Biogeochemistry of the Transition Elements in a Forested Landscape (beech, *Fagus sylvatica* L.) with the Granite Bedrock

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ABSTRACT: Geochemistry of the transition elements (TE) has been studied in the soil profile derived from the granitic rocks in the area of the Lesni potok catchment near the town of Říčany. The TE's distribution in surface water, atmospheric deposition and throughfall of the area have been discussed, too.

Relative mobility of the transition metals, derived from their concentration in the soil profile and in surface water, decreases in following sequence: Mn>Ni>Sc>Co>>Zn> >Cu>Fe>Cr>V>Ti. Recent annual load of the studied catchment by the transition metals, comparable with rural areas of southern Norway, indicates decreasing trends of their emission sources. Extent of other than natural terrigenic sources of the metals in bulk precipitation, expressed by their crustal enrichment factor (CEF, normalised to Fe), decreases in following order: Zn>Cu>Ni>V=Mn>Sc=Co=Cr>Ti. Higher values in the first four metals are attributed to their technogenic origin, CEF value of Mn is affected by the metabolic activity of the forest vegetation, surrounding the sampling locality. Impact of the metabolic activity of forest trees on the ambient redistribution of TE's, assessed by means of the EF_{TH} (the enrichment factor of the metals in beech throughfall), was clearly proved only in Mn.

KEY WORDS: transition elements, catchment, forest, granite bedrock, soil profile.

Introduction

Elements of the first transition series, scandium, titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper (and zinc) with the successively filled 3d electron orbital, constitute about 40 wt% of the Earth and they occur in most minerals of the crust. Their behaviour is very complex even in pure abiotic crustal geochemical processes such as the chemical rock weathering, as well as in the course of soil formation. It often differs
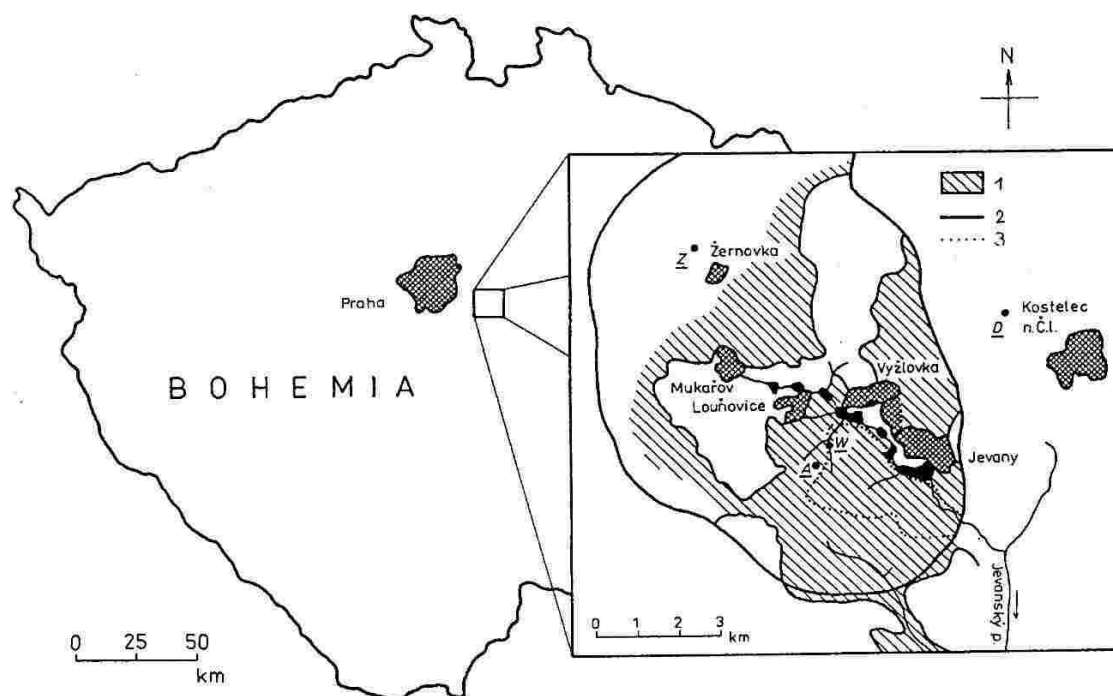

Fig. 1. Map of the Černokostelecko region, location of the sampling sites. 1 - afforested areas; 2 - boundary of the Říčany granite; 3 - area of the Voděradské bučiny State Nature Reserve; A - location of the abandoned Kaménka quarry; Z - location of the operated quarry near Žernovka; W - closing weir of the Lesní potok catchment, localities of the throughfall sampling; D - localities of bulk precipitation sampling near Kostelec n. Černými lesy.

markedly from those of the non-transition metal ions with similar sizes and oxidation state. Throughout the alteration, oxidation state of the transition metal compounds is susceptible to change (excluding the end members Sc and Zn) and it is very difficult to explain their geochemical distribution by conventional crystallochemical principles based on the ion size, charge and bond type criteria. Several geochemical characteristics of these elements were interpreted successfully by the crystal field theory (Burns 1970). Redistribution of elements, liberated by the chemical weathering depends upon the physical and chemical properties of their ions in the aqueous phase. Generally, the rock forming minerals are hydrolysed to very poorly soluble hydrosilicates and hydrated oxides. More soluble ions are leached, transported away and then adsorbed or precipitated (in environments, where concentration of the particular species exceeds their solubility product). In order to account for the behaviour of the transition elements in the abiotic systems, relative stability of the hydrated and complex ions in solution, as well as the redox potential of multivalent elements have also to be assumed. Cycling of these elements in the natural environments is even more complicated by the impact of living organisms and by the human activities. Majority of the transition elements (probably with the exception of Sc and Ti) is essential for numerous metabolic processes and all of them are very important and they are exploited often in vast amounts in numerous modern technologies.

The purpose of this study is to investigate and compare the mobility of elements of the first transition series in a given environmental setting, namely in a small forested catchment on granite bedrock without any direct anthropogenic activity. The presented paper involves also the evaluation of sources of the elements in the studied system and it discusses the importance of the three basic groups of processes which mediate the cycling of elements: the abiotic, biotic and anthropogenic one.

Materials and Methods
Studied area
Cycling of the transition elements was studied in the Lesní potok catchment (LPC) 30 km SE from Prague in Central Bohemia, the Czech Republic. The area has been characterised in previous papers (Minařík et al. 1998, Skřivan et al. 2000). It covers 0,765 km² and it is situated in the Nature State Reserve Voděradské bučiny with the bedrock of the Říčany and Jevany granite (Fig. 1). Its south boundary is at 500 m a.s.l., while the altitude of the closing profile (with the Thomson weir) is at 406 m a.s.l. (Fig. 2). The mean annual precipitation is 635 mm and the mean annual temperature is 7.3 °C.

