HEAVY METALS IN SOIL AND VEGETATION AT SHALLEE MINE, SILVERMINES, CO. TIPPERARY

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ABSTRACT

Samples of soil, three higher plant species (*Teucrium scorodonia*, *Primula vulgaris*, and *Succisa pratensis*) and two moss species (*Hylocomium splendens* and *Rhytidiadelphus loreus*) were collected in 1995 from around some of the disused buildings and surrounding area of Shallee mine, Silvermines, Co. Tipperary. The samples were analysed for lead, copper and zinc, using flame atomic absorption spectrophotometry. Results indicated high lead levels in all soil and moss samples, but copper and zinc levels were similar to levels found in uncontaminated areas. Although mosses are used extensively for monitoring the aerial heavy metal contamination, correlations were found here between lead levels in mosses and their adjacent soil. This suggests possible local aerial lead deposition.

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INTRODUCTION

The Silvermines area has a long and well-known mining history. It dates back over 700 years, to when European miners arrived there in 1289 (Cole 1922). The geology comprises Devonian Old Red Sandstone at the surface while the valley floor consists of carboniferous limestone and shale (Gillmore 1971; Andrew 1986). During the 18th and 19th centuries, the mining at Shallee, (Irish Grid reference R7070) concentrated on vein deposits, mostly of barytes, galena and quartz. In this century, Shallee was an important source of lead. In the 1950s, the mine yielded 355,000 tonnes of ore, producing 6,500 tonnes of lead until production at Shallee ceased in 1958 (Mulvihill 1990). Shallee, is the proposed site of Ireland's first National Mining Heritage Centre.

Although advances in technology in the 20th century have greatly increased the quantity and quality of metal production world-wide, mining remains one of the main sources of heavy metal pollution. In sites with aerial contamination, the detectable metals in vegetation appear as a blanket deposit of fine particles on leaf surfaces (Davies and Holmes 1972; Little 1973), while in metal-contaminated soils, vegetation growing on such soils can take up metals via the roots, and these metals are firmly bound to the plant tissues (Rühling and Tyler 1968, 1970, 1971). Higher plants previously were used as collectors of airborne dusts and heavy metals (Goodman and Roberts 1971; Lacasse and Treshow 1976). However, such plants are likely to contain heavy metals obtained from the soil via their root systems as well as from aerial deposition. Unless rates of plant metal uptake and soil levels are known, it is difficult to interpret data based on plant leaf analyses alone. Primitive plants such as mosses have either poorly-developed or non-existent root systems and therefore absorb most of their nutrients directly from the atmosphere, via either wet or dry deposition. As a result, they have been used extensively for monitoring various aerial pollutants, including heavy metals (Rühling and Tyler 1968; Bruning and Kreeb 1993; Markert 1993; Türkan *et al.* 1995, Gaare and Steinnes 1996).

The two moss species used in this study were *Hylocomium splendens* and *Rhytidiadelphus loreus*. *Hylocomium splendens* is a moss species that is commonly used in the biomonitoring of airborne heavy metals. For example, Rühling and Tyler (1970, 1971) used it to biomonitor heavy metal deposition in Scandinavia, Grodzinska (1978) used it to biomonitor heavy metals in twelve Polish national parks, while Halleraker *et al.* (1998) used it to biomonitor heavy metals in the Barents Euro-Arctic region. In all cases increased heavy metal content of the moss related well to locations near industrialised centres, and strong correlations were found between the annual sum of precipitation and heavy metal levels in the mosses.

The aim of this study was to investigate heavy metal levels (lead, zinc and copper) in soil and three higher plant species (*Teucrium scorodonia*, *Primula vulgaris*, and *Succisa pratensis*) and two moss species (*Hylocomium splendens* and *Rhytidiadelphus loreus*) sampled from around some of the disused buildings and surrounding area of Shallee mine.

MATERIALS AND METHODS

Sampling of plants

The choice of species was determined partly by availability and partly to compare sources of contamination, that is whether it was from the soil (higher plants) or from aerial deposition (mosses). In February 1995, fifteen samples were taken from each of the five plant species—the leaves from three herbaceous plants, *T. scorodonia*, *P. vulgaris* and *S. pratensis*, and the green shoots from two moss species, *H. splendens* and *R. loreus*. Soil samples from the adjacent top soil (10cm) were taken as well as samples from barren soil that had no plants or mosses. All soil and vegetation species were analysed for lead, zinc and copper levels, and the pH of the soil samples was also measured.

