

## The role of forest vegetation in the hydrochemistry of selected transition metals

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**Abstract** The comparative study of the Mn, Fe, Co, and Ni hydrochemistry was carried out in a forested catchment in central Bohemia. Relative mobility of the elements in soils was assessed from their distribution throughout the soil profile. Internal cycling of elements driven by metabolic activities of the vegetation was compared through the chemistry of bulk precipitation and throughfall. Relative mobility of the elements was estimated from their mass balance and through their proportional index (PIME) related to Fe as the most common element. Increased concentrations of the elements in the humic soil layer indicate their origin in the litterfall and throughfall. Atmospheric inputs of the elements (mainly Mn) are strongly affected by forest vegetation. The outputs through surface and subsurface discharge document the relative mobility of the elements, which decreases in order Mn>Ni>Co>Fe.

**Key words:** Manganese, iron, cobalt, nickel, hydrochemistry, catchment, cycling, mobility

### Introduction

Manganese (Mn), iron (Fe), nickel (Ni) and cobalt (Co) are typical transition elements with mutually akin chemical characteristics. Manganese, Fe and Co, occur in the environment at least in two oxidized states what strongly affects their mobility in soils and surface water sediments and determines their availability for plants. The abundance of the elements varies from very abundant major element Fe, minor Mn, to trace elements Ni and Co. All the elements are also essential for living organisms with distinct, crucial roles in the metabolism.

Forest ecosystems represent an important link between the atmospheric and aqueous environment. The biogeochemical studies oriented on similar ecosystems have been repeatedly involved in numerous monitoring projects [7, 18]. Forest ecosystems that evolved on nutrient poor soils (e.g. derived from the granite bedrock with low content of base elements) often encounter the deficiency of numerous important essential elements. The situation has been recently even impaired by additional losses of the life important elements from soils through the acidified precipitation containing strong inorganic acids of anthropogenic origin.

The task of our work was to assess the major sources of Mn, Fe, Co and Ni in the forest soils and to estimate the balance of their main inputs and outputs in the studied ecosystem. Relative extent of the individual pathways of the element within the system is compared through "proportional indices" ( $PI_{Me}$ ) in individual compartments and fluxes within the experimental forested catchment. The "proportional index" is related to the element iron,

as the most common element. To assess the role of forest vegetation in the biogeochemical cycles of studied elements, the internal cycle of the elements, involving the root uptake, throughfall and litterfall has been assessed in this study. Last but not least, the aim of this paper was also to determine the chemical forms of the elements present in surface water and to assess their role for the dynamics of studied elements in the ecosystem.

### Site description

The Lesni potok catchment (LP) is situated 30 km southeast of Prague in central Czech Republic. It covers area of 0.765 km<sup>2</sup> (Fig. 1). The bedrock of the catchment is composed of two types of the Říčany pluton granite, bright syenogranite (generally in the lower half of the catchment) and darker and coarser monzogranite. The mineralogical composition of both types is almost identical: ~27% quartz, ~29% orthoclase, ~35% plagioclase and ~6% biotite [11, 17]. Weathered granites sampled in the LP catchment usually contain kaolinite.

Closing profile equipped with a Thomson weir for the discharge measuring and sampling of surface water is at 406 m a.s.l. (locality LP6, Fig. 1). Adjacent to the weir is situated a well (4 m deep, equipped with inert material) for sampling of the shallow groundwater. The highest point of the catchment is at 500 m a.s.l.

Mean annual precipitation height during the period 1994 - 2006 was 735 mm and the runoff height during the same period was 96 mm. Mean annual temperature is 7.0°C. The catchment is almost completely forested with deciduous

(53%) and coniferous (45%) trees with prevailing European beech (*Fagus sylvatica*) and Norway spruce (*Picea abies*).



Figure 1. Map of the sampling sites in Lesni Potok catchment

## Materials, methods

Atmospheric inputs of elements were monitored through bulk samples of atmospheric precipitation (further *bulk precipitation*), involving both the wet and dry deposition on an open place. The extent of the internal cycle was indicated through the precipitation below the tree canopies (further *throughfall*) and the litterfall. The output of elements was monitored through the surface and subsurface water runoff. Surface water, bulk precipitation and beech throughfall have been sampled monthly since 1994. Spruce throughfall has been sampled monthly since 1997 and the subsurface water was sampled for 22 months in 1999 and 2000. Surface water sampling has been performed at the Thomson weir (loc. LP6, Fig.1). Samples designated for the determination of studied elements in bulk precipitation were collected at sites TR and ARB (Fig. 1). Beech throughfall was sampled at LP6 close to the Thomson weir of the catchment and spruce throughfall was collected approx. 200 m N from LP6 in a small spruce stand (LP 7, Fig. 1). The methods of bulk precipitation and throughfall sampling were described in detail elsewhere [20]. Sampling bottles were exchanged in one-month periods. They were sealed in PE bags to prevent their contamination during the transport into the laboratory. All pieces of the equipment were carefully cleaned by diluted nitric acid, hot distilled- and bidistilled water prior to their installation at the locality. Absence of contamination during the transport of samples between the laboratory and sampling locality, as well as during

the sample elaboration was verified by blank procedures with the bidistilled water.

