

PROFILE DISTRIBUTIONS OF LEAD, ZINC, AND COPPER IN DYSTRIC CAMBISOLS DEVELOPED FROM GRANITE AND GNEISS OF THE SUDETES MOUNTAINS, POLAND

CEZARY KABAŁA* and LESZEK SZERSZEŃ

*Institute of Soil Science and Agricultural Environment Protection, Agricultural University of
Wrocław, 50-357 Wrocław, Grunwaldzka 53, Poland*

(* author for correspondence, e-mail: kabala@ozi.ar.wroc.pl, fax: +48-71-3284849)

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Abstract. Total contents of Pb, Zn and Cu were examined in twenty-five soil profiles of forested Dystric Cambisols developed from granite and gneiss in the area of the Sudetes Mountains (SW Poland). Sequential extraction of heavy metals was also carried out to study relations between metal content and soil compounds. Profile distribution differed among the metals examined: Pb concentrations decreased gradually from surface with depth, whereas those of Zn increased with depth of soil profile, obtaining their maximum in the bedrock horizon. Cu was found to accumulate in topsoil and decrease with depth, but showed secondary increase of the concentration in bedrock. Organic matter was found to be a crucial factor of Pb binding and distribution, while iron oxides played the most important role in Zn binding. Both organic matter and oxides were important factors of Cu distribution. The results of sequential extraction show that all studied elements are mobile under strong acidic conditions in investigated Cambisols. Thus, total contents of Zn and Cu in bedrock cannot be used as geochemical background or as reference levels for assessing the contamination of soil surface with these metals.

Keywords: copper, lead, mountain soils, profile distribution, zinc

1. Introduction

Trace metals concentration and distribution in soils are influenced by several factors, such as particle size distribution, organic matter content, drainage, soil horizonation, vegetation (Kabata-Pendias and Pendias, 1992; Lee *et al.*, 1997). The overall content of heavy metals in any soil also depends on the geochemical nature of the parent material, since soil inherits from its parent rock a certain stock of elements that is then redistributed by pedological processes (Davies, 1980). The natural background of heavy metals in uncontaminated soils is usually at the level of trace amounts, following their low content in most of igneous and sedimentary rocks. Only mafic and ultramafic rocks are known as a rich source of some heavy metals, for example nickel and chromium (Kabata-Pendias and Pendias, 1992).

In the last centuries, and particularly in the last few decades, human activity has continuously increased the level of heavy metals circulating in the environment. Therefore, contamination of ecosystems with trace elements has become an im-



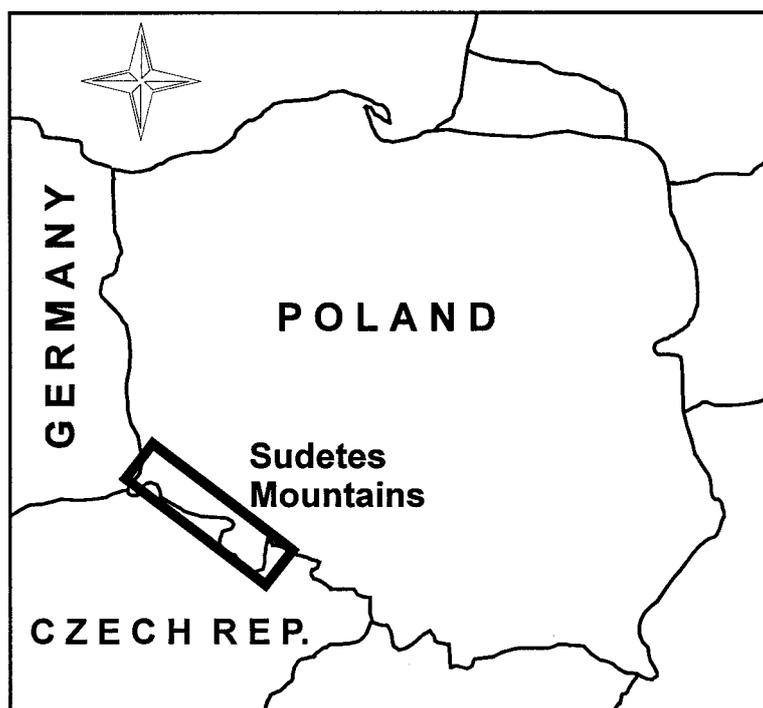


Figure 1. Location of the research area, the Sudetes Mountains, SW Poland.

portant topic of investigations, since many trace metals are toxic to terrestrial and aquatic organisms.