Bedrock
The crystalline bedrock is formed by the granitic rocks of the Říčany massif, the petrography and geochemistry of which are given in the preceding paper (Skřivan et al. 1999 ibid.) Table 1. shows the content of transition elements in both principal rock types of the Říčany massif. Content of the studied TE in the host rock and in the main rock-forming minerals separated from monzogranite of the Říčany type (locality Srbín) is shown in the Table 2. and in the Fig. 3

Soil
Soil developed from the granite bedrock is classified as a Gleyic Cambisol (Spaargaren 1994). The fractions <0,01 mm and <0,001 mm have been studied separately. Identical mineral association (in the order of the decreasing amount) was deter-
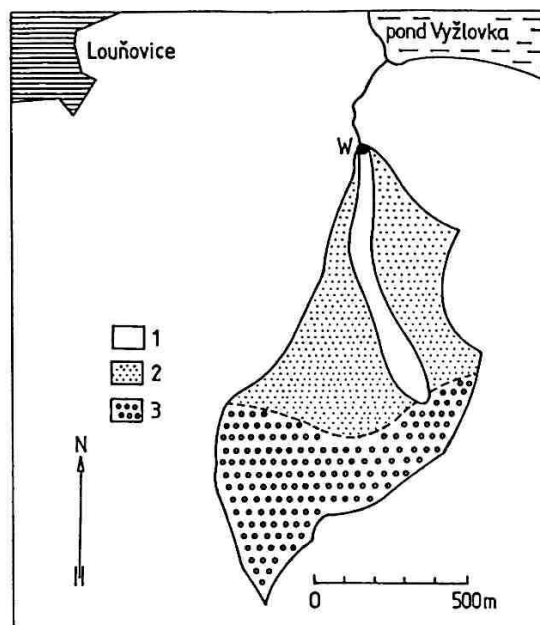

Fig. 2. Lesní potok catchment. Areas of the rock types derived from the geologic map of the Czech Republic 1:50 000, section Říčany. 1 - deluviofluvial sand loam sediments; 2 - syenogranite (Jevany type); 3 - monzogranite (Říčany type). W - Thomson weir and limnigraph for surface water sampling, plot of beech throughfall sampling.

mined in all the 14 soil samples, collected near the closing profile of the catchment: quartz, kaolinite, illite, K- feldspar, plagioclase and minor content of smectite, the structure of which has not been distinguished. Beech (and hornbeam) growth formed the vegetation cover of the sampling localities of soil The bedrock granite of the catchment could not be the source of this clay mineral. Some more basic material transported from the surroundings outside the granite massif should be its parent
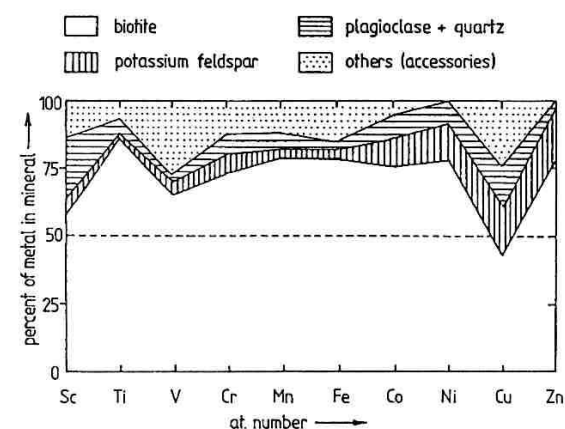

Fig. 3. Distribution of the transition elements in the main rock-forming minerals of the parent monzogranite. (see also the Table 2).

	bedrock		
element	monzogranite (Říčany type)	syenogranite (Jevany type)	low-Ca granite average[*]
Sc	4,8	4,0	7,0
Ti	1402,0	511,0	1200,0
V	15,0	2,9	44,0
Cr	10,9	8,7	25,0
Mn	191,0	96,0	390,0
Fe	9452,0	2991,0	14200,0
Co	3,3	1,2	1,0
Ni	12,2	6,6	4,5
Cu	14,7	13,9	10,0
Zn	86,0	35,0	39,0

[*]/ Turekian and Wedepohl (1961)

Table 1. Distribution of the transition metals in the parent rocks (μg.g^{-1}) of the Lesní potok catchment.

element	host rock	biotite 8.1% vol.	K-feldspar 32.7% vol.	plagioclase + quartz 27.5%, 24.8% resp.
Sc	7,20	50,7	1,32	3,22
Ti	1902,00	20190,0	120,00	180,00
V	25,90	208,0	3,40	0,20
Cr	24,50	221,0	4,74	3,27
Mn	237,00	2310,0	17,10	26,20
Fe	10940,00	105500,0	1186,00	551,00
Co	2,91	26,8	0,98	0,52
Ni	8,87	85,1	3,74	1,50
Cu	17,40	92,0	9,80	4,90
Zn	45,20	435,0	24,00	4,80

Table 2. The TE's content in the host rock and in the main rockforming minerals separated from monzogranite of the Říčany type (quarry Srbín) - in μg.g^{-1}.

material. The main morphological characteristics of the soil are presented in the profile description:

A (depth 0 - 15 cm) - very dark brown, moist, loamy sand, moderate coarse granular, very friable, abundant very fine and fine roots, abrupt, smooth boundary, density r = 0.78 g.cm^{-3}.

AB (15 - 33 cm) - yellowish brown, moist, loamy, moderate medium angular, friable, abundant very fine roots, clear, smooth boundary, r = 1.23 g.cm^{-3}.

Bw (33 - 48 cm) - yellow, moist, loamy sand, structure-less, non- coherent, clear, smooth boundary, r = 1.80 g.cm^{-3}.

Gr$_{1-4}$ (48 - 101 cm) - light grey, moist, loamy, structure-less, plastic, small soft spherical reddish brown iron-rich nodules, r= 1.62 g.cm^{-3}.

The diagram in Fig. 4 shows the soil profile and its grain size distribution to the depth of 1 m. More detailed informations are given in Minařík et al. 1998.

Vegetation cover of the catchment

Deciduous trees with dominant beech (*Fagus sylvatica* L.) prevail (52,98%) in the almost completely forested area of the catchment, whereas spruce (*Picea abies* L. Karst) is the most frequent among the coniferous (45,43%) trees (Sequens 1998). Further details are presented in (Skřivan et al. 1999).

Sampling and separation of the rock-forming minerals and soils

Part of the parent rock sample was treated for the separation and analysis of major minerals. The fraction with grain size 0,16 to 0,25 mm was employed for the magnetic separation of biotite on a Cook isodynamic separator. Purity of the concentrate after the manual cleaning under the microscope was in range 98-99%. The impurities consisted mainly of apatite in the form of inclusions. X-ray powder diffraction did not disclose presence of any phase other than biotite.

Large fenocrystals of the potassium feldspar were isolated by hand from the roughly crushed parent monzogranite. Crystals of the K-feldspar isolated in this way still contained minute amount of enclosed plagioclases as an impurity. Nevertheless, plagioclase was not identifies on the X-ray records.

The remaining material (after the magnetic separation of biotite and manual isolation of K-feldspar) contained a mixture of quartz and plagioclase. These salic minerals have not been further separated one from the other because of their close den-

sity range (2600 - 2650 mg.cm^{-1}) and they were used for the subsequent analysis together.