All the collected liquid samples were filtered (pore size 0.45  $\mu\text{m}$ ) in the field or in a laboratory and then stabilized with 1ml of diluted (1:3)  $\text{HNO}_3$  (suprapur, Merck) per 100 ml sample. Solid samples (soils, wood and assimilatory organs) were wet decomposed in a microwave oven (MLS 1200 Mega, Milestone, Italy) in  $\text{HNO}_3$  (65%) and HF (40%) mixture (3:1 v/v, Suprapur, Merck). Natural liquid samples were analyzed with AA Spectrometry (Varian SpectrAA 300, using flame technique FAAS mainly for Mn, Fe and graphite furnace GFAAS for Mn, Ni, Co determination). The detection limits for flame determination of Mn and Fe equals to 20  $\mu\text{g.L}^{-1}$ , and 30  $\mu\text{g.L}^{-1}$ , respectively. The GFA determination limit of Mn, Co and Ni equals to 0.5  $\mu\text{g.L}^{-1}$ . The wet decomposed samples were analyzed with the ICP-OES spectrometer (Thermo Elemental, Intrepid Duo) with axial plasma and ultrasonic CETAC nebulizer (model U-5000AT+). The concentration of elements was quantified using the lines Mn 259.3 nm; Fe 259.9 nm; Co 228.6 nm (under conditions recommended by manufacturer). Measured detection limits were for Mn 2.0  $\mu\text{g.L}^{-1}$ ; Fe 0.6  $\mu\text{g.L}^{-1}$ ; Co 0.6  $\mu\text{g.L}^{-1}$ ; Ni 0.4  $\mu\text{g.L}^{-1}$ . Calibration curves were obtained from a blank and four standards covering whole range of concentrations measured. The standards were obtained by diluting 1000  $\text{mg.L}^{-1}$  standard solutions Mn, Fe, Co, Ni in 2% (v/v)  $\text{HNO}_3$  (Analytika, Czech Republic).

Sampling localities of tree tissues were selected to be representative for the area of the whole catchment. Samples of the tree rings of Norway spruce (*Picea abies* L. Karst.) and European beech (*Fagus sylvatica* L.) were collected in summer season (July) from 3 trunks in each locality of trees approx. 60 years old in a height 130 cm above ground. The wood cores were extracted from the tree boles up to the stem axis with the increment borer (Haglöf, Sweden, PTFE coated) after the rough bark and phloem were removed. Beech leaves and spruce twigs with needles were cut off by plastic scissors and sealed in polyethylene bags. All samples were then dried up to a constant weight at 80° C in a flow box. Needles of spruce were then removed from the twigs by plastic tweezers. Samples of the assimilatory organs were purposely neither digested nor washed before their analysis. Thin poles of the wood mass from the borer were divided into three parts (inner, middle and outer), which were then analyzed separately. Further details concerning sampling, processing and analyses were presented in the paper of [20].

The content of leachable forms of elements in soils was determined after the digestion of soil fraction <1 mm with 0.1 M  $\text{HNO}_3$  (V/m = 200, 24hrs, room temperature).

The proportional index PI for each element was calculated to compare the individual biogeochemical cycles. We related this index to Fe, as the most abundant element of the studied ones.

$$PI_{Me} = Fe(\text{rock})/Me(\text{rock}) * Me(X)/Fe(X),$$

where X denotes the examined pool or flux

## Results

### Pools

Content of individual studied elements in soil, bedrock and assimilatory organs is presented in Table 1. The concentrations of studied elements in granite bedrock are generally low. The only exception is Fe, which is the most abundant heavy metal in the Earth's crust. Compared to the mean for low Ca-granites [22], the content of Fe in the bedrock of the LP catchment is lower. Content of Co and Ni in the monzogranite is higher than the mean values for low Ca-granites. Manganese, Fe, Co, and Ni are enriched two to three times in the monzogranite rock type compared to the syenogranite. All the studied elements are concentrated in biotite, because additional mafic and sulphide minerals containing the studied elements were not identified in the bedrock [5]. Manganese, Co and Ni are located in the structure of biotite as divalent ions in octahedral coordination to oxygen, similarly to  $Mg^{2+}$  and  $Fe^{2+}$ .