The first step in investigating of soil contamination is to define the range of trace elements concentrations typical for uncontaminated soils (Davies, 1980). Extensive research has been conducted in several countries to determine background levels of heavy metals (Kabata-Pendias and Pendias, 1992; Holmgren *et al.*, 1993), focussing generally on soils under agricultural cultivation, usually developed from sedimentary, unconsolidated parent materials.

Determination of the heavy metals reference level in mountain soils is generally more difficult because of diversity of geological and morphological formations, as well as the zonality of climatic conditions and vegetation. In addition, the Sudetes Mountains are partially exposed to atmospheric pollution caused by brown coal power plants, believed to be a source of soil contamination in the high elevated parts of the massif (Borkowski *et al.*, 1993).

The objectives of this study were to: (i) characterize Pb, Zn, and Cu profile distribution in forest soils developed from granite and gneiss in the Sudetes Mountains, (ii) establish the main soil factors influencing the distribution of these metals, and (iii) assess the level of soil contamination.

2. Area Description, Methods and Material Studied

Several varieties of granite and gneiss are the most common parent rocks of soils in the Sudetes Mountains (Figure 1). According to FAO-WRB soil classification (1998), Dystric Cambisols, Haplic Podzols, Dystric Regosols and Lithic Leptosols are the most frequent soil groups developed on this substratum.

Twenty-five profiles of soils covered with spruce forests, located at altitudes of 425–1200 m a.s.l. were investigated. Soil sampling sites were selected so as to minimize the risk of direct anthropogenic contamination. Locations were chosen in old forests at considerable distance from field/forest boundaries, in areas where neither lime, mineral fertilizers, nor sewage sludge were applied. However, long-distance airborne contamination cannot be excluded, since the Sudetes massif creates an orographic barrier for air masses polluted by the emissions from brown coal power plants.

Soil samples (including forest litter) were collected separately from all soil horizons down to the parent material. Soil horizons were distinguished and designated according to the FAO-WRB classification system (1998). Particle size distribution was determined (a) by the hydrometer method for silt and clay fractions, and (b) by sieving for sand fractions (Reeuwijk, 1995). Organic carbon in mineral horizons was analyzed by the wet oxidation method (with external heating). The approximate content of organic matter in forest litter was analyzed by the loss on ignition method. The value of pH was measured in soil:water mixtures at a 1:2.5 ratio. The total contents of Pb, Zn and Cu were determined by the flame atomic absorption spectrometry, after digestion of samples with concentrated (70%) perchloric acid.

General relationships between metal contents and soil properties were compared with the results of sequential extraction carried out according to the method of Zeien and Brümmer (1989). This method was chosen from among several other (Tessier *et al.*, 1979; Sposito *et al.*, 1982; Shuman, 1985; Keller and Vedy, 1994), as it makes possible to separate different reducible fractions, such as those occluded in Mn-oxides, in amorphous Fe-oxides and in crystalline Fe-oxides. Altogether, seven operationally defined fractions were determined and conventionally described as mobile (unspecifically adsorbed), exchangeable (specifically adsorbed), occluded in Mn-oxides, organically complexed, occluded in amorphous Fe-oxides, occluded in crystalline Fe-oxides, and residual (Table I). The soil profile chosen for sequential extraction of trace elements was selected from Dystric Cambisol developed from gneiss. It showed typical patterns of basic soil properties (texture, pH, organic matter distribution) and soil morphology.