The separated fractions of biotite, K-feldspar and the mixture of quartz with plagioclase were then pulverised in a corundum ball mill, decomposed in HF + HClO$_4$ mixture and analysed by AA spectrometry (Varian SpectrAA 300). Flame- or graphite furnace technique were used for the Cr, Mn, Co, Ni, Cu, and Zn determination. Ti and Fe content in the individual minerals was determined by the electron microprobe from the polished thin section of the original parent rock. X-ray diffractograph Philips PW 3710 was used for the identification of mineral phases in soil samples. The samples were studied in natural state, treated with ethylene glycol and heated at 550° C for one hour. Fractions < 10mm and < 1 mm were prepared by sedimentation method. This material was used to prepare oriented aggregates, which were X-rayed.

The rock and soil samples were crushed and pulverised in a mechanical agate mill and after the homogenisation they were decomposed in a mixture of HF + HNO$_3$, and HCl acids. The total content of the transition elements was determined by ICP-MS spectrometry using a Varian UltraMass instrument, in the laboratories of the Analytika Ltd., Prague. The accuracy and precision of our data were verified by measuring of the certified reference materials.

The loosely bound forms of the transition elements in soil were determined after the extraction of soil particles < 1mm in 0,1 M nitric acid (Merck, Suprapur) for 24 hrs. at room temperature (V/m = 200, see also Minařík et al. 1998). Tab. 3. shows both the total content and the loosely bound forms of transition elements in soil.

Sampling and analyses of surface water

Surface water of a small brook draining the catchment was sampled at the Thomson weir in monthly periods since 1993 till the end of 1997. All samples of surface water were filtered in the field through the Filter Holder Sartorius SM 165 10 (equipped with the cellulose nitrate filter Sartorius 11306-47-N, pore size 0,45 mm), coupled with the manual vacuum piston pump Nalgene. The filtrate was immediately stabilized with diluted (1:3 v/v) nitric acid (Merck, Suprapur, 1ml of diluted HNO$_3$ per 100 ml of sample). Samples of this type contain forms of elements dissolved in water at the moment of sampling. Analyses of surface water, as well as of the bulk precipitation and throughfall, were again performed by means of the ICP-MS spectrometry (Varian UltraMass, laboratories of the Analytika Ltd., Prague). Major anions were analysed by the HPLC method.

horizon	1/A	2/AB	3/B$_w$	4/Gr$_1$	5/Gr$_2$	6/Gr$_3$	7/Gr$_4$
depth(m)	0-0.15	0.15-0.33	0.33-0.48	0.48-0.67	0.67-0.74	0.84-0.87	0.90-1.00
density$_{(g.cm^{-3})}$	0,78	1,23	1,8	1,62	1,62	1,62	1,62
Sc	4,90	6,70	4,10	11,30	9,50	4,00	8,30
	0,12	0,18	0,18	0,42	0,56	0,48	1,46
Ti	3741,00	4354,00	1536,00	4863,00	4492,00	1809,00	3194,00
	4,09	3,45	2,44	4,70	4,40	2,77	3,73
V	28,90	41,40	14,40	60,60	53,90	17,00	34,70
	1,73	1,53	0,99	3,41	3,33	1,44	2,50
Cr	25,60	40,60	15,40	58,70	48,20	15,10	32,20
	0,38	1,18	0,76	1,42	1,43	0,63	0,80
Mn	119,00	193,00	75,00	193,00	151,00	57,00	103,00
	17,90	15,80	7,70	5,21	5,51	3,10	2,70
Fe	3292,00	5998,00	2658,00	7901,00	7390,00	2488,00	5179,00
	653,00	742,00	591,00	657,00	657,00	294,00	506,00
Co	1,90	5,60	1,70	6,20	5,20	1,60	3,70
	0,14	0,21	0,16	0,22	0,28	0,13	0,41
Ni	8,80	15,50	7,50	23,00	21,80	7,90	13,50
	0,90	0,32	0,14	0,28	0,44	0,21	0,54
Cu	26,80	28,50	10,80	37,90	35,60	13,40	24,50
	1,23	0,54	0,39	0,92	1,45	0,51	0,98
Zn	48,90	69,40	24,20	98,90	81,10	28,30	53,20
	5,42	3,64	1,71	4,42	4,39	1,73	2,34

Table 3. Total and leachable content of the transition metals in the soil profile ($\mu g.g^{-1}$) - Lesní potok catchment.

Sampling of the bulk precipitation and throughfall

Bulk samples of the atmospheric precipitation were collected on a monthly basis (1995-1998) in a forest clearing at the locality Truba situated approx. 5,5 km NE from the catchment, at least 50 m away from the trees (Fig. 1, locality signed D). Sampling and sample preparation prior to the analysis by ICP-MS were described in an earlier paper (Skřivan et al. 1995; Skřivan et al. 1999). The procedure is similar to that of Berg et al. 1994. Diluted nitric acid was inserted into the polyethylene 1L samplers prior to their exposure at the site, to prevent adsorption of dissolved forms of studied elements onto the walls of the sampling bottle. The analysed liquid portion of samples represents the sum of soluble forms of elements present in the precipitation together with their forms weakly bound to the solid particles of the deposition.

Samples of beech throughfall were collected (since April 1996 till October 1998) into a set of sampling devices at a sampling plot situated by the northern tip of the Lesní potok catchment (Fig. 2, locality signed W). The locality has a background
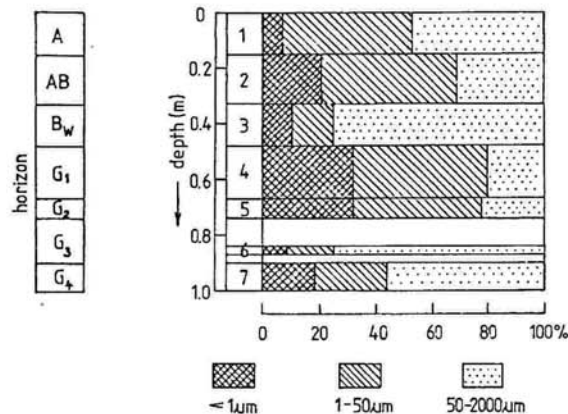

Fig. 4. Description of the soil profile and the grain size distribution in the individual horizons.

character, considering the Central European standards. Samples were collected in new GCTC (Glass Cone Throughfall Collector) devices (for further details, see also Skřivan et al. 1999). These collectors minimise losses of the atmospheric aerosol and they also record the true throughfall events only, as they do not sample the solid state precipitation (in the form of snow).

Prior to their installation on the sampling sites, all recycled PE bottles were carefully washed out (hot distilled water, 0.5% HNO$_3$, distilled and bidistilled water). The bottles were replaced at the end of each sampling period by new ones and they were transported in sealed PE bags into the laboratory. The bottles were weighed so that we might check up the volume of the liquid and the liquid samples were then filtered using a 0.45 mm membrane filter (see above). The filtrate was stored at +4 °C in a cooler until the analysis. In the case of throughfall, aliquot of samples prepared for the trace element determination were acidified (after the bulking of the average throughfall samples), and 1 day later they were filtered through the membrane filters. Samples of bulk precipitation determined for the evaluation of bulk chemical composition and for the laboratory pH measurements were collected separately.