Analytical procedure

All vegetation and soil samples were air-dried at ambient laboratory temperature. Soil samples were sieved to pass through a 2-mm sieve. Vegetation samples were ground and homogenised in a blender before weighing aliquots for total heavy metal content.

The samples were then dried at 70°C, until a constant weight was reached. Digestions of both soil and vegetation samples (1g) were carried out in 10ml concentrated HNO_3–HCl solution (3:1, analar grade) at approximately 125°C. Digested samples were then filtered and subsequently diluted with de-ionised water and the clear supernatant was analysed. All glassware was acid-washed using 10% nitric acid before use. Blanks and standards were made up using the same method. All determinations were carried out by means of a Varian Plus atomic absorption spectrophotometer using an air–acetylene flame.

The pH of the soil was measured using a soil sample added to distilled water in a ratio 1:2 (soil:water) on a volume basis. The data was analysed using SPSS (Statistical Package for Social Science) for Windows.

RESULTS

The maximum, mean ($\pm$ S.E.) and minimum total heavy metal levels found in the analysed soil, vegetation and moss samples, and the soil pH are given in Table 1. The Cu, Zn and Pb levels analysed from plant samples and their corresponding soil samples are illustrated in Fig. 1.

Heavy metal levels in higher plant and soil samples

Overall soil Cu levels ranged from 2.45mg/kg dry wt. (*T. scorodonia*) to 96.6mg/kg dry wt. (*P. vulgaris*), while overall Cu vegetation levels ranged

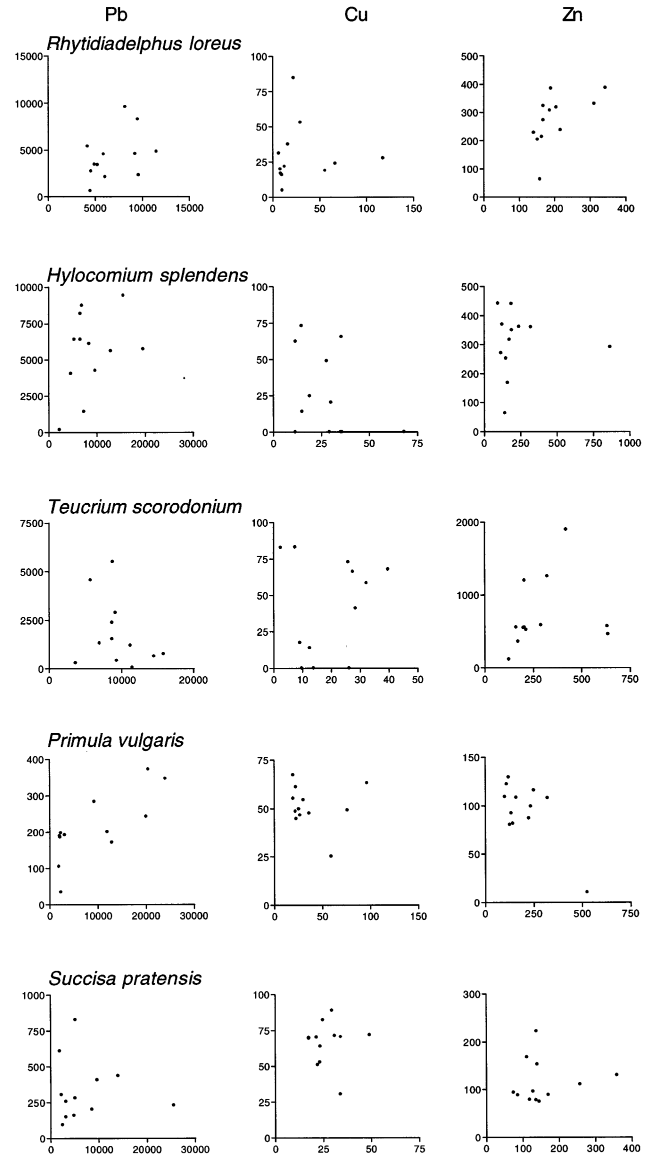

Fig. 1—Soil and vegetation levels of Cu, Zn and Pb analysed for *Teucrium scorodonia*, *Primula vulgaris*, *Succisa pratensis*, *Hylocomium splendens* and *Rhytidiadelphus loreus* from Shallee mine.

from non-detectable levels (*T. scorodonia*, *H. splendens*) to a maximum of 89.03mg/kg dry wt. (*S. pratensis*). *Teucrium scorodonia*, *S. pratensis*, and *P. vulgaris* all had higher mean Cu vegetation levels than their corresponding soil levels, whereas only *T. scorodonia* had a higher mean Zn vegetation level (721mg/kg dry wt.) than its soil Zn level (299mg/kg dry wt.). Although mean soil Zn levels were less than or equal to 308mg/kg, levels as high as 637mg/kg, 525mg/kg and 360mg/kg, respectively, were analysed from soil samples adjacent to *T. scorodonia*, *P. vulgaris* and *S. pratensis*.

