). Fifteen percent of total Zn was EDTA-extractable at Shallee against 5% at Magcobar.

4.2.2. *Areas where soil contamination is related to groundwater (2 km^2)*
Areas of shallow groundwater table occur (1) along the mountain foot and are marked by stream sources, and (2) along the river valley, where fens have developed. Though total metal concentrations in these areas are within the range of concentrations in soil affected by surface runoff from the mine site (Table I), EDTA-extractable metal concentrations are on average twice greater. The EDTA-extractable metal concentrations exceeded the guidance values by a factor of up to 36 for Pb and 17 for Zn. As a result, the ratio between EDTA-extractable and total metals was high and comparable with those in acidic soil at Shallee (53% for Pb and 13% for Zn) (Table II).

TABLE II
The proportion of metal concentration which is exchangeable in soil within various locations (%)

Metal	Soil on floodplains	Soil within groundwater seasonal seepage area	Soil affected by surface runoff	
			Magcobar site	Shallee site
Cd	66	74	77	77
Pb	46	53	22	60
Zn	7	13	5	15

4.3. AREAS WHERE SOIL CONTAMINATION IS RELATED TO SURFACE WATER: FLOODPLAINS (3.5 KM^2)

Pb and Zn concentrations in soil on floodplains were found to be comparable with those from the mine sites (Table I). Their total concentrations were up to 20 (Pb) and 50 (Zn) times greater than threshold values. All tested metals exceed guidance values for EDTA-extractable concentrations by up to six times (Cd), 150 times (Pb) and 85 times (Zn).

5. Metal bioavailability in soil

The biological availability of metals in soil is not only dependent on metal speciation but also on the receptors of soil contamination, such as different types of vegetation and living organisms. It is assumed that the EDTA-extractable metals concentration correlates closely with the concentration of metals available for uptake by vegetation (grass). Grazing animals are at risk from consumption of contaminated grass (function of bioavailable metal) and direct ingestion of attached soil (function of total metal).

5.1. METAL IN GRASS

Metal concentrations in grass leaves are given in Table III. It was assumed that metal concentrations in grass leaves rather than roots provide an indication on

TABLE III
The range of metal concentrations in grass leaves and grass roots

Hot spot class	Cd, mg kg^{-1}		Pb, mg kg^{-1}		Zn, mg kg^{-1}	
	Leaves	Roots	Leaves	Roots	Leaves	Roots
3RO						
Magcobar	0.11–0.23	0.31–0.83	30–45	70–100	14–28	67–149
Shallee	0.10–0.21	0.38–0.87	40–80	90–210	4–12	39–230
4GW	0.05–0.40	0.20–1.30	50–70	40–260	5–87	63–290
5SW (floodplain)	0.16–1.98	0.63–3.20	50–80	70–800	9–90	47–480
Animal requirement	Nil		Nil		20–100	
Uncontaminated Irish herbage	0.01–0.3		0.5–20		20–60	

metal availability in soil. Because of the limited extent of dust emission from mine sites, metal concentrations in leaf samples from the Silvermines area are believed to be little influenced by metal compounds adhering to their surface. Thus higher metal concentrations in grass leaves with similar coefficient of metal translocation from soil to leaves are found where metal bioavailability in soil is greater.

Within the sampled area Pb concentration in grass is 1.5–4 times greater than in uncontaminated herbage, typical for Irish environmental conditions ($>20\,mg\,kg^{-1}$) (Fleming and Parle, 1974). Zn content in grass on floodplains and in areas of groundwater seasonal seepage also exceeded the values for unpolluted Irish herbage ($>60\,mg\,kg^{-1}$). However, Zn is still within the animal requirement limits (20–100 $mg\,kg^{-1}$). Cd concentration greater than that in unpolluted Irish herbage ($>0.3\,mg\,kg^{-1}$) was found only in grass collected from the floodplains and in the zone of shallow groundwater table occurrence.