Results and Discussion
Content of elements in rock and soil
Scandium

The Sc- content in both types of the parent rock (monzo- and syenogranite) is very similar and it is moderately lower than the value given by Turekian and Wedepohl (1961) for Sc in low - Ca granites (Tab. 1). The distribution of scandium in the soil profile suggests that the highest total Sc contents are associated with the horizons abundant in the fine - grained fraction of soil. The leachable Sc content depends on the depth of the horizon. It increases from the topsoil (A horizon) towards the bottom of the profile (Gr$_4$ horizon), where it achieves more than 17% of the total Sc content (see Tab. 3). This trend could be explained either by the selective uptake of the mobile Sc- fractions by plants in the upper horizons of the soil profile, or, more probably, by its leaching and transport to the lower part of the profile by the acid atmospheric precipitation. Similar tendency has been observed during the study of rare earth elements distribution in the same profile (Minařík et al. 1998).

Titanium

The Ti - content of the parent monzogranite in the FBC is very close to the average 0.14% value given by Turekian and Wedepohl (1961) for Ti in the low - calcium granites. Syenogranite, the second main rock type in the studied area, is poor in Ti. This deficiency may reflect the lower proportion of biotite, which is the only mafic component of the rock.

Distribution of Ti between the rock - forming minerals of unaltered monzogranite showed that the major titanium - bearing mineral is the biotite, which bound more than 80% of the total Ti - content (Tab. 1).

On the contrary, soil material above the granites in abundant in Ti. The accessory Ti- oxide (rutile) and ilmenite, which are very resistant against weathering, are probably the main source of Ti in the residual soil. Titanium may be partly associated also with the secondary minerals as kaolinite (Dolcater et al. 1970). A very large enrichment of Ti in the fine fraction is observed in the soil profile. Content of leachable Ti in the soil horizons is the lowest of all the transition elements (< 0.2% of

the total Ti - content - see the Tab. 3) and thus it verifies the immobility of titanium in the course of interaction of soils with the acid precipitation.

Vanadium

Individual species of V in the parent rocks of the catchment were not determined in this study. However, its crystallochemistry and the abundant analytical data (e.g., Wedepohl 1978) suggest that this element tends to follow iron during the formation of primary minerals in igneous rocks. We assume that the main part of the total V - content is bound in the ferro - magnesian phase.

Both the types of the parent rock of the studied catchment are poor in vanadium. The deficiency is especially significant in the syenogranite, where some leaching of this element may be assumed. However, the residual soil covering the granite contains relatively more V and its median (see the Tab. 1) is very similar to the value presented by Turekian and Wedepohl (1961) for Ca - poor granites. The total V- content is the highest in the horizons abundant in the fine silt- and clay fractions. These results suggest that vanadium can be incorporated in newly formed mineral structures (e.g. smectite, chlorite) or adsorbed in the iron oxide coatings. The leachable V content in soil is not dependent on the depth of the particular horizon (Tab. 3). The highest amount of mobile V is observed in G_{r1} and G_{r2} horizons with reducing regime, whereas the upper aerobic horizons A, AB, and B_w are poor in V. The mobility of V in the soil samples is intermediate (4 to 8% of its total content is leached under the chosen conditions).

Chromium

Parent rocks of the catchment are relatively poor in chromium. More than 70% of the total Cr content is bound in biotite and approximately 13% in feldspars. The other host phase can be the accessory Ti - minerals and magnetite. In comparison to granites, the residual soil is Cr enriched. The distribution of total chromium content in the soil profile is strongly dependent on the grain size of the samples. The horizons abundant in the clayey fraction (Gr_1 and Gr_2) contain more Cr than the others. We observe this trend in the geochemical distribution of all transition elements of our study. The Cr/V ratio is almost constant and close to 1 in the soil samples. The leachable amount of Cr is very low in the whole soil profile (Tab. 3). This can be attributed to the resistance of the minerals containing Cr during the weathering and soil formation and to the association of Cr with amorphous ferric oxyhydroxides in oxic environment (Koons et al. 1980).

Manganese

The analyses of the major rock-forming minerals separated from the fresh monzogranite showed that almost 80% of Mn is bound in biotite. Approximately 8% of Mn is associated with plagioclase + quartz and less than 5% with potassium feldspar. The parent rocks (especially the syenogranite) of the catchment are poor in this element. Residual soil developed on granite is also low in Mn. The total Mn - content varies in the range 57 to 193 mg.kg-1 with the maximum in clay abundant soil horizons Gr_1 and Gr_2 (Tab. 3). The position of Mn in the weathering products and soil components has not been identified, but analyses by the electron microprobe have shown that the most abundant secondary host minerals of Mn are smectite and chlorite which contain as much as 4100 ppm of MnO.
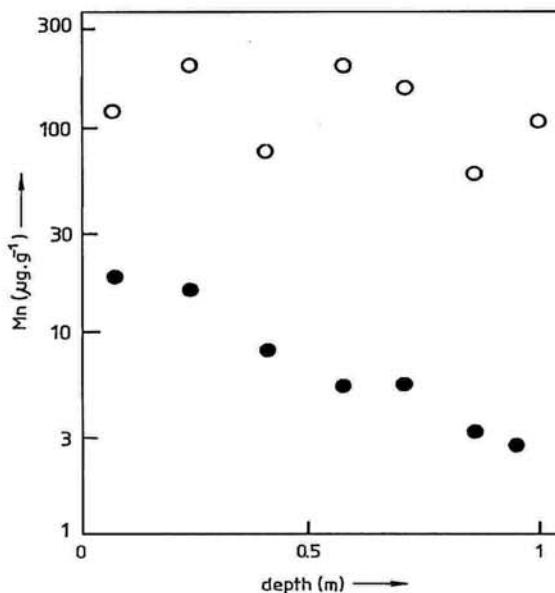

Fig. 5.   Variation of the Mn content with depth; circles: total Mn content, dots: leachable Mn content.

Leachable portion of the Mn - content in soil is relatively high (3 to 15%), but there is strong dependence of Mn distribution on the depth of the particular soil horizon. Fig. 5. documents the continuing decrease of the extractable Mn content from the topsoil towards the bottom of the profile. The aerobic upper horizons are in average much more enriched in Mn, than those in the reducing environment. The results of our previous study have documented strong influence of metabolism of the forest vegetation on the Mn - cycling and its distribution in the soil profile. A detailed study of the manganese behaviour in this catchment is given in Skřivan et al. (1997).

Iron

Fe, the most abundant heavy metal in the Earth's crust, is not accumulated in the parent rocks of the catchment. Out of them, syenogranite is especially low in iron. The partitioning of Fe between the various rock-forming minerals shows many similarities with manganese: high content in the biotite (70 to 80% of the total Fe - rock content) and less than 10% in the other coexisting minerals (both feldspars and quartz). The soil above the granites is also poor in Fe (2500 - 8000 mg.kg-1). The highest total iron content is associated with clay abundant soil horizons. The main host secondary phases are smectite and chlorite, according to the data from the electron microprobe. Part of the Fe total soil content is present in the form of iron oxyhydroxide coatings on the partly decomposed primary minerals (el. microprobe).

