FACTORS AFFECTING THE TRACE ELEMENT DISTRIBUTION IN A SOIL DEVELOPED ON GRANITE BEDROCK IN CENTRAL BOHEMIA (CZECH REPUBLIC)*

J. Martínek, A. Žigová, P. Skřivan

Institute of Geology, Academy of Sciences of the Czech Republic, Prague, Czech Republic

Distribution of As, Be, Cd, Cu, Mn, Pb, Sr, and Zn was studied in a soil profile developed on the alluvium of the granitic bedrock in a forested watershed "Lesní potok" SE from Prague. Geochemistry of the bedrock shows considerable enrichment in As, Be and Pb. Four horizons, A, Bw, Go and Gr, were distinguished in a soil described as Gleyic Cambisol. Total content of Mn, Fe, Zn, and Cu in the individual soil horizons is proportional to their clay content and cation exchange capacity. Distribution of the forms of elements in the soil profile, extractable in 0.1 M HNO₃ reveals the pattern resulting from their migration characteristics, origin, and the impact of the acid atmospheric deposition. The uppermost A soil horizon is enriched in the extractable forms of As, Cd, Mn, Pb, Sr, and Zn. Anthropogenic industrial aerosol is the most probable source of As, Cd and Zn, whereas the aerosol of vehicular emissions represents the main input of Pb. Metabolic activity of the forest vegetation, manifested in considerably enhanced fluxes of Mn, Sr (Zn) in throughfall, is the most probable reason for their enrichment in the A horizon. Decrease in the overall content of Be, as well as in the content of extractable Be and Sr towards the upper parts of the soil profile results from the enhanced leaching of these elements through the acid atmospheric precipitation, which is also documented in high concentrations of these elements in the surface discharge.

watershed; soil; profile; trace elements; distribution

INTRODUCTION

The bonding and vertical distribution of minor and trace elements in soils have been intensively studied from several reasons: First, they can provide

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valuable information on possible risks of the mobilisation of elements into the ground waters and surface streams. On the other hand, they can give evidence on the accessibility of soil chemical components for the vegetation, which is important especially in agriculture. There are several factors which affect the status and mobilisation of trace elements in soils: chemical character of the particular element, its origin, structural and chemical composition of soil, dispersity of its particles, and the external effects. Among them, the acid atmospheric precipitation is the most important effect in our studied system.

Aim of this work was to compare the behaviour of several typical minor and trace elements in a soil profile which evolved in an alluvial deposit with granitic bedrock in the experimental forested watershed "Lesní potok" in Central Bohemia. Selection of elements pursued the possibility to choose various types of them with differing mobilisation characteristics, role in the plant metabolism and origin, including the anthropogenic one.

MATERIAL AND METHODS

Site description

The soil characteristics and distribution of selected elements in the soil profile were studied at the closing profile of the experimental catchment "Lesní potok watershed" (LPW) in the Černokostelecko region, Central Bohemia. Small brook of the watershed is draining the northern part of the Nature State Reserve "Voděradské bučiny" and it is situated approximately 30 km SE from the centre of Prague. It covers an area of 0.765 km² and it is completely forested (prevailing beech, hornbeam and Norway spruce). The southern boundary of the catchment reaches 500 m above sea level and the closing weir at its northern part is 406 m a.s.l. Mean annual precipitation is 635 mm and the average stream runoff is 134 mm (3.2 L.s⁻¹). "Lesní potok watershed" is underlain by the granitoids of the Říčany massif. The LPW is included in an integrated biogeochemical monitoring system of small watersheds (covering the western part of the Czech Republic) managed by the Czech Geological Survey. Chemistry of bulk precipitation, throughfall and stream runoff is monitored there since 1994 (bulk precipitation since 1989). Soil profile was studied in a distance 5 m NE from the Thomson weir, where the stream runoff and its chemistry are measured, in an 1 m deep pit. Total content of the selected elements (As, Be, Cd, Cu, Fe, Mn, Pb, Sr, Zn) and content of their extractable forms (determined through the digestion in 0.1 M HNO₃) were measured in the soil sampled from the pit.

Bedrock of the watershed

The LPW watershed is underlain by two types of granitic rocks. They represent part of the late Variscan Central Bohemian Pluton as its most recent members. The northern half of the catchment is underlain by a light coloured fine-grained two mica syenogranite (the Jevany type), while the southern part is built of a coarse- to medium-grained biotitic monzogranite (the Říčany type) (M i n a řík et al., 1998). The studied soil profile (in the northern part of the catchment) is therefore underlined by syenogranite. The profile, however, is of alluvial origin (floodplain of the "Lesní potok" brook) and the studied soil profile is therefore probably derived from both types of the described rocks.

Characteristics of the soil profile

The sampled soil profile is formed by the alluvial deposits with the overall thickness 10 m (Hons et al., 1990). The soil profile (LP 33) has been sampled 5 meters NE from the Thomson weir and the pit was dug into 1 m depth on 4 June 1996. The main morphological characteristics of the individual horizon are presented in the soil profile description:

A: 0-15 cm Very dark brown (10 YR 2/2) moist, loamy sand, moderate coarse granular, very friable, abundant very fine and fine roots, abrupt, smooth boundary;

Bw: 15-33 cm Yellowish brown (10 YR 5/4) moist, loam, moderate medium angular, friable, abundant very fine roots, clear, smooth boundary

Go: 33-48 cm Yellow (10 YR 8/6) moist, loamy sand, structureless, non coherent, clear, smooth boundary;

Gr: 48-101 cm Light grey (5Y 7/1) moist, loam, structureless, plastic, small soft spherical reddish brown iron nodules.