Table III includes the range, arithmetic mean and sample standard deviation, as well as the geometric mean for the entire data set. Original values were converted to logarithms because the frequency distributions of transformed data were more symmetrical (normal) than those of original data. Thus, geometric mean is reported as the better measure of central tendency of log-normally distributed data. The

TABLE I

Reagents used in sequential extraction according to Zeien and Brümmer (1989)

Fraction	Reagent	pH
1. Mobile (unspecifically absorbed)	1 M NH ₄ NO ₃	7.00
2. Exchangeable (specifically observed)	1 M NH ₄ OAc	6.00
3. Occluded in MnOx	0.1 M NH ₂ OH-HCl + 1 M NH ₄ OAc	6.00
4. Organically complexed	0.025 M NH ₄ -EDTA	4.60
5. Occluded in amorphous FeOx	0.2 M NH ₄ -oxalate	3.25
6. Occluded in crystalline FeOx	0.2 M NH ₄ -oxalate + 0.1 M ascorbic acid	3.25
7. Residual (structurally bound in some silicates)	Concentrated HClO ₄ /HNO ₃	–

arithmetic mean and sample standard deviation were included for comparison as indexes widely used in similar studies.

3. Results and Discussion

Soil profiles selected for investigation represented Dystric Cambisols with a shallow surface ochric horizon and a well developed cambic horizon. Forest litter horizons were usually present. The important feature of all soils examined was their high acidity, with pH value ranging between 3.0 and 5.3 (Table II). The lowest pH occurred in surface horizons and significantly increased with depth in soil profiles. Organic carbon content was the highest in surface layers of forest litter (up to 54.3%) and gradually decreased with depth in soil profiles. The relatively high organic carbon contents in B, BC and C horizons were probably connected with the high mobility of low-molecular products of litter decomposition in a strongly acidic soil environment (McBride, 1994). Characteristic features of texture included a considerable contribution of coarser rock fragments, low clay content, and medium to high silt content (sandy loam or silty loam textural classes). No variability was found in clay distribution within soil profiles.

Relatively high Pb concentrations in surface horizons decreased rapidly with depth in soil profiles (Table III). An average Pb concentration in surface mineral A horizons exceeded those found in bedrock almost threefold. Even a superficial

TABLE II

Range of pH values, organic carbon and clay contents of investigated Dystric Cambisols developed from granite and gneiss in the Sudetes Mountains

Soil horizon	Organic carbon (%)	Clay (%)	pH in H ₂ O
O horizon (forest litter)	20.2–54.3 ^a 43.1 ^b	–	3.1–5.0 3.8
A horizon (mineral humus-rich surface horizon)	2.1–15.4 8.3	2–10 5	3.0–4.9 3.6
B horizon (cambic - horizon of intense weathering)	1.2–7.4 3.3	2–11 5	3.3–5.0 4.0
BC horizon (transitional layer)	0.2–4.6 1.7	2–9 5	3.4–5.2 4.2
C horizon (bedrock layer)	0.2–2.5 1.0	2–11 5	3.7–5.3 4.3

^a Range of results: minimum–maximum.

^b Arithmetic mean.

comparison indicated a strong connection between Pb and organic matter distribution within soil profiles, that was confirmed by a high correlation coefficient $R = 0.74$ at a significance level $P < 0.001$ (Table IV). No significant correlation was found between Pb and clay content, which is perhaps a result of textural homogeneity of soils. A significant correlation between Pb and pH value seems to be a secondary consequence of the interrelationship between a decrease of humus content and an increase of pH in the soil profile.

The results of sequential extraction confirmed the importance of organic matter for Pb distribution. With a relatively constant level of residual fraction (ca. 12–17 mg kg⁻¹) corresponding with clay content stability, a decrease in organically bound Pb fraction resulted in a decrease of total Pb concentration in subsequent horizons (Figure 2). The organic fraction made up to 44% of Pb (in A horizon), whereas iron oxides (mainly amorphous) bound below 25% of total Pb. Weakly bound fractions (mobile and exchangeable) were negligible in deeper soil horizons, probably due to higher pH values. The sum of Pb occluded in Fe-oxides and residual fractions in C-horizon (parent material) – ca. 23 mg kg⁻¹ – corresponds to Pb content of granite and gneiss rocks – 15–24 mg kg⁻¹ (Kabata-Pendias and Pendias, 1992). It may imply that higher Pb content in the soils examined (in their surface horizons particularly) results from Pb input with organic matter. This hypothesis is

TABLE III

Total contents of lead, zinc, and copper in soil horizons of Dystric Cambisols developed from granite and gneiss in the Sudetes Mountains