The leachable Fe - content is the highest of all transition elements (8 to 22% of the total Fe content), and especially the AB horizon is abundant in Fe. There is no correlation between the iron concentration and the depth in the soil profile. It seems that the mobility of this element varies in dependence on the change of pH and Eh of the system soil - water rather than with the mineralogy of the sampled material.
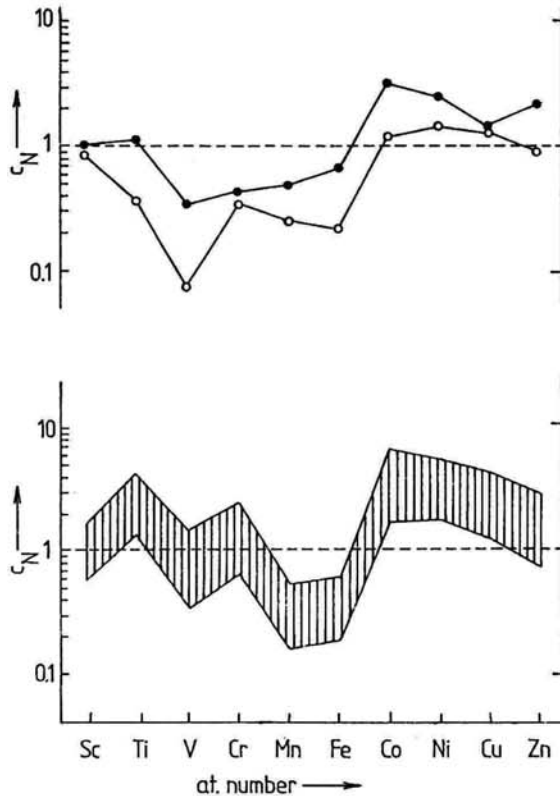
Fig. 6. above TE's distribution in two main rock types of the catchment (normalised to the mean Ca-low granite - see also the Table 1); circles: syenogranite of the Jevany type, dots: monzogranite of the Říčany type.

Fig. 6. below Normalised TE's distribution in the soil profile (range of seven samples).

Cobalt

Contrary to Fe and Mn, both the parent granite rocks are relatively abundant in Co (Fig. 6). Approx. three quarters of the total Co - rock content are bound in the biotite and 20% is associated with the other rock-forming minerals(K- feldspar, plagioclase and quartz). Residual soil seems to be also enriched in Co. Cobalt, like iron and the other transition elements of the first series, shows preferential enrichment in the soil samples abundant in clay fraction. The host secondary phase may be the chlorite and smectite. In comparison to Fe and Mn, leachable portion of Co is slightly lower and the variations are not dependent on the depth of the soil profile. In average, however, the horizons with reducing regime (from G_{r1} to G_{r4}) contain more leachable Co than the upper horizons (Tab. 3). The distribution is here similar to that of Fe.

Nickel

The content of Ni in both the rock types is also higher than the value given by Turekian and Wedepohl (1961) for nickel in low Ca- granites. More than three quarters of total Ni - rock content are bound in the biotite, 14% of it in K- feldspar and less than 10% in plagioclase and quartz. As well as the granites, residual soil is abundant in Ni (7.5 - 23.0 mg.kg⁻¹). The highest total Ni

content is associated with fine - size soil samples (horizons Gr_1 and Gr_2). The leachable Ni - content is especially high in the humic A horizon (Tab. 3). The accumulation of the loosely bound Ni in the topsoil could be most probably attributed to the atmospheric deposition and to the metabolic incorporation of Ni in the vegetation (tree assimilation organs) rather than by the natural rock weathering. Nickel and cobalt, two geochemically similar elements, show very different distribution in our profile. The differences could be explained by varying stabilities of their complexes with organic soil matter and bby easier oxidation of the Co^{2+} ion (Stevenson and Ardakani 1972).

Copper

The Cu - contents in both the main rock types of the parent material in the catchment are mutually similar and they are slightly higher than the average for copper in low Ca - granites (Turekian and Wedepohl 1961). The partitioning of Cu between the individual rock-forming minerals shows that only 43% of the total Cu rock content is associated with the biotite, approx. 18% with K - feldspar and 15% with plagioclase and quartz.

The residual soil on the granite is also abundant in Cu. A comparison of copper concentrations in the individual soil horizons indicates the accumulation in samples enriched by the silt - clay soil fraction. This enrichment of Cu in the fine fraction of soil suggests that most of Cu is in a finely dispersed form, perhaps in clay minerals (Tab. 3). The Cu distribution in soil profile is very similar to that of Ni, where the leachable Cu - content is the highest in the uppermost humic A - horizon, and also similar to that of Ni. Combined effect of the enhanced atmospheric input through the anthropogenic immissions, together with the formation of stabile Cu- complexes with organic matter (Gamble and Schnitzer 1973), are evidently the reason of the observed trend. Variations of the content of leachable Cu forms throughout the lower horizons of the profile are not dependent on the depth.

Zinc

The Zn - content in the parent monzogranite is high whereas the syenogranite is less abundant in zinc. Its content corresponds to the value for Zn in low - Ca granites (Turekian and Wedepohl 1961). The distribution of Zn between the different host rockforming minerals is similar to that of Ni: 78% of the total Zn - rock content is bound in biotite, 17% in K- feldspar and the remainder is associated with plagioclase and quartz. The total Zn content in the soil profile shows a wide range of values for the particular horizons (24 to 99 mg.kg⁻¹). The higher values correspond to the samples abundant in the silt - clay fraction (Gr_1, Gr_2) (Tab. 3). Direct correlation was found between the total Zn and Cu - content in the soil profile. The leachable Zn content is especially high in humic A horizon, suggesting here the same origin of this typical anthropogenic metal. Accumulation of the loosely bound Zn in the topsoil might rather result from the atmospheric input, than from weathering of the parent material or from the internal metabolic cycling of the essential Zn within the forest vegetation.

The distribution of the total- and leachable forms of all transition elements in the soil profile is depicted in Figs. 7a to 7j.

Concentration of the elements in surface water of the catchment

Bulk chemistry of the surface water of the catchment, characterised from its relative content of individual major cations and

anions (see the Table 4), corresponds to the calcium - magnesium sulphate type.

Content of the studied transition elements in the surface stream is shown in the Table 5. The Table contains also values of the "Relative Mobility Potential" (RMP) of the individual studied elements (see the last column). This denomination was defined as a ratio of the median value of the concentration of element in surface stream (in $mg.L^{-1}$) divided by its mean concentration ($mg.kg^{-1}$) in the soil profile normalised to the least mobile element - Ti:

$$RMP = \frac{Cw_{Me}.Cs_{Ti}}{Cs_{Me}.Cw_{Ti}} ,$$

where Cw is the concentration of an element (Ti) in water, and Cs is the mean concentration in the soil profile.