All soil samples showed extremely high Pb levels. Lead soil levels ranged from 1,862mg/kg dry wt. (*S. pratensis*) to 25,539mg/kg dry wt. (*S. pratensis*,). Lead vegetation levels were also high with *T. scorodonia* having the highest mean Pb vegetation level (800mg/kg dry wt.), compared to *P. vulgaris* (211mg/kg dry wt.) and *S. pratensis* (332mg/kg dry wt.).

Spearman's rank order correlation coefficients were calculated for metal levels in plants, their associated soils and soil pH. Similar significant correlations were obtained between metals in soils associated with *P. vulgaris* and *S. pratensis*. In soil from both species Pb was positively correlated with both Zn ($P < 0.01$) and Cu ($P < 0.01$). In soils associated with all three higher plant species, Zn was positively correlated with Cu although this had a higher significance in soils associated with *P. vulgaris* and *S. pratensis* ($P < 0.001$) than with *T. scorodonia* ($P < 0.05$). Significant negative correlations were obtained between soil pH and soil metal levels. The only correlation between vegetation metal levels and their corresponding soil metal levels was found in *P. vulgaris*, where Pb soil levels were significantly correlated ($P = 0.004$) to Pb vegetation levels.

Heavy metal levels in moss species

Both *H. splendens* and *R. loreus* showed varying metal levels, although *H. splendens* had a higher overall mean level for all metals. Copper levels ranged from < 0.1mg/kg dry wt. to 73.2mg/kg dry wt. in *H. splendens* and from 4.9mg/kg dry wt. to 84.9mg/kg dry wt. in *R. loreus*, Zn levels ranged from 64.1 mg/kg dry wt. to 443mg/kg dry wt. in *H. splendens* and from 63.7mg/kg dry wt. to 389mg/kg dry wt. in *R. loreus*, and Pb levels ranged from 1,425mg/kg dry wt. to 9,427mg/kg dry wt. in *H. splendens* and from 647mg/kg dry wt. to 9,632mg/kg dry wt. in *R. loreus*.

Results from soil samples taken in the vicinity of the mosses showed similar metal levels to those found in the soil around the higher plants (see Table 1). Spearman's rank order correlation coefficients were also calculated between metal levels in mosses, their associated soils and soil pH. In soils, Zn was positively correlated with Cu although this had a higher significance in soils taken from the vicinity of *R. loreus* ($P < 0.001$), than with *R. loreus* ($P < 0.05$). Soils around *R. loreus* showed a positive significant correlation ($P < 0.05$) between Pb and Cu and between Pb and Zn. No correlations were found between metals in *H. splendens*, although *R. loreus* showed a positive significant correlation ($P < 0.001$) between Pb and Cu. In *H. splendens* a positive correlation ($P < 0.05$) was found between Pb levels in the soil and Zn levels in the moss.

DISCUSSION

Metal levels in soil

The levels of Cu and Zn found in soil samples taken from Shallee mine (Table 1) can be compared to values commonly reported in literature for uncontaminated areas. For example, Cu,

Table 1—Minimum mean (± S.E.) and maximum levels of Pb, Zn and Cu (mg/kg dry wt.) found in *Teucrium scorodonia*, *Primula vulgaris*, *Succisa pratensis*, *Hylocomium splendens* and *Rhytidiadelphus loreus*, their corresponding soil samples and in bare soil, and soil pH from the Shallee area.