Soil horizon	Parameter	Trace metal (mg kg ⁻¹)		
		Pb	Zn	Cu
O horizon	Range	47.0–217.0	30.0–76.7	8.2–44.2
	GM ^a	105.8	46.4	19.4
	AM±SD ^b	114.7±45.4	47.9±12.6	21.2±8.9
A horizon	Range	50.2–165.0	28.2–137.0	7.0–34.5
	GM	86.8	50.4	15.1
	AM±SD	92.4±33.7	56.4±30.5	17.2±9.0
B horizon	Range	23.0–101.0	30.0–100.0	2.0–37.5
	GM	55.3	52.0	11.6
	AM±SD	59.5±22.3	58.0±20.8	13.9±8.7
BC horizon	Range	21.9–45.0	27.2–135.0	1.0–42.5
	GM	34.2	59.5	10.3
	AM±SD	34.9±6.9	65.5±30.1	14.3±11.3
C horizon	Range	16.5–51.0	54.5–137.0	6.5–43.0
	GM	33.8	80.8	13.7
	AM±SD	35.0±9.1	84.9±28.3	16.0±10.2

^a Geometric mean.

^b Arithmetic mean±sample standard deviation.

confirmed by the polynomial regression equation (significant at $P < 0.05$), in which the constant value of 23.5 corresponds well to the sum of stable Pb fractions:

$$Pb_t = 23.5 + 12.4C - 0.46C^2,$$

where

Pb_t = Total concentration of lead (mg kg⁻¹);

C = Organic carbon content (%).

The average Pb concentration in surface horizons of Cambisols examined in this study was generally significantly higher than those reported from arable (Kabata-Pendias and Pendias, 1992; Holmgren *et al.*, 1993) or other forested sites (Friedland and Johnson, 1985; Herrick and Friedland, 1990; Billett *et al.*, 1991; Maciejewska, 1993). A similarly high level (48–94 mg kg⁻¹) was reported by Schwarz *et al.* (1999) from central Slovakia as indicating airborne pollution of soils. This comparison suggests the contamination of surface horizons of studied soils with Pb. Both atmospheric deposition and plant uptake may result in an accumulation of trace metals in surface horizons. But since it is not an essential element for

TABLE IV

Coefficients of correlation between soil properties and trace metals contents within mineral horizons (data for forest litter excluded)

	OC ^b	pH	Clay	Pb	Zn
Pb	0.74 ^a	-0.62 ^a	-0.19		
Zn	-0.42 ^a	0.18	-0.27	-0.23	
Cu	0.01	0.09	-0.25	0.21	0.56 ^a

^a Level of statistical significance $P < 0.001$.

^b Organic carbon.

plants, Pb should not be subject of biological accumulation at such a high level (Kabata-Pendias and Pendias, 1992).

Completely different from that of Pb was the pattern of Zn distribution within the studied soil profiles. The highest Zn concentrations were found in bedrock while the lowest were in the forest litter and mineral A horizons. The prevalence of the deepest C horizons over surface mineral A horizons (nearly 60%) does not correspond to the findings of Friedland and Johnson (1985), Herrick and Friedland (1990), Lee *et al.* (1997), and Maciejewska (1993) who reported enrichment of surface layers in comparison to bedrock.

Zn concentration correlated negatively with organic carbon content (Table IV) and did not show any significant relation either to clay content or soil pH. A positive correlation between Zn and Cu, however, does appear to be statistically significant.

The organically bound Zn fraction was negligible in the total Zn content (Figure 2), while Shuman (1985), reported a high percentage of this fraction in other soils. Residual Zn was a dominant fraction in mineral horizons, in all cases making up over 50% of the total content. This result draws a parallel with a high correlation between total soil Zn and clay content reported by Lee *et al.* (1997). Considerably high percentage of Zn (up to 35% in C-horizon) was found as fraction occluded in Fe oxides, both amorphous and crystalline, with a prevalence of the latter. The high affinity and selective absorption of Zn on Fe oxides were widely reported by Shuman (1985), Iyegar *et al.* (1981) and Ramos *et al.* (1994). Relatively high concentrations of weakly adsorbed or 'mobile' Zn fractions were found in all horizons with a maximum in surface layers. This confirms the high mobility of Zn in the soil profile, very likely at low pH, in particular of surface horizons (McBride, 1994). Kabata-Pendias and Pendias (1992) pointed out that acid leaching is a crucial factor in Zn mobilization and may lead to losses of this metal from some horizons, particularly of podzols and brown acid soils derived from sands.