The value of RMP provides useful pieces of information concerning the actual differences in the ability of individual elements to migrate in dissolved forms. The group of transition elements can be arranged in a line from the most- to the least mobile element: Mn>Ni>Sc>Co>>Zn>>Cu>Fe>Cr>V>Ti. The ability of the transition elements to enter the aqueous phase under common conditions of the system depends in particular on their oxidation state. Bivalent ions of Mn, Ni, Co, and Fe are much more mobile than their trivalent counterparts, because of higher solubility of their hydroxides and poorer adsorption on the solid matter of the surface stream, caused mainly by lower charge

and larger ionic radii of the Me^{2+} forms. Values of the standard electrode potentials of the half-reactions $Me^{2+} \Leftrightarrow Me^{3+} + e^-$ at neutral or slightly acidic conditions are -0,41, -0,26, +0,77, +1,51, and +1,82V for Cr, V, Fe, Mn, and Co, respectively (Krauskopf 1979). Out of these elements, Cr and V exist even in higher oxidation state in forms stable in the oxic systems. The mentioned standard electrode potentials indicate that Mn, Co (and also Ni, Cu and Zn) equilibrated in surface water with access of atmospheric oxygen exist prevailingly as free Me^{2+} ions (Turner et al. 1981). In examining the plausible oxidation state of the elements in surface waters, it is noteworthy also to take into account the kinetics of the redox reactions. Their reaction rate at minute concentrations of elements in solution is very low, so that the condition of equilibrium in the headwaters of a stream is scarcely reached (Cherry et al. 1979). Scandium and titanium, on the other hand, are elements existing in a single (3+ and 4+, respectively) oxidation state at natural conditions. Speciation of Sc is widely variable, depending on the pH value and concentration of F^- and CO_3^{2-}/HCO_3^- ions. Relatively high mobility of scandium, derived from its increased concentrations in surface water, is then probably caused by the formation of strong complexes of Sc with the fluoride ion. Log K values of these complexes are similar to those of Al. Tetravalent Ti, on the other hand, is fully hydrolysed in the form of sparingly soluble hydroxide, (Turner et al. 1981), which strongly limits its mobility in the surface water.

parameter	n	mean	st.dev.	median	min.	max.
Na^+	56	8,370	1,332	8,290	3,290	11,780
K^+	56	1,437	0,925	1,340	0,410	7,250
Mg^{2+}	56	7,755	1,363	7,750	3,070	11,170
Ca^{2+}	56	20,335	3,981	19,755	7,080	30,410
NH_4^+	54	0,028	0,053	0,010	0,010	0,330
F^-	54	0,775	0,131	0,770	0,350	1,040
Cl^-	56	4,718	1,200	4,565	1,820	7,970
SO_4^{2-}	54	84,230	12,907	83,200	57,600	111,000
NO_3^-	55	3,109	2,658	2,510	0,100	11,000
pH	123			4,910	4,330	7,160

Table 4. Bulk chemistry of surface water, sampling site LP6, years 1993-97, concentration in $mg.L^{-1}$.

element	n	mean	st.dev.	median	min.	max.	CEF
Sc	7	0,23	0,26	0,12	0,080	0,80	4,50
Ti	8	2,14	1,56	1,90	4,360	1,23	0,44
V	22	0,86	0,44	0,74	0,060	4,36	8,50
Cr	21	0,29	0,23	0,26	0,001	0,68	3,20
Mn	16	20,20	24,30	8,05	2,030	85,40	8,30
Fe	21	56,50	41,90	45,00	15,000	150,00	1,00
Co	21	0,08	0,05	0,07	0,020	0,23	4,20
Ni	16	0,85	1,33	0,51	0,030	5,56	9,14
Cu	16	2,55	2,87	1,58	0,500	12,30	34,70
Zn	16	14,00	5,91	13,40	5,030	25,70	167,00

Tab. 6. Concentration of the transition elements in bulk precipitation ($\mu g.L^{-1}$), together with their crustal enrichment factor (CEF) normalised to Fe (see the text).

element	n	mean	st.dev.	median	min.	max.	RMP
Sc	6	6,47	2,28	7,20	1,90	8,19	258,00
Ti	8	14,10	2,91	13,64	9,86	19,26	1,00
V	21	0,47	0,33	0,38	0,09	1,22	2,65
Cr	21	0,56	0,45	0,53	0,01	2,03	3,93
Mn	16	366,00	132,00	314,00	201,00	666,00	618,00
Fe	21	408,00	615,00	190,00	71,00	2600,00	9,53
Co	21	3,55	1,51	3,53	0,39	6,75	239,00
Ni	17	25,81	6,74	25,20	17,40	36,50	450,00
Cu	16	1,45	0,89	1,15	0,76	4,35	11,30
Zn	16	21,46	6,30	20,55	11,00	40,20	89,30

Tab. 5. Concentrationn of the transition elements in surface water of the catchment ($\mu g.L^{-1}$), values of their RMP (relative mobilisation potential), see the text.

	$F_{Me}/*$		
element	Truba/96	Nordmoen/90	Osen/90
Sc	70	n.d.	n.d.
Ti	1130	n.d.	n.d.
V	440	570	360
Cr	150	170	220
Mn	4800	1800	4100
Fe	27000	22000	23000
Co	49	23	24
Ni	300	470	430
Cu	940	350	1300
Zn	7900	4300	4600

$F_{Me}/*$ – values for Norway stations Nordmoen and Osen in 1990, calculated from Berg et al. (1994).

Tab. 7. Annual load of the catchment by transition elements (F_{Me}, $\mu g.m^{-2}$) through the bulk precipitation in 1996.

Concentration of the elements in bulk precipitation and beech throughfall.

Table 6 shows main statistical data concerning the content of transition metals in samples of the bulk precipitation collected in 1996-97. Last column of the Table 6 presents (for comparison with the data of Berg et al. (1994) the crustal enrichment factor CEF of selected elements normalised to Fe, with respect to their content in the Earth crust (Roessler and Lange 1972). Values of CEF close to 1 (Sc, Ti, Cr, Fe, and Co) characterise the elements with terrigenous dust being their prevailing source in the atmosphere. On the other hand, the higher the CEF of the other elements, the stronger should be the impact of their anthropogenic atmospheric emissions. This principle holds with the exception of Mn: metabolic activity of the surrounding forest vegetation probably represents its main source in samples of the bulk precipitation (see the Tab. 6). This effect was observed previously (Skřivan et al. 1995) and it is ascribed to the contamination of the wet precipitation by small droplets of water generated throughout the collision of rain with surface of the tree assimilation organs. Other elements with high values of CEF (V, Ni, Cu, Zn) are the typical technological metals whose industrial and other anthropogenic emissions markedly exceed their flux in comparison to their natural sources (Nriagu 1989).

Annual load of the catchment by transition elements (expressed in mg Me.m^{-2}) in bulk atmospheric precipitation in 1996, calculated from their median concentrations and annual precipitation height (593 mm) is shown in the Table 7. Our figures are compared with those of Berg et al. (1994), as the sampling and evaluating procedures of both the data sets are similar. The Tab. 7 contains values of the flux of selected elements at two rural Norwegian stations with intermediate and continental climate (Nordmoen, Osen) collected in 1990. Both the sets of data are in good agreement, indicating that the quality of atmospheric deposition at rural stations in southern Norway and in the Czech basin is comparable. It is necessary, however, to take into account the more intensive wash-out effect of the atmosphere in Norway due to higher values of the annual precipitation height (822 mm and 711 mm, respectively). Our slightly higher values for Mn can be explained by the proximity of forest trees (and effects of their metabolism, see above). Higher flux of Zn can be attributed to the urban and industrial activities of the densely populated central Bohemia, namely of proximity of Prague,

which stretches NW from the sampling station, windward to the direction of prevailing winds.