Metal (mg/kg)	*T. scorodonia*		*P. vulgaris*		*S. pratensis*		*H. splendens*		*R. loreus*		*Bare soil*
	Soil	*Plant*	*Soil*	*Plant*	*Soil*	*Plant*	*Soil*	*Plant*	*Soil*	*Plant*	
Pb											
Minimum	3,632	71	1,830	35.6	1,862.58	95.65	2,189	181.8	4,173	647	3,436
Mean (± S.E.)	9,498 ± 988.5	1,800 ± 502.2	9,335 ± 2,417	211 ± 27.05	7,132 ± 1,970.99	331.66 ± 61.31	8,751 ± 1,425	5,553.9 ± 797	6,929 ± 728	5,690 ± 738	8,996.9 ± 1,537.2
Maximum	15,1823	5,524	24,019	373	25,539	830.28	19,608	9,427	1,148	9,632	17,635
Zn											
Minimum	125	120	101	10.69	75.1	75.17	95	64.1	141	63.7	7.81
Mean (± S.E.)	299 ± 50.85	721 ± 141.56	204 ± 35.23	195.68 ± 8.94	155.77 ± 22.79	115.77 ± 13.04	230.6 ± 60.4	308 ± 31.4	200 ± 18.3	274 ± 26.3	106 ± 15.37
Maximum	637	1,904	525	130	359.77	222.67	866.9	443	342.8	389	182
Cu											
Minimum	2.5	< 0.01	19.7	25.4	17.6	30.5	11.3	< 0.01	6.58	4.9	4.3
Mean (± S.E.)	19.6 ± 3.4	42.07 ± 9.76	38.1 ± 7.34	51.2 ± 3.13	27.3 ± 2.57	66.2 ± 4.42	27.8 ± 4.56	25.82 ± 8.36	30.3 ± 9.7	29.9 ± 6.1	26.65 ± 5.45
Maximum	39.8	83.2	96.6	67.4	49.2	89.0	68.1	73.2	117	84.9	77.9
pH											
Minimum	5.62		6.32		5.49		5.52		6.77		4.35
Maximum	7.05		7.27		7.46		7.56		7.48		7.54

Zn and Pb generally vary in the ranges 5–80mg/kg dry wt., 20–300mg/kg dry wt. and 2–200mg/kg dry wt., respectively (Fleming and Parle 1977; Gardiner 1980; Alloway 1990a,b). However, all soil samples showed extremely high lead levels, indicating lead-contaminated soil in the area sampled.

Spearman's rank order correlation coefficients were observed between metal levels in soil and soil pH. Significant negative correlations ($P = 0.000$) were found between Cu levels and pH in soil samples and between Cu ($P = 0.004$) and Pb ($P = 0.019$) levels and pH in the soil samples taken adjacent to *T. scorodonia*. Although similar trends have been reported by Alloway (1990a,b), Brady (1990) and Stanners and Bourdeau (1995), it should be noted that not all soil metal levels showed a correlation with levels in vegetation, either positive or negative, which suggests that pH is not the only controlling factor in plant metal uptake (see also Sanders 1983; Jones and Burgess 1984; McBride 1989; Bell *et al.* 1991).

Copper and lead levels also correlated in all soils sampled from around higher plants and mosses. This was to be expected as both the higher plants and the mosses were sampled within the same area, and therefore the soil was subjected to the same physico–chemical processes.

Metal levels in higher plants

Normally, plant metal levels for Cu, Zn and Pb vary in the ranges of 5–20mg/kg dry wt., 25–200mg/kg dry wt. and 1–12mg/kg dry wt., respectively (Fleming and Parle 1977). Abnormally high levels of Pb and Zn were observed for *T. scorodonia* (mean Pb and Zn levels 1800.44mg/kg and 721mg/kg dry wt., respectively). Although values similar to those found in *T. scorodonia* have been known to substantially reduce plant growth (Black 1968; Jones and Burgess 1984; Leita *et al.* 1989), no such toxicity was visible in the plants sampled. This may indicate the possible presence of metal resistance through tolerance of Zn and Pb in *T. scorodonia* as suggested by Brooks *et al.* (1979) and Baker (1981).

Chambers and Sidle (1991) found that plant metal levels were highly variable when related to soil metal levels and, according to Fleming and Parle (1977), the uptake of heavy metals varies widely depending on the plant species being studied. They also found that metal uptake was controlled by such variables as pH, organic matter content, and the degree of soil moisture. Generally, most heavy metals were less available to plants under alkaline conditions, than under acid conditions (Hesse 1971). The fact that Cu plant levels were found to be higher than soil levels in all of the higher plant species analysed, may indicate that Cu uptake by plants is not restricted at this site by pH or other factors.