Higher metal content was found in grass on floodplains ($Cd_{av} = 0.63\,mg\,kg^{-1}$, $Pb_{av} = 62\,mg\,kg^{-1}$, $Zn_{av} = 40\,mg\,kg^{-1}$) while the lowest were mainly found in areas affected by runoff from the Magcobar AMS ($Cd_{av} = 0.17\,mg\,kg^{-1}$, $Pb_{av} = 38\,mg\,kg^{-1}$, $Zn_{av} = 19\,mg\,kg^{-1}$) (Figure 6). Pb and Zn concentrations in grass leaves from the area affected by groundwater seepage downgradient from the AMS ($Pb_{av} = 60\,mg\,kg^{-1}$ and $Zn_{av} = 42\,mg\,kg^{-1}$) are comparable to grass from the floodplains, which indicates higher Zn and Pb bioavailability in these areas (Figure 6). Cd is also found to be more biologically available in areas of groundwater seepage. Cd concentration in grass collected from soil with a similar range of EDTA-extractable Cd concentration (0.8–1.5 $km\,kg^{-1}$), demonstrated highest values for areas of seasonal groundwater seepage and lowest values in areas affected by surface runoff from the AMS (Figure 7). Pb uptake by grass leaves was also greater on more acidic soil ($Pb_{av} = 54\,mg\,kg^{-1}$ at the Shallee site).

Pb and Zn concentrations in grass leaves correlate with soil metal concentrations. Where EDTA-extractable Pb concentrations in soil were greater than guideline values ($>50\,mg\,kg^{-1}$), Pb in grass leaves exceeded the range for unpolluted herbage in Irish conditions. Zn concentrations in grass leaves also correlated with EDTA-extractable Zn in soil, but in the grass leaf concentrations fall within animal requirement limits, even where Zn concentration in soil is the highest (for instance, on floodplains $Zn_{EDTA} = 1695\,mg\,kg^{-1}$ and $Zn_{grass} = 63\,mg\,kg^{-1}$). This and the fact that potentially bioavailable Zn composes the smaller proportion of total Zn confirmed that in the Silvermines area Zn is likely to be less mobile and therefore less bioavailable than Cd and Pb.

Cd concentration in leaves exceeds the range for Cd concentration for uncontaminated herbage, only when EDTA-extractable Cd concentration in soil is higher than $1.3\,mg\,kg^{-1}$. This suggests that in the Silvermines area the threshold value for EDTA-extractable Cd, indicating some level of contamination in soil is likely to be higher than the general $0.8\,mg\,kg^{-1}$ guideline, as is recommended in Ireland (Fleming and Parle, 1974).