The concentration of elements in beech throughfall (Table 8) reveals limited impact only on the cycling of the group of the transition elements, with the exception of Mn. The moderately increased concentrations of Ni, Zn, Cu, and Co in throughfall could be attributed both to the interception of atmospheric aerosol by the tree crowns, as well as to the leaching of these essential elements from the tree assimilation organs (Heinrichs and Mayer 1980). The mechanism of metabolic cycling through the root uptake, transport in sapwood into the leaves and leaching by the acid wet precipitation is extremely strong in Mn. This is shown in its high value of EF_{TH}, the enrichment factor of the element in throughfall.

Conclusions

The mass balance calculations of separated rock-forming minerals and host rock show that 45 to 86% of the TE's are accumulated in biotite, the only mafic component representing about 8% vol. of the unaltered parent rock (the monzogranite). This relatively unstable phase is destroyed during the rock weathering, and most of the transition metals are released into the soil. This phase becomes enriched with TE in comparison with the underlying parent rock. The comparison of the variations in the total TE content in the individual soil layers shows that the distribution is controlled by the amount of clay fraction in the particular soil horizons. Generally, the horizons abundant in the fine fraction contain more TE's than those with the predominance of silty and sandy fraction.

The loosely bound species of the TE (extractable in 0.1 M HNO_3) represent only a small part of their total content in soil (0.1% Ti, 22% Fe). Their distribution is not dependent on the grain size of the soil samples. It was observed that the amount of leachable Sc increases with the depth of the profile. We assume that the mobile fraction of this element is leached and transported into the deeper zones of the soil profile by acid atmospheric precipitation whose pH increases with depth. The Sc distribution in surface- and subsurface waters draining the terrain of the catchment supports this geochemical interpretation. On the contrary, trend of the leachable Mn content in the soil profile is antithetic to that of Sc, as manganese is attached in the uppermost part of the soil profile where it is continually cycled by the metabolic activity of the surrounding forest vegetation.

The biogeochemistry of individual transition metals considerably differs one from another. Their general characteristics can be summarized into the following paragraphs:

· Relative content of V, Cr, Mn, Fe (Sc) in monzogranite is lower than in low - Ca granites. The same, including Ti, holds for syenogranite. On the other hand, contents of Co, Ni, Cu (and Zn) are in both rock types enriched.

· Biotite is the host mineral of more than 75% of Ti, V, Cr, Mn, Fe, Co, Ni and Zn. Majority of the remaining part of the elements is bound in both types of feldspars, the Cu content in feldspars almost equals to that in biotite. Host mineral of Sc in unknown.

· All the elements are enriched in the clay soil fraction. Chlorite and smectite are the host secondary phases for V, Mn, Fe and Co. Vanadium is probably also adsorbed on the iron oxide coatings. Titanium in soil is abundant, bound probably in accessory Ti- oxides and ilmenite.
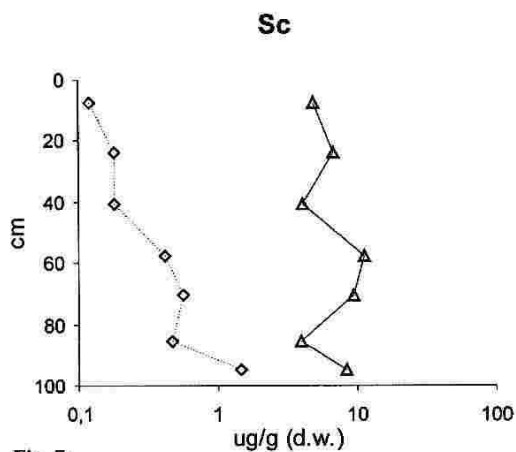
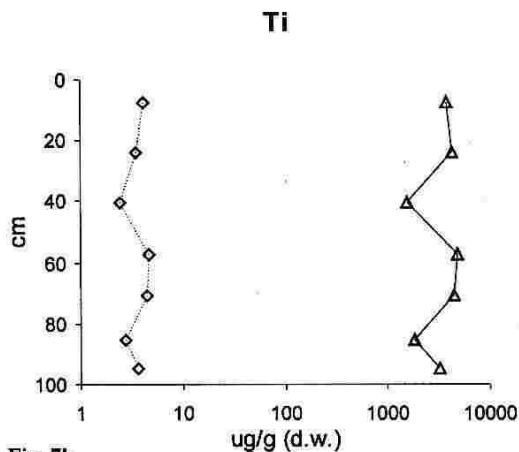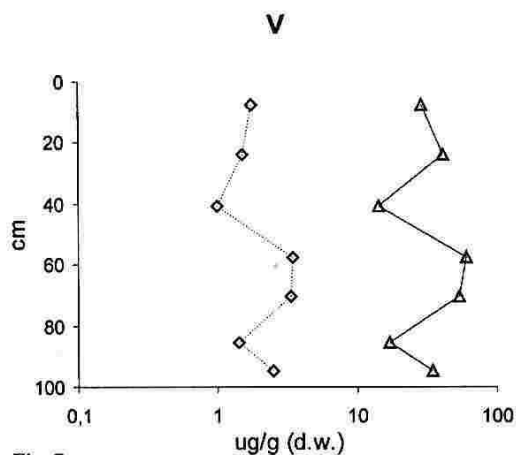| element	n	mean	st.dev.	median	min.	max.	EF_{TH}
Sc	5	0,17	0,07	0,140	0,090	0,27	1,21
Ti	9	1,84	1,09	1,450	0,650	3,63	0,76
V	26	1,13	0,49	0,981	0,530	2,28	1,33
Cr	15	0,38	0,16	0,360	0,126	0,64	1,41
Mn	18	184,10	132,00	148,500	54,200	459,10	18,50
Fe	9	85,20	31,50	83,900	48,800	137,50	1,86
Co	26	0,17	0,09	0,140	0,050	0,42	1,93
Ni	21	2,04	1,26	1,630	0,660	5,08	3,18
Cu	21	3,45	1,59	3,010	1,160	7,70	1,91
Zn	21	29,60	16,12	26,300	9,809	74,30	1,96

Tab. 8. Content of the transition elements in beech throughfall (μg.L^{-1}), together with their enrichment factor (EF_{TH}) with respect to the bulk precipitation (see the text).

Sc

Fig. 7a.

Ti

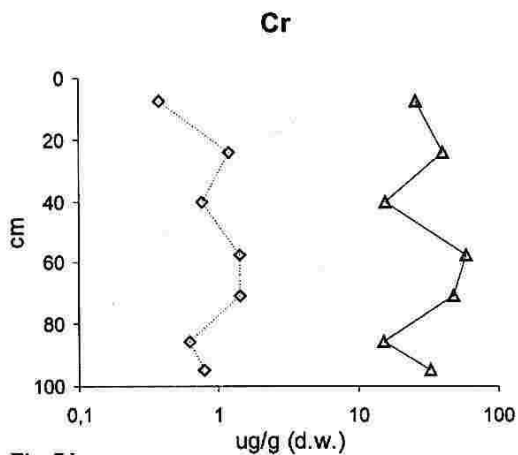Fig. 7b.