Depth of the groundwater table is approx. 1.7 m.

Solid rock, the Jevany syenogranite, was found by drilling in depth of approx. 10 m.

The soil is classified according to the World Reference Base for Soil Resources (1994) as a Gleyic Cambisol.

Samples of the soil profile were analysed from four horizons, A, Bw, Go, Gr (this one with 4 subhorizons). The pH value, humus content, cation exchange capacity – T_M , exchangeable H_m^+ (according to Mehlich), particle size distribution (see Table I) and physical properties (bulk density, particle density, suction, water capacity, maximum capillary capacity, retention water capacity, porosity, semicapillary porosity, minimum air capacity and volume changeability – see Table II) were determined by procedures according to

| 5 | I. The individual characteristics of the LP 33 profile (pHH20, pHKC1, organic carbon, cation exchange capac | city – T _M , exchangeable H ⁺ _M , particle |
|---|---|---|
| | size distribution) | |

| Soil horizon | Average depth | рН _{Н-О} | рН _{КСІ} | T _M | H_{M}^{+} | Humus | < 0.01 mm | < 0.001 mm | 0.001– 0.01 mm | 0.01– 0.05 mm | 0.05– 0.25 mm | 0.25– 2.00 mm |
|-----------------|---------------|-------------------|-------------------|----------------|-------------|-------|--------------|---------------|-------------------|------------------|------------------|------------------|
| norizon | cm | - 1120 | | mmol/100 g | mmol/100 g | % | % | % | % | % | % | % |
| Α | 7.5 | 3.80 | 3.00 | 24.00 | 26.50 | 8.19 | 19.0 | 6.8 | 12.2 | 33.7 | 12.5 | 34.8 |
| Bw | 24.0 | 4.04 | 3.46 | 13.70 | 15.50 | 0.78 | 35.6 | 20.5 | 15.1 | 32.9 | 13.6 | 17.9 |
| G ₀ | 40.5 | 4.14 | 3.79 | 5.10 | 6.50 | 0.41 | 14.8 | 10.4 | 4.4 | 10.1 | 12.5 | 62.6 |
| Gr ₁ | 57.5 | 4.00 | 3.41 | 15.20 | 17.00 | 0.48 | 44.6 | 32.2 | 12.4 | 35.8 | 11.8 | 7.9 |
| Gr ₂ | 70.5 | 4.05 | 3.38 | 14.60 | 15.00 | 0.21 | 43.6 | 32.0 | 11.5 | 34.1 | 9.2 | 13.2 |
| Gr ₃ | 85.5 | 4.26 | 3.54 | 3.80 | 5.00 | 0.07 | 14.6 | 9.0 | 5.6 | 10.8 | 7.6 | 67.0 |
| Gr ₄ | 95.0 | 4.33 | 3.43 | 5.70 | 6.50 | 0.14 | 23.3 | 18.1 | 5.3 | 20.3 | 14.6 | 41.8 |

II. The physical properties of the LP 33 profile

| Soil | Average depth | S | WC | MCC | RWC | BD | PD | Р | SP | MAC |
|-----------------|---------------|--------|--------|--------|--------|-------------------|-------------------|--------|--------|--------|
| horizon | cm | % vol. | % vol. | % vol. | % vol. | g/cm ³ | g/cm ³ | % vol. | % vol. | % vol. |
| Α | 7.5 | 55.78 | 56.68 | 56.22 | 54.36 | 0.78 | 2.36 | 67.03 | 2.32 | 16.48 |
| Bw | 24.0 | 42.67 | 42.19 | 41.94 | 39.66 | 1.23 | 2.52 | 51.19 | 2.54 | 11.15 |
| G ₀ | 40.5 | 33.69 | 32.13 | 31.60 | 28.72 | 1.79 | 2.58 | 30.46 | 3.39 | 7.04 |
| Gr ₁ | 57.5 | 41.63 | 38.39 | 37.76 | 35.01 | 1.63 | 2.54 | 35.89 | 3.39 | 3.17 |
| Gr ₂ | 70.5 | 43.89 | 42.70 | 42.38 | 38.96 | 1.61 | 2.53 | 36.62 | 3.73 | 1.64 |
| Gr ₃ | 85.5 | 43.89 | 42.70 | 42.38 | 38.96 | 1.61 | 2.53 | 36.62 | 3.73 | 1.64 |
| Gr ₄ | 95.0 | 43.89 | 42.70 | 42.38 | 38.96 | 1.61 | 2.53 | 36.62 | 3.73 | 1.64 |

S - suction, WC - water capacity, MCC - maximum capillary capacity, RWC - retention water capacity, BD - bulk density, PD - particle density, P - porosity, SP - semicapillary porosity, MAC - minimum air capacity

Hraško et al. (1962), modified by Research Institute for Soil and Water Conservation, Prague.