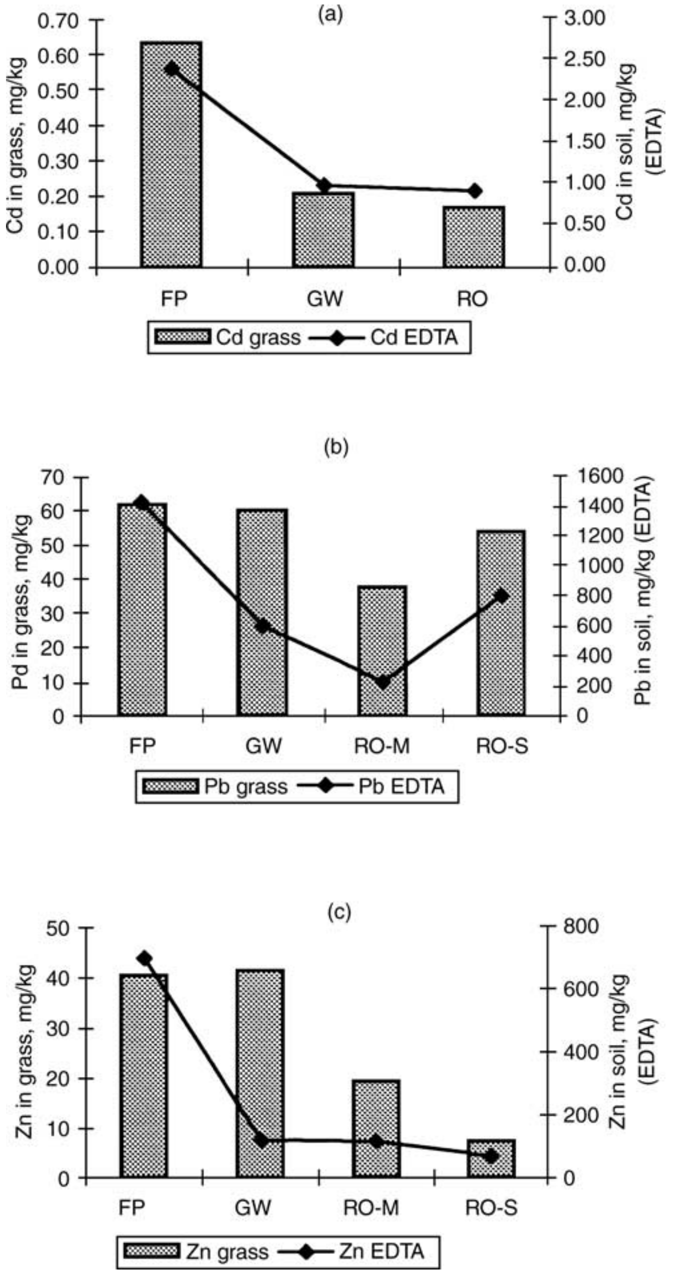

Figure 6. Average Cd (a), Pb (b) and Zn (c) concentrations in grass leaves and soil within various areas: FP – floodplains; GW – seasonal groundwater seepage; RO – surface runoff in the Magcobar and Shallee areas.

Therefore high bioavailability of the studied metals, as indicated by EDTA-extractable metal in soil and metal concentration in grass leaves, suggests that high bioavailability of studied metals is associated with three particular

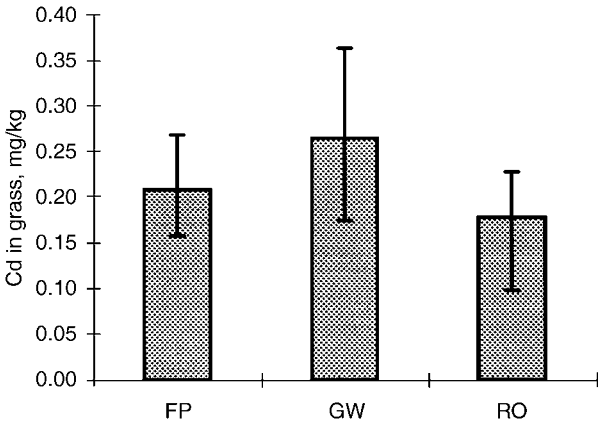

Figure 7. Average Cd (a) concentrations in grass leaves collected from soil with similar EDTA-extractable Cd concentration (0.85–1.5 mg kg^{-1}) in various areas: FP – floodplains; GW – seasonal groundwater seepage; RO – surface runoff.

circumstances:

(a) Where metal concentration in soil is extremely high (floodplains or mine sites).
(b) Where soil pH is low (particularly for Pb).
(c) Groundwater discharge zones, where metal compounds were deposited in soluble forms.

Since metal uptake by various types of vegetation is specific to individual species (Merian, 1991), metal uptake by grass may be considered only as an indicator for metal bioavailability in the area. Due to the local predominance of grazed pasture in the area, the results adequately describe environmental risk related to the major type of land use. They also allow assessment of the risks for grazing animals, which is considered next.

5.2. METAL INTAKE BY GRAZING ANIMALS

In the prevailing pastoral grazing landuse environment, uptake of metals by vegetation allows metals to enter the food chain. In order to assess the risk for cattle, the potential consumption of metals from contaminated zones in the Silvermines area was considered. A few assumptions were made (Ferguson *et al.*, 1998).

1. During grazing, intake of soil by cattle may reach up to 10% of fodder by weight. Consumption of grass leaves and roots were taken to be in a ratio of 50:50.
2. Cattle on average consume 15–20 kg per animal per day.

3. Pb may cause different degrees of poisoning depending on the method of intake.
   (a) Lethal poisoning in cattle results from ingestion of about 10 g Pb.
   (b) The same result occurs when animals receive feed with lead concentrations of 300–400 mg kg^{-1} dry matter for a period of over two weeks.
   (c) Symptoms of intoxication in ruminants can be expected in the case of feed concentrations over 50 mg kg^{-1} dry matter over a period of several months.
4. Zn poisoning may occur when the concentration in feed is about 1000 mg kg^{-1} dry matter.
5. Cd poisoning by a single oral dose of 5–10 mg kg^{-1} body weight is lethal, which on average for cattle is 2.5–5 g. Concentrations in feed of 25 mg kg^{-1} can cause bone metabolism in farm animals disorders after six months.