Total concentrations of Fe, Co and Ni in soil at LP catchment were higher than those found in the bedrock. The highest leachable concentrations of the elements, (except for Fe), were found in the top (organic) layers of the soil profile.

Another significant pool of the elements in the forest ecosystems is represented by the biomass [4]. With respect to biogeochemical fluxes of the element, it was necessary to assess its content in the assimilatory organs of the dominant tree species in LP catchment. Comparing the leachable concentrations in soil and vegetation tissues enables to get an idea of uptake for the selected elements.

### Inputs, outputs, internal cycling

The major mineral source of Fe, Mn, Ni and Co in LP catchment is the biotite. The hydrolysis and dissolution of biotite occurs from the edges of crystals inward and secondary minerals such as Fe oxide are precipitated mostly at the edges, with only a few secondary phases precipitated on the basal surfaces [12]. This observation suggests that released Fe (II) and/or Mn (II) are precipitated in aerobic conditions before they diffuse into the bulk solution. Additional ions in the biotite structure such as  $Ni^{2+}$  and  $Co^{2+}$  can be sorbed onto the Fe and Mn oxides at the biotite edges or can be released into the soil solution. The dissolution rate of biotite is a function of solution pH, temperature, organic ligand concentration, Al concentration, and saturation state or reaction affinity (e.g [13]).

Chemical weathering of biotite has been found to be similar to plagioclase in both laboratory [1, 2, 8, 21] and field experiments [3]. We applied these experiences for the estimation of Fe, Mn, Co and Ni release from biotite that should be proportional to the rate of plagioclase chemical

Table 1 The concentration of the elements in different environmental pools

		Mn		Fe		Co		Ni	
Bedrock	Monzogranite (mg.kg <sup>-1</sup> )	191		9452		3.3		12.2	
	Syenogranite (mg.kg <sup>-1</sup> )	96		2991		1.2		6.6	
	Biotite, 8,1 % vol.	2310		105500		26.8		85.1	
Soil concentration	Horizon	Tot	Leach	Tot	Leach	Tot	Leach	Tot	Leach
	Of (0 - 10 cm)	74	45.4	4501	576	2.1	0.4	49.2	3.6
	A (10 - 27 cm)	33	4.0	3528	392	1.3	0.5	9.6	3.0
	AB (27-51 cm)	43	1.8	3166	86	1.4	0.0	5.6	0.3
	Bv (51-71 cm)	68	1.6	7114	746	1.7	0.1	10.7	0.3
	Bc (71-111 cm)	85	5.8	4371	344	1.9	0.1	10.9	0.2
	Mean	<b>61</b>	<b>12</b>	<b>4536</b>	<b>429</b>	<b>1.7</b>	<b>0.2</b>	<b>17.2</b>	<b>1.5</b>
Assimilatory organs	Spruce needles (mg.kg <sup>-1</sup> )	416		33		0.12		0.87	
	Beech leaves (mg.kg <sup>-1</sup> )	1047		102		0.14		1.21	
	Spruce - wood (mg.kg <sup>-1</sup> )	184		137		N/A		1.86	
	Beech - wood (mg.kg <sup>-1</sup> )	48		65		N/A		1.82	
	Spruce needles/soil ratio	8.42		0.03		0.13		0.13	
	Beech leaves/soil ratio	17.87		0.05		0.13		0.16	

Table 2 Pools of the elements in catchment soils (mg.m<sup>-2</sup>), mean annual inputs and outputs (mg.m<sup>-2</sup>.yr<sup>-1</sup>)

Medium		Locality	Mn	Fe	Co	Ni
Soil pool			42 246	3 870 755	1 232	8 909
Inputs	Bulk precipitation	ARB	16.5	29.6	0.0396	0.260
	Rock weathering	av. LP	13.0	203.0	0.0700	0.300
Outputs	Surface discharge	LP6	22.1	16.7	0.0470	0.763
	Subsurface discharge	LP6	13.5	118.4	0.1195	0.125
Net change			<b>-6.12</b>	<b>97.6</b>	<b>-0.057</b>	<b>-0.329</b>

weathering. Chemical weathering rate of plagioclase was calculated using a mass balance equation for Na that is not significantly affected by the ion exchange in soil and by the biomass uptake [19, 23].

On basis of the mean concentration of elements in the LP catchment bedrock (Table 1) and the pattern of chemical weathering of plagioclase, the calculated annual chemical weathering flux of Fe from biotite was estimated to be 203 mg.m<sup>-2</sup>.yr<sup>-1</sup>, Mn - 13 mg.m<sup>-2</sup>.yr<sup>-1</sup> [16], Co - 0.07 mg.m<sup>-2</sup>.yr<sup>-1</sup>, and Ni - 0.3 mg.m<sup>-2</sup>.yr<sup>-1</sup>.