The soil profile is very acid. The organic carbon shows the decrease from the umbric A horizon to gleyic Gr horizon – and it mirrors the irregularities in the clay content (< 0.001 mm, see Table I) reflected in the cation exchange capacity – T_M . Content of the exchangeable H_M^+ in the sorption complex is high and it corresponds to the Gleyic Cambisol.

Results of the particle size distribution correspond to the allochtonous origin of the parent material, which in the horizons Go and Gr3 has significant portion of the 0.25–2.00 mm fraction and in the horizons Bw, Gr1, Gr2 has significant portion of the < 0.001 mm fraction. We define the individual horizons with respect to the texture classes – as follows: A – loamy sand, Bw – loam, Go – loamy sand, Gr1 – loam, Gr2 – loam, Gr3 – loamy sand, Gr4 – loamy sand.

Knowledge of the mobilization and redistribution of elements requires the definition of physical characteristics of soil (see the Table II). The bulk density BD considerably increases in the Go horizon, in the underlying horizons having similar values. Opposite course was observed in the porosity P, that is the characteristics, as well as bulk density, which correlates to the humus content of the soil profile. The Gr, as it is described bellow, shows abrupt and significant changes in comparison to the upper part of soil profile. The value of suction S reaches higher values than the porosity, which documents the enhanced swelling of soils. The values of water capacity WC reach values of suction, which means that majority of the semicapillary pores SP is filled with water. This characterisation of soil is also confirmed by the fact, that at growing volume of the semicapillary pores the values of minimum air capacity MAC are lowering. Proportion between the retention water capacity RWC and the porosity is unfavourable for further development of soil, too. Values of the physical properties, as well as their course show, that the pedogenesis proceeds in the upper part of the soil profile under oxidising conditions, which change in the depth approx. 48 cm (the boundary between the Go and Gr horizons) into the reducing ones. Conditions of the lower part of the profile have led to the evolution of horizons with gleyic properties.

Chemistry of the soil profile

The total content and content of the mobile forms was determined in the soil sampled from the probe (LP33) described above. Total content of studied elements was determined (Analytika Co. Ltd., Prague, analyst J. Bendl) through wet decomposition of soil samples in a mixture of conc. HNO₃ and HF under pressure in a microwave oven and through analysis of the solution

by ICP-MS. Content of the extractable (loosely bound) forms of elements were determined through digestion of the soil samples (fraction < 1 mm) in 0.1 M HNO₃ (1 g of solid in 200 ml of acid solution, duration 24 hrs). The extracts were – after the membrane filtration (Sartorius, pore size < 0.45 m) – analysed by AAS (M. Burian, in a laboratory of the Institute of Geology, CAS, Prague).

RESULTS

Inputs and outputs of elements of the catchment

Bulk atmospheric precipitation

Sampling of the bulk precipitation is carried out at the experimental station of the Faculty of Forestry, Czech Agricultural University (locality "Truba") which is situated 5 km from the LPW. It is sampled on a forest clearing, at least 50 m from the full-grown trees. The procedure of the bulk precipitation sampling is in principle similar to that published by B e r g et al. (1994) and it was previously described by S k \check{r} i v a n and V a c h (1993).

Mean annual pH of atmospheric precipitation is 4.2 and the average composition is sampled monthly since May 1989. Data summarising the bulk precipitation samples from the point of view of the selected elements content are presented in Table III (from May 1994, like the following throughfall data).

Throughfall

Beech-hornbeam throughfall is sampled in the closing profile of the LPW, e. g. in the same site as the stream runoff and soil profile. Sampling of this type of atmospheric deposition started in May 1993. The throughfall is collected monthly, too, and the sampling procedure was described by S k \check{r} i v a n et al. (1994). Mean pH of the throughfall samples is 4.7. Data of the beechhornbeam throughfall are summarised in Table III, together with the bulk precipitation data.

Output by the surface discharge

Surface water discharge is one of the most significant outputs (together with the subsurface discharge and exploitation of wood) from the catchment. The average runoff during the last 3 hydrological years (1994–1996) was 134,1 $L.m^{-2}.yr^{-1}$ and the average pH was 4.8 during the same period. The

III. Mean concentrations (μ g.l⁻¹), mean fluxes (μ g.m⁻².day⁻¹) and mean annual fluxes (μ g.m⁻².year) of selected elements in samples of the bulk precipitation, beech-hornbeam throughfall and surface discharge (n = 32 for all of these sampled media)

| Bulk precipitation | | | | | | | | | | |
|--------------------|-------|---------|----------|----------|-------|-------|-------|--------|------|--|
| Element | Cu | Mn | Fe | Zn | Pb | Be | As | Sr | Cd | |
| Mean concentration | 2.08 | 22.26 | 89.47 | 16.84 | 4.63 | 0.02 | 1.85 | 2.45 | 0.15 | |
| Mean flux | 3.07 | 31.59 | 125.65 | 22.26 | 7.90 | 0.03 | 3.16 | 2.72 | 0.24 | |
| Mean annual flux | 1 122 | 11 531 | 45 863 | 8 125 | 2 882 | 11.9 | 1 153 | 994 | 86.3 | |
| | | Beech | -hornbea | m throug | hfall | | | | | |
| Element | Cu | Mn | Fe | Zn | Pb | Be | As | Sr | Cd | |
| Mean concentration | 3.02 | 293.11 | 56.15 | 33.74 | 2.50 | 0.09 | 1.98 | 7.75 | 0.23 | |
| Mean flux | 3.57 | 292.73 | 68.25 | 32.37 | 3.15 | 0.07 | 2.68 | 4.55 | 0.27 | |
| Mean annual flux | 1 303 | 106 845 | 24 910 | 11 817 | 1 151 | 26.1 | 978 | 1 662 | 98.1 | |
| | | S | urface d | ischarge | | | | | | |
| Element | Cu | Mn | Fe | Zn | Pb | Be | As | Sr | Cd | |
| Mean concentration | 1.09 | 382.50 | 370.06 | 19.06 | 0.42 | 8.01 | 1.30 | 201.28 | 0.48 | |
| Mean flux | 0.21 | 93.84 | 33.23 | 8.18 | 0.17 | 3.27 | 0.49 | 78.98 | 0.19 | |
| Mean annual flux | 77.3 | 34 250 | 12 130 | 2 987 | 61.6 | 1 193 | 180 | 28 829 | 69.4 | |