On this basis, the amounts of Cd, Pb and Zn, which may be consumed by cattle during grazing, were estimated. Pb was found to be the most hazardous of the three metals studied. In a number of locations, cattle could receive a lethal Pb dose during a single day of grazing (Figure 8). These sites are mainly located within the floodplains and also in the groundwater seepage zone downgradient from the Shallee tailings pond. Conditions for cattle grazing on some fields have the potential to cause lethal doses over a two week period. At all other sampling locations within the potential pollution pathway zones, cattle grazing over several months within pollution hot spots may suffer some symptoms of poisoning. Cd does not represent a significant risk for cattle outside the mine sites. Intake by cattle of Zn at a level causing poisoning was found on floodplains.

Therefore high metal concentrations in soil may become a significant threat to farming activity. Areas where Pb concentrations in soil are above 3000 km kg^{-1}

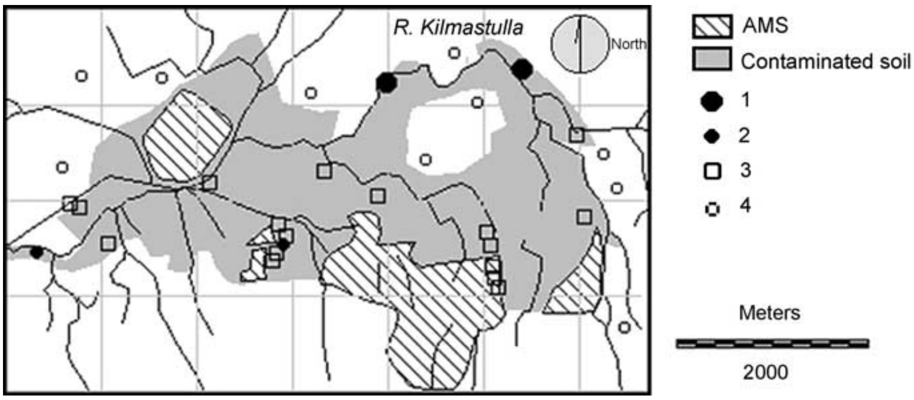

Figure 8. Risk of Pb intake by grazing cattle (1 – extremely high risk (single day of grazing may result in intake of lethal Pb dose); 2 – high risk (two weeks of grazing may result in intake of lethal Pb dose); 3 – moderate risk (symptoms of intoxication may occur in several months of grazing); 4 – low risk.

pose a high risk and use for grazing should be restricted. Those in the Silvermines area include the AMS and floodplains downstream from the AMS.

6. Environmental risk assessment

Environmental risk assessment is based on the hazard posed to defined receptors. Depending on the assessment aims, the risk may be rated to trigger values for metal concentrations in various environmental media, specific pollutants, endangered attributes of environment, or pollution targets.

Preliminary investigation of soil contaminated by Cd, Pb and Zn in the vicinity of the Silvermines AMS, Co. Tipperary, Ireland, and analysis of effects on vegetation and grazing animals allowed identification of zones of high environmental risk. Water related pathways are the most important means of pollutant transport in the area. The adopted investigation methodology, based on the initial delimitation of potential contamination zones, allowed an optimised sampling programme and provided a basis for the generalisation of the results.

Apart from soil within the mine sites, extremely high levels of total metal concentration were found in soil on floodplains downstream from the AMS (Pb more than 10 000 mg kg^{-1}; Zn up to 35 000 mg kg^{-1}). This is related to redistribution of fluvial sediment, which is the most polluted media in the Silvermines area with concentrations of Cd, Pb and Zn reaching 28, 6400 and 20 000 mg kg^{-1} respectively (Aslibekian and Moles, 2001). Soils were also found to be polluted by Pb and Zn in areas affected by surface runoff from the AMS, and in areas of seasonal groundwater seepage, where Pb and Zn concentrations were greater than 530 and 720 mg kg^{-1} respectively. Outside those areas soil contamination was not detected.