Zinc levels analysed from *P. vulgaris* and *S. pratensis* plant samples were well within those normally encountered in plants growing in uncontaminated soil (Fleming and Parle 1977; Türkan *et al.* 1995), those plants having mean Zn levels of 116mg/kg and 104mg/kg dry wt., respectively. Although Pb levels were higher than normal (mean 332mg/kg and 211mg/kg dry wt.), they were well below those found in *T. scorodonia*. This may suggest a tolerance mechanism working within both plant species that allows these plants to grow and survive in this site despite the high Pb levels in the soil, although more research is needed to confirm this, because metal tolerance was not investigated in this study.

Overall the normal levels of Cu, Zn and Pb in plants growing in uncontaminated areas have been reported to vary in the ranges 5–20mg/kg dry wt., 25–200mg/kg dry wt. and 2–10mg/kg dry wt., respectively (Fleming and Parle 1977; Türkan *et al.* 1995). Taking these ranges into account, the results of this study showed that, by comparison, the area is polluted by Pb, assuming that the normal levels for the area were not naturally high before mining disturbance.

Metal levels in mosses

Mosses absorb heavy metals from air particles and both *H. splendens* and *R. loreus* have been used to investigate or biomonitor airborne heavy metals (Rühling and Tyler 1970). Changes in heavy metal levels in mosses are usually taken to indicate uptake from external sources through a process of ion exchange and chelation (Manning and Feder 1980; Gaare and Steinnes 1996; Gregurek *et al.* 1998). *Hylocomium splendens* is commonly used as a biomonitor for heavy metals. Mosses are used as biomonitors of atmospheric heavy metal deposition because the levels of metals in the moss are closely correlated to atmospheric deposition (Rühling and Tyler 1973; Stanners and Bourdeau 1995).

Spearman's rank-order correlations showed similar correlations occurring in both soil and *R. loreus*, i.e. Pb was correlated with Cu ($P < 0.05$ in soil; $P < 0.001$ in moss). As heavy metal uptake by mosses occurs via wet or dry deposition from the atmosphere and not from the soil, since contact with the ground is minimal (Rühling and Tyler 1968, 1970, 1971; Goodman and Roberts 1971; Gaare and Steinnes 1996), these correlations may suggest the occurrence of local aerial deposition although confirmation of this needs further investigation.

Rhytidiadelphus loreus and *H. splendens* differ in metal levels because they take up metals at different rates, although the overall pattern stays the same, i.e. excessively high lead deposition, relatively low Zn and normal Cu deposition.

CONCLUSIONS

Levels of Cu and Zn are not high enough to cause environmental pollution. However, Pb levels are above the normal range both in soil and vegetation species. The correlations obtained between metals in the soils, along with those obtained for metals in mosses, may suggest that local metal deposition occurs in the area, although further study is needed to confirm this.

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REFERENCES

Alloway, B.J. 1990a Soil processes and the behaviour of metals. In Alloway, B.J. (ed.), *Heavy metals in soils*, 11–37. London. Blackie.

Alloway, B.J. 1990b The origin of heavy metals in soils. In Alloway, B.J. (ed.), *Heavy metals in soils*, 38–57. London. Blackie.

Andrew, C.J. 1986 The tectono–stratigraphic controls to mineralization in the Silvermines area, County Tipperary, Ireland. In C.J. Andrew, R.W.A. Crowe, S. Finlay, W.M. Pennell and J.F. Pyne (eds), *Geology and genesis of mineral deposits in Ireland*, 377–407. Irish Association for Economic Geology.

Baker, A. 1981 Accumulators and excluders—strategies in the response of plants to heavy metals. *Journal of Plant Nutrition* **3**, 643–54.

Bell, P., James, B., and Chaney, R. 1991 Heavy metal extractability in long-term sewage sludge and metal salt amended soils. *Journal of Environmental Quality* **20**, 468–81.

Black, C. 1968 *Soil–plant relationships*. Wiley and Sons.

Brady, N.C. 1990 *The nature and properties of soils*, 10th edn. London. Macmillan Publishing Company.

Brooks, R., Morrison, R., Reeves, R., Dudley, T. and Akman, Y. 1979 Hyperaccumulation of nickel by *Alyssum L* (Cruciferae). *Proceedings of the Royal Society of London* **203**, 387–403.

Bruning, F. and Kreeb, K.H. 1993 Mosses and biomonitors of heavy metal contamination within urban areas. In B. Markert (ed.), *Plants as bioindicators, indicators for heavy metals in the terrestrial environment*, 395–401. Weinheim. VCH Publishers.

Chambers, J. and Sidle, R. 1991 Fate of heavy metals in an abandoned lead–zinc tailings pond: 1. vegetation. *Journal of Environmental Quality* **20**, 745–58.