average stream runoff of the selected elements is presented in the following Table III, too.

Mineralogy and chemistry of the bedrock

Mineralogy, bulk chemistry and content of selected minor and trace elements in both types of the parent rocks are summarised in Table IV.

Chemistry of the soil profile

Chemical data from the probe are summarised in Table V. It contains the total content of studied elements, together with their mobile forms and the ratio of mobile/total content, expressed in %.

DISCUSSION

Inputs and outputs

Higher concentration of some elements in throughfall (the precipitation collected after it has passed through the tree canopy) in comparison with

| Rock type | Syenogranite (Jevany type) | Monzogranite (Říčany type) | Rock type | Syenogranite (Jevany type) | Monzogranite (Říčany type) |
|------------------|-------------------------------|-------------------------------|--------------------------------|-------------------------------|-------------------------------|
| Mineral | vol. % | vol. % | oxide | wt. % ¹⁾ | wt.% ²⁾ |
| Quartz | 26.42 | 24.76 | SiO ₂ | 70.62 | 69.64 |
| K – feldspar | 40.61 | 32.70 | TiO ₂ | 0.29 | 0.35 |
| Plagioclase | 20.05 | 27.53 | Al ₂ O ₃ | 14.80 | 15.24 |
| Biotite | 5.79 | 8.10 | Fe ₂ O ₃ | 0.57 | 0.72 |
| Muscovite | 0.47 | 0.18 | FeO | 1.28 | 1.48 |
| Kaolinite | 6.22 | 6.60 | MnO | 0.04 | 0.05 |
| Chlorite | 0.18 | 0.06 | MgO | 1.08 | 1.42 |
| Accessories | 0.16 | 0.07 | CaO | 1.36 | 1.43 |
| Σ | 99.98 | 100.00 | Na ₂ O | 3.92 | 3.50 |
| Element | mg.kg ⁻¹ | mg.kg ⁻¹ | K ₂ O | 5.09 | 5.40 |
| As ⁴⁾ | 24.0 | 11.0 | P ₂ O ₅ | 0.24 | 0.35 |
| Be ³⁾ | 7.0 | 13.0 | H ₂ O ⁺ | 0.41 | 0.43 |
| Cd ⁴⁾ | 0.19 | 0.56 | H ₂ OPPP | 0.23 | 0.27 |
| Cu ⁴⁾ | 13.9 | 14.7 | Σ | 99.93 | 100.28 |
| Pb ⁴⁾ | 64.0 | 68.0 | | | |
| Sr ⁴⁾ | 28.0 | 807 | | | |
| Zn ⁴⁾ | 35.4 | 85.8 | : | | |

IV, Modal- and bulk chemical composition of the parent rocks

1) mean values of 11 analyses

2) mean values of 16 analyses, both by Palivcová et al. (1992)

3) mean concentratin by Němec (1978)

4) concentration by J. Bendl, Analytika Co. Ltd., ICP-MS (unpublished)

samples of the bulk precipitation collected on an open place (see Table III) follows from the fact that throughfall contains - in addition to the solutes of the incoming precipitation - also solutes from the leached metabolites of the foliage and the dissolved species from the so called "occult deposition" (Drever, Clow, 1993). This term is used to cover the deposition from mist and fog and the dry deposition (both solid and gaseous) taken up by surfaces of foliage. Occult deposition is the probable source of As, Be, Cd, (Cu and Zn) in throughfall, whereas the tree metabolism is responsible here for the elevated concentrations of Mn, Sr and perhaps essential Cu, Zn (He in richs, Mayer, 1980; Atteia, Dambrine, 1993). On the other hand, lower concentration of Fe in throughfall can be attributed to the lower