Potentially bioavailable metal concentrations (EDTA-extractable) are also high in acidic soil (Shallee) and groundwater seepage zones, which are comparable with those on floodplains. EDTA-extractable concentrations for all studied metals, including Cd, were greater than guideline values for polluted soils. The ratio of EDTA-extractable to total Cd was greatest and for Zn was the lowest of the three metals studied.

There is a clear correlation between EDTA-extractable metal concentrations in soil and grass. Bioavailability of metals was found to be higher in the areas of groundwater seepage and in soil with lower pH (at Shallee). This indicates that metal mobility and therefore environmental risk may be expected not only in the areas where total metal concentration in soil is extremely high (such as floodplains), but also where soil pH is low and where seepage of contaminated groundwater occurs.

Cd concentration in grass indicated pollution when EDTA-extractable Cd was greater than 1.3 mg kg^{-1} in soil. Zn concentration in grass did not exceed the animal requirement level for this element (20–100 mg kg^{-1}) even in the most polluted zones. Pb concentration in grass indicated herbage pollution in those locations where EDTA-extractable Pb concentration exceeds the guidance values.

Due to soil and grass intake during grazing, cattle exposure to metals, particularly Pb, is hazardous in the Silvermines area. In some locations cattle may consume a lethal dose of Pb ($>10\,g\,day^{-1}$) during a single day of grazing.

Overall Pb is considered as the most hazardous pollutant in the Silvermines area, which can cause a significant environment risk through vegetation uptake and direct exposure to soil. Zn being an essential metal has a lowest impact on the environment. A low portion of total Zn being EDTA-extractable, results in low grass uptake of Zn from soil, and Zn in grass on most polluted soil does not exceed the guideline level of Zn for animals. The direct exposure of farm animals to Zn in soil is not likely to result in intoxication. Cd uptake by vegetation may cause a certain risk in the areas of floodplains and shallow occurrence of groundwater table.

Investigation based on the consideration of pollution pathways may also assist the management practice for the contaminated land. Floodplains are considered as most hazardous areas for cattle grazing, tillage or gardening. Here sheep farming may be adopted as a better land use option, since the mechanism of grazing results in less soil being ingested than for cattle which pull grass, roots and attached soil. Areas of shallow groundwater should be excluded from tillage or gardening due to the high content of biologically available metals. Here drainage measures, aiming to lower the groundwater table, and simultaneous measures for metal leaching from soil may be applied to reduce environmental risk. Tillage and gardening practice in the area of acidic soils occurrence should incorporate measures to increase soil pH in order to reduce biologically available metals. Since these areas were delimited, the extent and cost of such measures may be easily estimated.

7. Conclusions

1. A process for preliminary evaluation of environmental risk, based on analysis of potential pathways of metal compound transport and deposition, was developed and implemented in the area of the Silvermines AMSs, where a long history of mining and mineral processing has resulted in elevated Cd, Pb and Zn soil concentrations not only within but also in mine surroundings.
2. Elevated soil metals are shown to be predominantly in areas where metal deposition in soil is associated with water related pathways (surface runoff, seasonal groundwater seepage and floodplains). Extensive areas of soil within preliminary delimited zones were classified as contaminated on the basis of Cd, Pb and Zn concentrations (both total and EDTA-extractable). The most affected areas, with metal concentrations in soil comparable with that within the AMS, were floodplains located 2–3 km downstream from the site.
3. Assessment of the sequential effects on grass and grazing animals indicates that Pb poses the greatest risk due to its high toxicity and high concentrations in soil. Within floodplain areas grazing cattle may intake a lethal dose of Pb.

4. On the basis of the investigation an approach to risk assessment was developed which allowed assessing the risks related to individual metals, areas of contamination and contamination targets. The approach allows optimising the site investigation, and may employ GIS methodologies.

References

Alloway, B.J. and Ayres, D.C.: 1993, *Chemical Principles of Environmental Pollution*, Blackie Academic & Professional, London.

Alloway, B.J. (ed.): 1995, *Heavy Metal in Soils*, Blackie Academic & Professional, London.

Aslibekian, O., Childs, P. and Moles, R.: 1999, Metal contamination of surface water in the vicinity of the Silvermines Abandoned Mine Sites (AMS), *Environmental Geochemistry and Health* **21**, 339–345.