The values of Zn concentration in surface organic horizons were lower than those found by Billett *et al.* (1991) in Scotland and similar to those reported by Herrick and Friedland (1990) from U.S.A. Zn contents in mineral horizons were

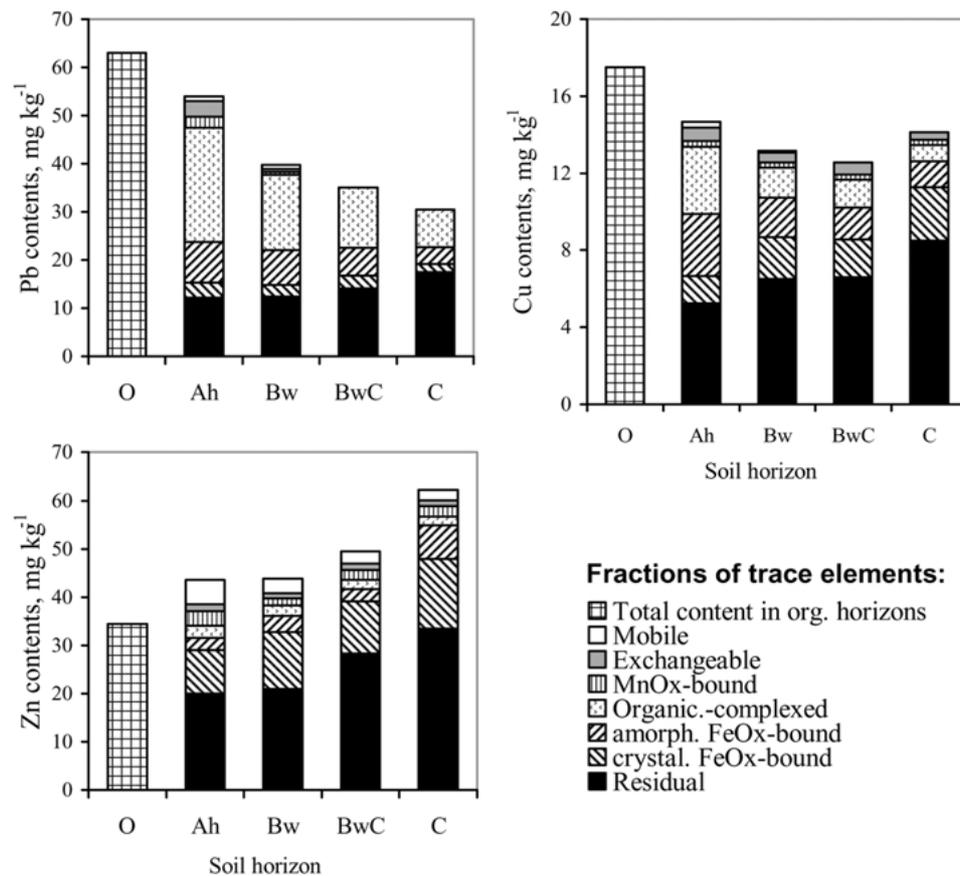


Figure 2. Distribution of Pb, Zn and Cu fractions in typical profile of Dystric Cambisol developed from gneiss.

within the range typical for unpolluted soils (Kabata-Pendias and Pendias, 1992; Holmgren *et al.*, 1993; Maciejewska, 1993), whereas the concentrations reported by Schwarz *et al.* (1999) in surface horizons of mountain soils in central Slovakia were as much as by twofold higher (90.5–128.7 mg kg⁻¹). Kabata-Pendias and Pendias (1992) reported the values of 40–60 mg kg⁻¹ as common Zn concentrations in granite and gneiss, which are considerably lower than those found in C horizons of the studied soils. This may support the thesis that higher Zn concentration in the deepest part of the studied soil profiles resulted from immobilization of this metal leached out from acid surface horizons. Thus, the total content of Zn in the deeper horizons of the soils studied cannot be used as a background level for assessing the contamination in soil surface horizons.