| Average depth | As (ppm) | Be (ppm) | Cd (ppm) | Cu (ppm) | Fe (ppm) | Mn (ppm) | Pb (ppm) | Sr (ppm) | Zn (ppm) |
|------------------|-------------|-------------|--------------|-------------|-------------|--------------|-------------|------------|------------|
| 7.5 cm | 35.3 / 0.68 | 3.75 / 0.14 | 0.79 / 0.100 | 26.8 / 1.16 | 3 292 / 730 | 118.7 / 18.2 | 67.1 / 30.0 | 223 / 2.36 | 48.9 / 4.6 |
| % m.f. | 1.93 | 3.73 | 16.66 | 4.33 | 22.17 | 15.32 | 44.74 | 1.06 | 9.41 |
| 24 cm | 43.1 / 0.18 | 5.43 / 0.60 | 1.05 / 0.010 | 28.5 / 1.10 | 5 998 / 862 | 192.9 / 15.2 | 58.6 / 12.6 | 210 / 0.36 | 69.4 / 3.2 |
| % m.f. | 0.42 | 11.05 | 0.95 | 3.86 | 14.37 | 7.88 | 21.50 | 0.17 | 4.61 |
| 40.5 cm | 30.6 / 0.22 | 6.33 / 0.55 | 0.86 / 0.010 | 10.8 / 0.14 | 2 658 / 714 | 75.1 / 7.8 | 47.9 / 10.0 | 265 / 0.32 | 24.2 / 1.0 |
| % m.f. | 0.72 | 8.69 | 1.16 | 1.30 | 26.86 | 10.37 | 20.86 | 0.12 | 4.14 |
| 57.5 cm | 39.6 / 0.27 | 6.21 / 1.11 | 1.25 / 0.017 | 37.9 / 1.00 | 7 901 / 815 | 192.9 / 5.3 | 76.4 / 26.0 | 175 / 0.62 | 98.9 / 3.8 |
| % m.f. | 0.68 | 17.87 | 1.36 | 2.64 | 10.32 | 2.75 | 34.04 | 0.35 | 3.84 |
| 70.5 cm | 42.2 / 0.32 | 6.03 / 1.39 | 1.26 / 0.040 | 35.6 / 1.29 | 7 390 / 838 | 150.8 / 5.6 | 93.1 / 26.0 | 203 / 1.01 | 81.1 / 3.6 |
| % m.f. | 0.76 | 23.05 | 3.17 | 3.63 | 11.34 | 3.71 | 27.93 | 0.50 | 4.44 |
| 85.5 cm | 28.1 / 0.34 | 6.30 / 0.60 | 1.00 / 0.008 | 13.4 / 0.44 | 2 488 / 466 | 56.8 / 4.2 | 40.1 / 11.0 | 245 / 0.72 | 28.3 / 1.0 |
| % m.f. | 1.21 | 9.52 | 0.80 | 3.27 | 18.73 | 7.39 | 27.42 | 0.29 | 3.54 |
| 95 cm | 35.1 / 0.52 | 7.38 / 1.22 | 1.19 / 0.016 | 24.5 / 0.88 | 5 179 / 630 | 102.7 / 3.8 | 66.8 / 16.2 | 280 / 2.46 | 53.2 / 2.2 |
| % m.f. | 1.48 | 16.53 | 1.34 | 3.59 | 12.16 | 3.70 | 24.26 | 0.88 | 4.13 |

V. Total content of the selected elements (in ppm – mg.kg⁻¹ and of their extractable forms (expressed in ppm, too) and % of the mobile forms from their total content – % m.f.

content of terrigenous dust inside the afforested area than in an open place. Lower concentration of Pb in throughfall is explained by the character of fine particles of the vehicular aerosol, which is attached to the foliar surfaces and then partly enters the tree tissues (H a g e m e y e r, S c h a e f e r, 1995). Part of the atmospheric Pb is then deposited on the ground only with the litterfall. Additionally – the locality Truba, where the bulk atmospheric precipitation is collected, is situated approx. 100 m from the road with relatively low traffic density and part of the Pb content may be derived from this road – like a vehicular lead (Martínek, Burian, 1996).

The deposition intensity of throughfall water is lower (owing to the tree canopy interception and evapotranspiration) than that of the bulk precipitation. Nevertheless, the inputs of Mn, Sr, Zn as the essential elements and Be, Cd, Cu as the washed out components of anthropogenic aerosols are higher than the inputs by the bulk precipitation from reasons mentioned above.

Surface discharge of Cu, Pb, As, Zn and Fe is much lower than their atmospheric inputs. On the other hand, the output of Sr and Be (weathering products of underlying rock) is much higher than their atmospheric inputs.

Differences among the pH values of the individual presented fluxes (bulk precipitation pH = 4.2, throughfall 4.69 and surface discharge 4.8) reflect the processes of interaction among rainfall water, tree canopy and soil profile. These values also indicate that the precipitation water is partly neutralised during its path into the stream, which, on the other hand, results in the depletion of soil profile cations and accelerates the weathering processes.

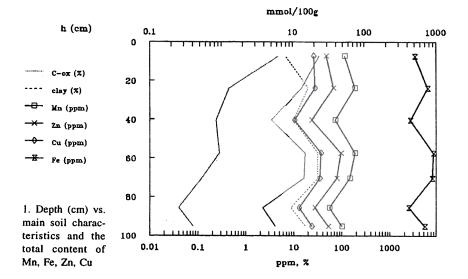
The data presented in Table III are the most important for the mass balance of the watershed.