Aslibekian, O. and Moles, R.: 2000, Environmental Contamination Related to Mine Drainage Distribution from Old Mine Sites by Waterways, in: *Mine Water and the Environment*. Proceedings of 7th IMWA Congress, Poland, 2000, pp. 49–58.

Aslibekian, O. and Moles, R.: 2001, An investigation of environmental contamination at the Silvermines AMS (Ireland) based on the preliminary delimitation of pollution hot spots using GIS methodology, *Mine Water and the Environment* **20**, 73–80.

Archer, G.B., Sleeman A.G. and Smith, D.C.: 1996, *Geology of Tipperary*, GSI, Dublin.

Bieber, A.: 1998, Aspects of Contaminated Sites and of the Reuse of Polluted Soil in Germany, in: Guercia, F. and Mariotti, C. (eds), *Risk Assessment and Risk Management of Contaminated Sites in Europe*. Proceeding of the International Workshop, ANPA, Rome, pp. 39–55.

Calco, R. and Perez, A.: 1994, Soils and acid mine waters, *Water, Air and Soil Pollution* **73**, 247–263.

Clark, M.W.: 1998, Management implications of metal transfer pathways from a refuse tip to mangrove sediments. *The Science of The Total Environment* **222**, 17–34.

Ferguson, C. *et al*. (ed.): 1998, *Risk Assessment for Contaminated Sites in Europe*. *Volume 1: Scientific Basis*, LQM Press, Nottingham, 165 pp.

Finch, T. and Gardiner, M.: 1993, *Soil of Tipperary North Riding*, National Soil Survey of Ireland, Teagasc.

Fleming, G.A. and Parle, P.J.: 1974, *Heavy Metal Studies*, Soil Research, An Foras Taluntais, Dublin.

Gallagher, V. and O'Connor, P.: 1997, Characterisation of the Avoca Mine Site: Geology, Mining Features, History and Soil Contamination Study, Technical Report, Geological Survey of Ireland, 1997.

Mariotti, C.: 1998, Legislative aspect and risk assessment for contaminated sites in Italy: the UNICHIM approach, in: Guercia, F. and Mariotti, C. (eds), *Risk Assessment and Risk Management of Contaminated Sites in Europe*, Proceeding of the International Workshop, 1998, ANPA, Rome, pp. 69–80.

Maskall, J., Whitehead, K. and Thornton, I.: 1995, Heavy metal migration in soils and rocks at historic smelting sites, *Environmental Geochemistry and Health* **17**, 127–138.

Merian, E. (ed.): 1991, *Metals and Their Compounds in the Environment: Occurrence, Analysis and Biological Relevance*, VCH, Cambridge, 1373 pp.

Minorco Lisheen EIS: 1995, *Environmental Impact Assessment*, Dublin.

Niagu, J.O. *et al.*: 1998, Saturation of ecosystem with toxic metals in Sudbury basin, Ontario, Canada, *The Science of The Total Environment* **223**, 99–117.

Rowell, D.L.: 1994, *Soil Science: Methods and Applications*, Addison Wesley Longman Ltd., UK.

O'Sullivan, K.: 1999, Human blood is tested for lead in Silvermines scare, *The Irish Time*, 2 September.

Smith, K., Plumlee, G. and Ficklin, W.: 1994, Predicting Water Contamination from Metal Mines and Mining Waste, *Open-File Report, USGS*, p. 112.

Steinborn, M. and Breen, J.: 1999, Heavy metals in soil and vegetation at Shallee mine, Silvermines, Co. Tipparery, in: *Biology and Environment*. Proceedings of the Royal Irish Academy, **99B**, pp. 37–42.

Thornton, I.: 1993, Environmental geochemistry and health in the 1990's: a global perspective, *Applied Geochemistry* **2**, 203–210.

Thornton, I.: 1995, Sources and pathways of arsenic in south-west England: health implications, in: Chappell, W. (ed.), *Exposure and Health Effect of Arsenic*, Volume 13, University of Missouri, pp. 93–103.

Thornton, I. and Abrahams, P.: 1983, Soil ingestion – a major pathways of heavy metals into livestock grazing contaminated land, *The Science of The Total Environment* **28**, 282–294.