Among the three elements compared, Cu occurred in the soils studied at the lowest concentrations. The special feature of this metal distribution was a significant variability in distinguished soil horizons (e.g. from 1.0 to 42.5 mg kg⁻¹ in

BC horizons). The high differences between the values of geometric and arithmetic means (up to 40% in BC horizon) and the high values of standard deviations are good indicators of this variability (Table III). Cu distribution within soil profiles showed certain similarities to Pb and Zn patterns. Cu maximal concentrations were found in surface horizons. Similarly to Pb, Cu content decreased with depth in soil profile, and increased again in parent rock horizon, which makes Cu and Zn pattern very similar. Cu content in C-horizons exceeded those found in overlying BC horizons by 35%.

The total Cu concentration in the soils studied did not indicate any significant dependence on pH, clay or organic matter contents in mineral horizons (Table IV). However, the coefficient of correlation between Cu and organic carbon content calculated for all of the material studied (including forest litter horizons) was positive ($R = 0.29$) and statistically significant at $P < 0.01$. Moreover, Cu correlated positively with Zn ($R = 0.56$ of $P < 0.001$).

The residual fraction was found to be the most significant part of total Cu as examined by sequential extraction (Figure 2). In surface horizons, however, the residual Cu accounted only for 35%, while Cu occluded in iron oxides ca. 30% and organically complexed 25% of the total Cu content. Ramos *et al.* (1994) reported that organically bound Cu was the most important form of Cu in unpolluted soils, whereas Shuman (1985) found Cu occluded in oxides to be a deciding factor in total Cu content. Keller and Vedy (1994) showed that organic matter in topsoil, and oxides in bedrock played the major role in Cu distribution in soils of the Swiss Alps similar to those examined in this study. This conclusion fits well with the soil profiles presented in this paper since the role of organically bound fraction decreased and that of the oxides-bound fraction increased with depth (Figure 2). It also explains the lack of a significant correlation between the total contents of Cu and organic matter in the soils studied. Higher Cu content in the lower horizons of the soils studied seems to be a result of immobilization of Cu leached out from acid surface horizons, in spite of the fact that Cu is considered rather stable (McBride, 1994).

Total Cu content in the Cambisols studied was rather low, comparable to that reported in unpolluted soils (Kabata-Pendias and Pendias, 1992; Holmgreen *et al.*, 1993; Maciejewska, 1993; Keller and Vedy, 1994). In organic horizons, however, it was generally higher than concentrations found by Billett *et al.* (1991) and by Herrick and Friedland (1990), and at the same time much lower than those reported by Schwarz *et al.* (1999) in Slovakia.

4. Conclusions

The distribution patterns of Pb, Zn and Cu in the profiles of strongly acidic Cambisols developed from granite and gneiss of the Sudetes Mountains were different for all elements examined. The total contents of Pb were the highest in surface

horizons, and gradually decreased with depth along with a decrease in organic matter. Pb concentrations found in the bedrock were similar to those reported for granite and gneiss rocks, and were not enriched by input from surface horizons. Zn concentrations were the lowest in surface horizons and increased with depth obtaining a maximum in the deepest layers of soil profiles. The amounts of mobile Zn in all horizons of soil profiles were significant. Iron oxides played a crucial role in Zn binding in the profile studied. The highest Cu accumulation occurred in surface horizons, decreased with depth, and increased secondarily in the bedrock layer. Cu distribution resulted from binding both by organic matter (particularly in topsoil) and iron oxides (in whole profile).

The results of sequential extraction showed that all elements examined were mobile under strongly acidic conditions in the soils examined. The mobility of metals seems to decrease in the following order: Zn > Cu > Pb. The total contents of Zn and Cu in bedrock layers, unlike that of Pb, resulted both from weathering of parent rock and from the immobilization of leached metals, thus they cannot be used as geochemical background or a reference levels for assessing the contamination in soil surface horizons.

Soils of the Sudetes Mountains contained elevated amounts of Pb in surface horizons, but there was no evidence of soil contamination with Zn and Cu.