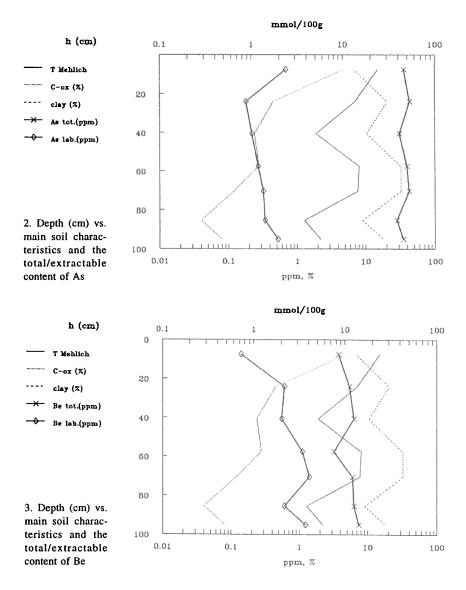
Content in parent rock and in soil

Underlying rock is generally the main source of elements in the corresponding soils. In our case, the composition of studied alluvial soil profile is derived from both types of the bedrock – the Říčany monzogranite and the Jevany syenogranite. These two types of bedrock are derived from the same source, which is documented by similar mineral and bulk chemical composition. On the other hand, they differ strongly in the content of several trace elements, as can be seen from Table IV. The difference is by far the largest in Sr and it is difficult to explain, as the content of plagioclases in both the rock types is similar. Results of Sr analyses were repeatedly confirmed and the high Sr content in monzogranite is necessary to ascribe to the local anomaly of the sampled rock. Remarkably high content of Pb in both types of rock results from its isomorphous substitution in K-feldspars. Total content of As, Cd, Cu, and Pb throughout the soil profile, however, is higher than that in both types of the bedrock. This fact has to be explained by the content of secondary clay minerals and amorphous Fe and Mn oxyhyroxides in the soil profile. These phases with unique properties and high specific surfaces represent favourable environment for the attachment of trace elements, which are liberated during the hydrolytical alteration of the primary rock forming minerals.

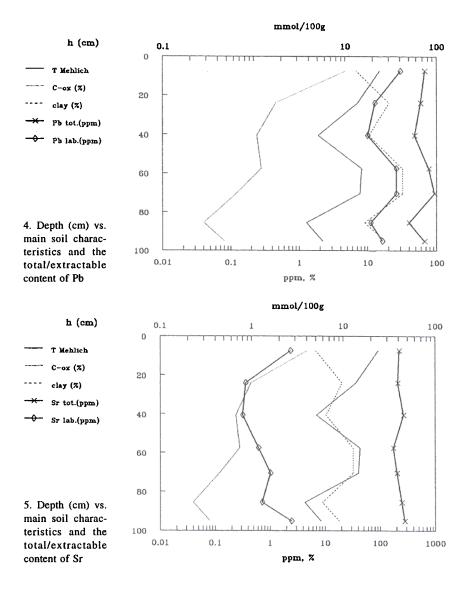
Soil profile

Total contents of studied elements (see Table V) indicate that the concentrations of Zn, Mn, Cu, Fe (Fig. 1) and partly As and Pb (see Figs. 2 and 4) correlate with the clay content (< 0.001 mm fraction) in the individual soil horizons. Content of these elements corresponds – in the deeper soil horizons – with the cation exchange capacity according to Mehlich, too. Discrepancies between the element content and the two mentioned soil characteristics in the A horizon can be explained by the enhanced content of organic matter, as it is well known that several trace elements, especially Cu, Pb and Zn are considerably retained by the organic matter. (Jenne, 1977; Harter, Naidu, 1995). Content of studied elements in the uppermost A horizon is mostly affected by the atmospheric inputs of anthropogenic dry deposition and by the solutes from throughfall.





Portion of the elements bound to the organic matter is mobilised – under applied experimental conditions – and enters the solution. This concerns, in our case, mainly the content of Pb, Mn, Cd, and Zn in the umbric A horizon. Low content of exctractable forms of arsenic (Fig. 2), in comparison to the



considerable portion of exctractable Fe and Mn throughout the whole soil profile, documents either the poor mobility of As anions at low pH or its presence in the relatively stabile inclusions – most probably in sulfidic phases – inside the grains of the rock forming minerals and in biotite (M i n a \check{r} i k

et al., 1997). The growing portion of the exctractable forms of Be, as well as of its total content (Fig. 3), towards the bottom of the profile follows from its high mobility under acidic conditions (Borovec, 1993; Veselý et al., 1989). This tendency verifies the gradual washout of this element by acid atmospheric precipitation and its depletion in the uppermost soil horizons. The enhanced output of Be is in good agreement with its relatively high content in the surface discharge (see Table III, Skřivan et al., 1996). It is necessary to point out, that the inputs of Be through the atmospheric deposition are negligible. The overall amount of Be is partly influenced - but not so markedly as in the other elements - by the clay content of the individual horizon. The abrupt decrease in the content of exctractable forms of Fe and Mn in the Gr horizon (see Table V), in spite of their higher total contents (which follows from the higher content of clay fraction), can be explained by the above discussed change of the redox conditions at the boundary between the Go and Gr horizons, which lead to the depletion of mobile forms of Fe and Mn.