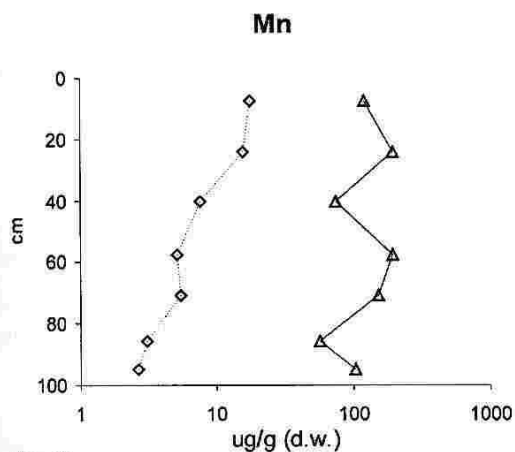## V

Fig. 7c.

Cr
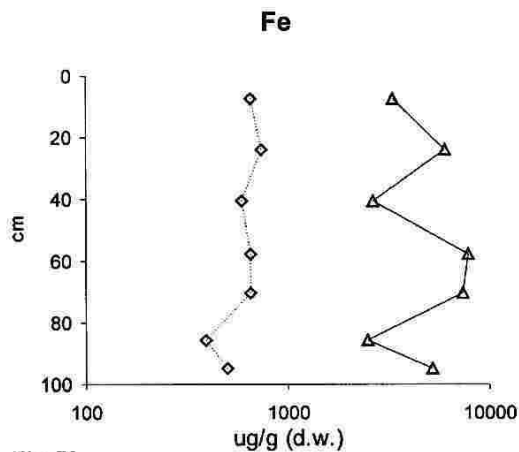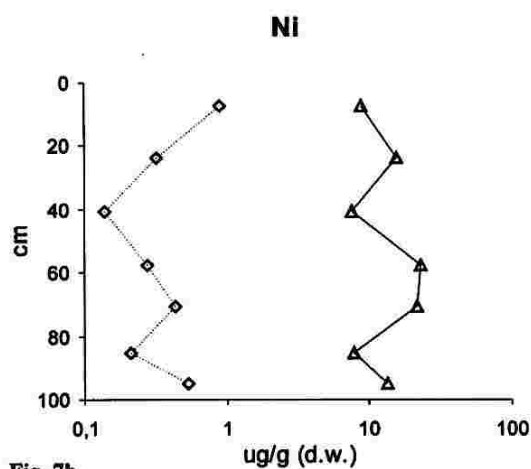

Fig. 7d.

Mn

Fig. 7e.

Fe

Fig. 7f.

Fig. 7a-f. Soil profile in the Lesní potok catchment: Variation of the total content and leachable forms of transition elements with depth. Full line: total content; dotted line: leachable forms (0.1M HNO₃).

Distribution of the mobile forms of Mn, Ni, Cu, Zn (and Fe) throughout the soil profile shows decreasing tendency with depth. The A-horizon of soil developed on the granite bed-

rock becomes enriched also in the soluble Ni, Cu and Zn, which are the typical technogenic metals with essential role in the metabolic processes of the vegetation. Distribution
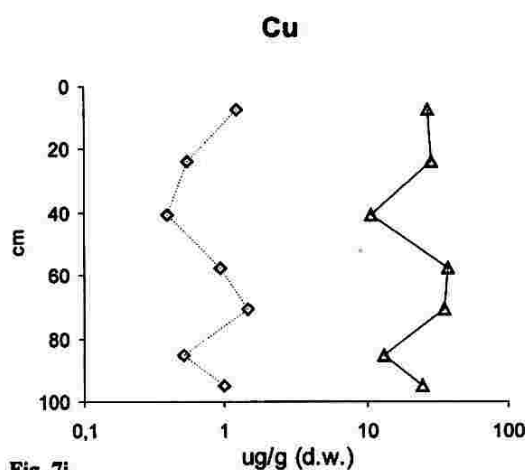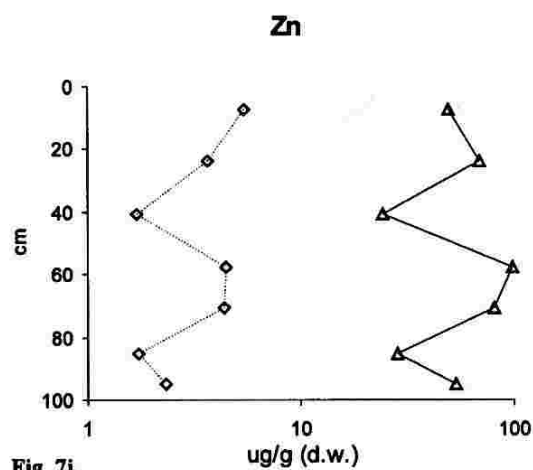
Co

Fig. 7g.

Ni

Fig. 7h.

Cu

Fig. 7i.

Zn
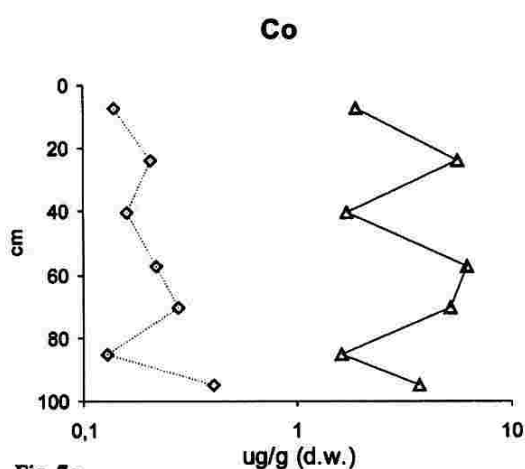
Fig. 7j.

Fig. 7g-j. Soil profile in the Lesní potok catchment: Variation of the total content and leachable forms of transition elements with depth. Full line: total content; dotted line: leachable forms (0.1M HNO₃).

of Sc shows increase with depth, whereas the content of Ti, V, Cr, Fe and Co is not dependent with depth of the soil profile. Relative content of the mobile forms is the highest in Fe, the lowest in Ti.

· Relative mobility of Sc, Mn and Ni is high, Co, Cu and Zn intermediate, and of Ti, V, Cr and Fe low (here depending on the Eh of the system).

· Sources of Sc, Ti, Fe (V, Cr, Co) in atmospheric precipitation are mostly terrigenic, of Cu, Zn (Ni, V, Cr, Co) affected by technogenic emissions. Content of Mn in precipitation, especially near the afforesed areas, is affected by metabolism of the vegetation.

·Extent of biotic cycling of Mn is very high, of Co, Ni, Cu and Zn moderate. The remaining transition elements show negligible (Sc, Ti, V, Cr) or low (Fe) biotic cycling.

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