References

- Billett, M. F., Fitzpatrick, E. A. and Cressen, M. S.: 1991, 'Long-term changes in the Cu, Pb and Zn content of forest soil organic horizons from north-east Scotland', *Water, Air, and Soil Pollut.* **59**, 179–191.
- Borkowski, J., Dietrych, A., Kocowicz, A. and Szerszeń, L.: 1993, 'Heavy Metals Contents in Soils and Plants of Karkonosze Mts.', in *Geological Problems of the Karkonosze Mts.*, Wrocław University Press, Wrocław, Poland, pp. 131–136 (in Polish, with English Abstr.).
- Davies, B. E.: 1980, 'Trace Element Pollution', in B. E. Davies (ed.), *Applied Soil Trace Elements*, John Wiley & Sons, New York, U.S.A., pp. 287–344.
- Friedland, A. J. and Johnson, A. H.: 1985, 'Lead distribution and fluxes in a high-elevation forest in Northern Vermont', *J. Environ. Qual.* **14**(3), 332–336.
- Herrick, G. T. and Friedland, A.: 1990, 'Patterns of trace metal concentration and acidity in montane forest soils of the north-eastern United States', *Water, Air, and Soil Pollut.* **53**, 151–157.
- Holmgren, G. G. S., Meyer, M. W., Chaney, R. L. and Daniels, R. B.: 1993, 'Cadmium, lead, zinc, copper, and nickel in agricultural soils of the United States of America', *J. Environ. Qual.* **22**, 335–348.
- Iyengar, S. S., Martens, D. C. and Miller, W. P.: 1981, 'Distribution and plant availability of soil zinc fractions', *Soil Sci. Soc. Am. J.* **45**, 735–739.
- Kabata-Pendias, A. and Pendias, H.: 1992, *Trace Elements in Soils and Plants*, 2nd ed., CRC Press, Boca Raton, FL, U.S.A., 528 pp.
- Keller, C. and Vedy, J. C.: 1994, 'Distribution of copper and cadmium fractions in two forest soils', *J. Environ. Qual.* **23**, 987–999.
- Lee, B. D., Carter, B. J., Basta, N. T. and Weaver, B.: 1997, 'Factors influencing heavy metals distribution in six Oklahoma benchmark soils', *Soil Sci. Soc. Am. J.* **61**, 218–223.

- Maciejewska, A.: 1993, 'The content of trace elements in acid brown soils developed from sandstone of the Swietokrzyskie Mountains', *Polish J. Soil Sci.* **26**(2), 111–117.
- McBride, M. B.: 1994, *Environmental Chemistry of Soils*, Oxford University Press, New York, Oxford, 782 pp.
- Ramos, L., Hernandez, L. M. and Gonzales, M. J.: 1994, 'Sequential fractionation of copper, lead, cadmium and zinc in soils from Donana National Park', *J. Environ. Qual.* **23**, 50–57.
- Reeuwijk, L. P. (ed.): 1995, *Procedures for Soil Analysis, Technical Paper 9*, 5th ed., ISRIC, Wageningen, The Netherlands, 156 pp.
- Schwarz, A., Wilcke, W., Kobza, J. and Zech, W.: 1999, 'Spatial distribution of heavy metal concentrations as indicator of pollution sources at Mount Krizna (Great Fatra, central Slovakia)', *J. Plant Nutr. Soil Sci.* **162**, 421–428.
- Shuman, L. M.: 1985, 'Fractionation method for soil microelements', *Soil Sci.* **140**, 11–22.
- Sposito, G., Lund, G. J. and Chang, A. C.: 1982, 'Trace metal chemistry in arid zone field soils amended with sewage sludge. I. Fractionation of Ni, Cu, Zn, Cd and Pb in solid phases', *Soil Sci. Soc. Am. J.* **46**, 260–264.
- Tessier, A., Campbell, P. G. C. and Bisson, M.: 1979, 'Sequential extraction procedure for the speciation of particulate trace metals', *Anal. Chem.* **51**, 844–851.
- World Reference Base for Soil Resources: 1998, *FAO World Soil Resources Report, No. 84*, Rome, Italy, 124 pp.
- Zeien, H. and Brümmer, G. W.: 1989, 'Chemische Extraktionen zur Bestimmung von Schwermetallbindungsformen in Böden', *Mitt. Dtsch. Bodenkundl. Gesellsch.* **59**, 1, 505–510 (in German).