Both the high total amount of Pb and content of its mobile forms (Fig. 4), mobilised at given experimental conditions, correspond in the whole soil profile to high Pb content in both types of the parent rock. Lead substitutes potassium in the structure of K-feldspar which is the dominant mineral component of the bedrock (see Table IV). The annual atmospheric input of Pb is not insignificant, as it is shown in Table III. It originates from the vehicular emissions of the engines, which burn the leaded gasoline. Nevertheless, the content of exctractable Pb forms in the uppermost 1 m of soil exceeds its annual input at least by 3 orders. This means that majority of mobile lead throughout the profile is of lithogenic origin. Only the umbric A horizon, which is directly influenced by the wet and dry atmospheric deposition, as well as by the litterfall, contains substantial amount of anthropogenic lead. The relative content of exctractable forms of the studied elements in the A horizon with respect to their total content is in the sequence Pb > Fe > Cd> Mn > Zn > Cu > Be > As > Sr (see Table V). It is necessary to point out that the sequence clearly reflects the conditions of the experimental determination of labile forms of studied elements. High relative content of mobile lead, in comparison with that of arsenic, stresses the significance of the chemical aspects of bonding of the compared elements. Lead, after its liberation from the crystal lattice of the aluminosilicates and sulphides, remains bound in secondary forms, whose mobilisation strongly depends on the pH of the system. Mobility of this element throughout the soil layer, under common natural conditions, is very low (Johnson et al., 1995). Arsenic has been most probably originally bound in separate sulfidic compounds. Mobility of its secondary oxidized phases (AsIII, AsV), which are mostly

bound to the Fe-oxyhydroxides, primarily depends on the Eh of the system (B o w e 11, 1994). It is evident that the applied experimental determination of the exctractable forms of all studied elements is tentative only and that it does not simulate the natural leaching processes precisely. Nevertheless, the field study confirmed that the mobility of both elements, Pb and As, is low, as it is documented by their content in the surface discharge. On the other hand, low content of exctractable forms of Sr throughout the soil profile (see Table IV and Fig. 5) results from their continual leaching (P o p o v et al., 1995) into the ground water and the surface stream (see high concentration of Sr in the surface discharge in Table III) under the really existing conditions which are strongly affected by the acid atmospheric precipitation.

CONCLUSIONS

Distribution of studied minor and trace elements (As, Be, Cd, Cu, Mn, Pb, Sr, Zn) troughout the soil profile of the LPW watershed is first of all affected by the bulk chemical and mineral composition of the bedrock, which determines the character of the individual soil horizons. The underlying granites are enriched in As, Be and Pb, content of the other elements corresponds to their common content in these rock types. Character of the studied soil profile is affected by its genesis, as it is formed by the alluvial deposits with changing modal composition and grain size distribution. Distribution of most of the studied elements, e.g. Zn, Mn, Cu, and Fe strongly correlates with the clay content of the individual soil horizons. Atmospheric input of vehicular Pb represents the only important source of elements besides their input through the rock weathering. The atmospheric deposition of technogenic As, Cd, Pb, and perhaps Zn contributes to their enhanced content of extractable forms in the soil A horizon, too. On the other hand, metabolic activity of the tree vegetation affects the distribution pattern throughout the profile strongly in Mn, and to a lesser extent in Sr (Zn). The influx of atmospheric protons, which is at least by one order higher than before the industrial revolution, significantly affects the pattern of Be and Sr, the elements which are increasingly leached into the surface water.

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References

ATTEIA, O. – DAMBRINE, E.: Dynamique d'éléments traces dans les précipitations sous le couvert de 2 pessieres peu polluées de Suisse romande. Ann. Sci. For., 50, 1993: 445–459.

SCIENTIA AGRICULTURAE BOHEMICA, 30, 1999 (1): 55-71

BERG, T. – ROYSET, O. – STEINNES, E.: Trace elements in atmospheric precipitation at Norwegian background stations (1989–1990) measured by ICP-MS. Atmosph. Envir., 28, 1994: 3519–3536.

BOROVEC, Z.: Partitioning of silver, beryllium and molybdenum among chemical fractions in the sediments from the Labe (Elbe) river in central Bohemia, Czech Republic. GeoJournal, 29, 1993: 359-364.

BOWELL, J. R.: Sorption of arsenic by iron oxides and oxohydroxides in soils. Appl. Geochem., 9, 1994: 279–286.

DREVER, J. I. – CLOW, D. W.: Weathering rates in catchments. In: Reviews in Mineralogy, 31, 1993: 464–483.

HAGEMEYER, J. – SCHAEFER, H.: Seasonal variations in concentrations and radial distribution patterns of Cd, Pb and Zn in stem wood of beech trees (*Fagus sylvatica* L.). Sci. Total Environ., 166, 1995: 77–87.

HEINRICHS, H. - MAYER, R. (1980): The role of forest vegetation in the biogeochemical cycle of heavy metals. J. Environ. Qual., 9, 1980: 111-118.

HARTER, R. D. - NAIDU, R.: Role of metal-organic complexation in metal sorption by soils. Adv. Agron., 55, 1995: 219-263.

HONS, R. - TIPKOVÁ, J. - MINAŘÍK, L. - ABSOLON, K.: Geochemical profile in the area of the Lesní potok stream in the Říčany district. In: Proc. Inst. Apl. Ecol. CZU, Prague, 1990: 85–95 (in Czech).

HRAŠKO, J. – ČERVENKA, L. – FACEK, Z. – KOMÁR, J. – NĚMEČEK, J. – POSPÍŠIL, F. – SIROVÝ, V.: Analyses of soils. Bratislava, SVTL 1962. 342 p. (in Slovak).