Cole, G.A. 1922 *Memoir of localities of minerals of economic importance and metalliferous mines in Ireland*. Dublin. Stationery Office.

Davies B.E. and Holmes, P.L. 1972 Lead contamination of roadside soil and grass in Birmingham, England, in relation to naturally occurring levels. *Journal of Agricultural Science* **79**, 479–84.

Fleming, G. and Parle, P. 1977 Heavy metals in soils, herbage and vegetables from an industrialised area west of Dublin city. *Irish Journal of Agricultural Research* **16**, 35–48.

Gaare, E. and Steinnes, E. 1996 Use of the moss *Hylocomium splendens* for the mapping of radiocaesium fallout from the atmosphere. *11th meeting of the Nordic Society for Radiation Protection, 26–29 August, 1996.*

Gardiner, M. 1980 *Soil associations of Ireland and their land use potential*. Soil Survey Bulletin no. 36. Dublin. An Foras Taluntais.

Gillmore, D. 1971 *A systematic geography of Ireland*. Dublin. Gill and MacMillan.

Goodman, G.T. and Roberts, T.M. 1971 Plants and soils as indicators of metals in the air. *Nature* (*London*) **231**, 287–92.

Gregurek, D., Reimann, C. and Stumpfl, E.F. 1998 Trace elements and precious metals in snow samples from the immediate vicinity of nickel processing plants, Kola Peninsula, northwest Russia. *Environmental Pollution* **102**, 221–32.

Grodzinska, K. 1978 Mosses as bioindicators of heavy metal pollution in Polish national parks. *Water, Air and Soil Pollution* **9**, 83–97.

Halleraker, J.H., Reimann, C., de Caritat, P., Finne, T.E., Kashulina, G., Niskaavaara, H. and Bogatyrev, I. 1998 Reliability of moss (*Hylocomium splendens* and *Pleurozium schreberi*) as a bioindicator of atmospheric chemistry in the Barents region: interspecies and field duplicate variability. *The Science of the Total Environment* **218**, 92–139.

Hesse, P. 1971 *A textbook of soil chemical analysis*. London. Murray.

Jones, R. and Burgess, M. 1984 *Environmental Science and Technology* **18**(10), 731–3.

Lacasse, N.L. and Treshow, M. 1976 *Diagnosing vegetation injury caused by air pollution*. US. Environmental Protection Agency.

Leita, L., Nobili, M., Pardini, G. and Sequi, P. 1989 Anomalous contents of heavy metals in soils and vegetation of a mine area in S.W. Sardinia, Italy. *Water, Air and Soil Pollution* **48**, 423–33.

Little, P. 1973 A study of heavy metal contamination on leaf surface. *Environmental Pollution* **5**, 159–72.

Manning, W. and Feder, W. 1980 *Biomonitoring air pollutants with plants*. Essex. Applied Science Publishers.

Markert, B. 1993 *Plants as biomonitors, indicators for heavy metals in the terrestrial environment*. Weinheim–New York–Tokyo. VCH Publishers.

McBride, M. 1989 Reactions controlling heavy metal solubility in soils. *Advances in Soil Science* **10**, 1–56.

Mulvihill, M. 1990 Mining our past for the future. *Technology Ireland*, April, 48–51.

Rühling, Å. and Tyler, G. 1968 An ecological approach to the lead problem. *Botaniska Notiser* **121**, 321–42.

Rühling, Å. and Tyler, G. 1970 Sorption and retention of heavy metals in the woodland moss *Hylocomium splendens* (Hedw.). Br. et Sch. *Oikos* **21**, 92–7.

Rühling, Å. and Tyler, G. 1971 Regional differences in the deposition of heavy metals over Scandinavia. *Journal of Applied Ecology* **8**, 497–517.

Rühling, Å. and Tyler, G. 1973 Heavy metal deposition in Scandinavia. *Water, Air and Soil Pollution* **2**, 445–55.

Sanders, J. 1983 The effect of pH on the total and free ionic concentrations of manganese, zinc and cobalt in soil solutions. *Journal of Soil Science* **34**, 315–23.

Stanners, D. and Bourdeau, P. 1995 *The Dobris Assessment*. Copenhagen. European Environmental Agency.

Türkan, I., Henden, E., Çelik, Ü. and Kivilcim, S. 1995 Comparison of moss and bark samples as biomonitors of heavy metals in a highly industrialised area in Izmir, Turkey, *The Science of the Total Environment* **166**, 61–7.