JENNE, E. A.: Trace element sorption by sediments and soils – sites and processes. In: Proc. Symp. Mo in the environment (eds. CHAPPEL, W. – PETERSON, K.), Vol. 2, 1977. 425 p.

JOHNSON, C. E. – SICCAMA, T. G. – DRISCOLL, C. T. – LIKEUS, G. E. – MOELLER, R. E.: Changes in lead biogeochemistry in response to decreasing atmospheric inputs. Ecol. Appl., 5, 1995: 813–822.

MARTÍNEK, J. – BURIAN, M.: Evaluation of the locality "Truba" (Kostelec n. Č. lesy) from the point of view of the bulk precipitation sampling. In: Workshop SCOPE Global changes and essential elements cycling in the environment, Prague, September 17–18, 1996, Geol. Inst. ASCR. Extd. Abs.: 6–7.

MINAŘÍK, L. – BURIAN, M. – NOVÁK, J. K.: Experimental acid leaching of metals from biotite of the Říčany monzogranite. Věstník ČGÚ, 72, 1997 (3): 239–244.

MINAŘÍK, L. – ŽIGOVÁ, A. – BENDL, J. – SKŘIVAN, P. – ŠŤASTNÝ, M.: The behaviour of rare-earth elements and Y during the rock weathering and soil formation in the Říčany granite massif, Central Bohemia. The Science of the Total Environment. 1998.

NÉMEC, D.: Genesis of aplite in the Říčany massif, central Bohemia. Neues Jahrb. Mineral. Abh., 133, 1978 (3): 322-339.

PALIVCOVÁ, M. – WALDHAUSROVÁ, J. – LEDVINKOVÁ, V. – FATKOVÁ J.: Říčany granite (Central Bohemian Pluton) and its ocelli- and ovoids-bearing mafic enclaves. Krystalinikum, 21, 1992: 33–66.

POPOV, V. Y. – KUTNYAKOV, I. V. – ZHIRNOV, V. G. – VICHRENKO, Y. P. – SIVE-RINA, A. A. – BOBOVNIKOV, T. I.: Vertical distribution of Sr-90 and Cs-137 in alluvial sod soils in the near zone of the Chernobyl Nuclear Power Station. Eurasian Soil Sci., 27, 1995 (11): 65–73. SKŘIVAN, P. – VACH, M.: Decreasing immissions of vehicular lead in central Bohemia? Acta Univ. Carol., Geol., 37, 1993: 45–55.

SKŘIVAN, P. – MINAŘÍK, L. – BURIAN, M. – VACH, M.: Cycling of beryllium in the environment under anthropogenic impact. Scientia Agric. Bohem., 25, 1994: 69–79.

SKŘIVAN, P. – ŠŤASTNÝ, M. – KOTKOVÁ, P. – BURIAN, M.: Partition of beryllium and several other trace elements in surface waters. Agric. Bohem., 27, 1996: 131–145.

VESELÝ, J. – BENEŠ, P. – ŠEVČÍK, K.: Occurrence and speciation of beryllium in acidified freshwaters. Water Res., 23, 1989: 711–717.

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MARTÍNEK, J. – ŽIGOVÁ, A. – SKŘIVAN, P. (Geologický ústav AV ČR, Praha, Česká republika):

Faktory ovlivňující distribuci stopových prvků v půdním profilu vyvinutém na granitické hornině ve středních Čechách (Česká republika).

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Distribuce As, Be, Cd, Cu, Mn, Pb, Sr a Zn byla sledována v půdním profilu vyvinutém na aluviu granitické horniny v povodí Lesní potok, nacházejícím se jihovýchodně od Prahy. Podložní hornina je značně obohacena As, Be a Pb. V půdě, určené jako glej kambizemní, byly odlišeny čtyři horizonty: A, Bw, Go, Gr. Celkový obsah Mn. Fe, Zn a Cu v jednotlivých půdních horizontech závisí na obsahu jílových minerálů a kationtové výměnné kapacitě. Distribuce forem prvků v půdním profilu. jež jsou extrahovatelné v 0,1 M HNO3, vypovídá o jejich migračních charakteristikách, původu a vlivu kyselé atmosférické depozice. Půdní A horizont je obohacen o extrahovatelné formy As, Cd, Mn, Pb, Sr a Zn. Antropogenní industriální aerosol je s nejvyšší pravděpodobností zdrojem As, Cd a Zn, zatímco aerosol z vehikulárních emisí představuje hlavní vstup olova. Metabolická aktivita stromové vegetace, již dokládají významně zvýšené toky Mn, Sr (Zn) ve srážkách pod korunami stromů, je neipravděpodobněiší příčinou jejich zvýšených koncentrací v půdním A horizontu. Snižování celkového obsahu Be i celkového obsahu extrahovatelného Be a Sr směrem k vrchním částem půdního profilu vyplývá ze zvýšeného loužení těchto prvků kyselými atmosférickými srážkami, což dokumentují jejich vysoké koncentrace v povrchovém odtoku.

povodí; půda; stopové prvky; distribuce

Contact Address:

Ing. Jaroslav Martínek, Geologický ústav AV ČR, Rozvojová 135, 165 00 Praha 6, Česká republika, tel.: 02/20 92 26 28, fax: 02/20 92 26 70, e-mail: skrivan@gli.cas.cz