Mean annual input and output fluxes of the elements (in mg.m<sup>-2</sup>.yr<sup>-1</sup>) are summarized in Table 2. Precise values of the net input of elements into the catchment, represented by the bulk precipitation, are however most probably biased by the impact of leached (mostly local) organic debris deposited from the nearby trees into the collectors. The extracts from the debris collected in the funnel of samplers are leached by subsequent precipitation and it could provide surplus amounts of the essential elements to samples of bulk precipitation, before all of Mn.

The outputs of elements through water runoff were monitored at site LP6. The outputs from the forest ecosystem of all four elements most probably exceed their inputs at LP catchment.

The crucial role of shallow groundwater output for Fe (and to a lesser extent for Mn) is due to very high Fe<sup>2+</sup> (and Mn<sup>2+</sup>) concentrations in solution collected below the water table level (sampled from the well). The groundwater outflow from the LP catchment usually amounts 10% annual streamwater flux from the catchment. The amount of subsurface water discharge was calculated using the mass-balance of Cl<sup>-</sup> ions described in Navrátil et al., [14]. The output of Ni, which occurs in aquatic systems solely in Ni(II) forms, is divided between the surface and subsurface water proportionally to their discharge flows (0.763 and 0.125 mg.m<sup>-2</sup>.yr<sup>-1</sup>, respectively).

## Discussion

The concentrations of studied elements in soils and in the bedrock in LP catchment (Tab. 1) reflect their relative mobility under the actual conditions of the system. Whereas the concentration of Mn is lower throughout the soil profile than that in the bedrock, the concentrations of remaining three elements on the contrary are always higher. This finding is in agreement with low mobility of Fe (and Co) under oxidizing conditions, resulting in enrichment of the elements in soils together with aluminum and other immobile elements such as REE, Pb, Ti and others [10, 15]. The enrichment of Ni in the soil profile is not clear, as the mobile Ni(II) form is relatively stable. The distribution of elements throughout the soil profile indicates effect of input of atmospheric protons which mobilize the metals towards deeper horizons, where the soil percolates become partly neutralized and the metals are subsequently immobilized. High concentration of leachable Mn

in the uppermost Of horizon results from its high content in the tree tissues (Tab.1), especially in the assimilatory organs and therefore in the litterfall. The distribution of Mn throughout the soil profile LP35 below the beech stands, especially the very low leachable Mn content in AB and Bv horizons is probably related to high level uptake of the element.

Moderately higher total Co and Ni concentrations in soil than in the bedrock and their distribution throughout the profile result probably from the residual products of partly weathered biotite and/or from their (mostly anthropogenic) input through atmospheric deposition. It also indicates a negligible root uptake of Co and Ni (which is in agreement with relatively low concentration of the elements in tree tissues). The highest total concentration of both elements in the uppermost Of horizon, which is particularly remarkable in Ni, should be attributed mainly to the atmospheric (mostly anthropogenic) input of the elements. Relatively low concentration of mobile forms of the elements in Of horizon indicates their strong binding to the organic matter, in contrast with the loosely bound (mostly metabolic) Mn.

Basic information concerning the net accumulation or loss of the elements in soils of studied catchment could be obtained from the mass balance of their inputs and outputs. The only directly measurable fluxes of the elements to and from the LP catchment are bulk atmospheric precipitation and the natural output from the catchment (represented by the surface- and subsurface discharge). Table 2 summarizes the soil pool of elements (provided the mean thickness of the soil layer is 0.7 m), and the mean annual deposition-, surface discharge- and subsurface discharge fluxes of the elements.

In spite of the probably overestimated Mn input through bulk precipitation (impact of mostly autochthonous organic particles), the net balance is negative - Mn is almost certainly lost from the catchment. The same results were found for Co and Ni. Soil pool of Fe on the other hand is increasing, mainly due to the relatively high input through rock weathering and low output. Crucial feature of Fe is its relatively easy oxidation to the poorly mobile Fe<sup>3+</sup> form.

Another tool used to reveal and compare the specific character of the biogeochemical cycling of the individually discussed elements is the concept of their *proportional indices* (PI's) related to the most common element Fe. The proportional indices are summarized in the Table 3.

Main characteristics of the elements derived from their PI's can be expressed as follows:

All the monitored atmospheric inputs are affected by the impact of metabolic leaching products of all the examined essential elements (Mn, Ni, Co), which results in altered chemical composition of the collected samples, mainly of throughfall. The strongest impact is observed in the chemistry of spruce throughfall. Moderately lower

PI's in beech throughfall can be attributed to relatively low specific surface of the assimilatory organs of deciduous trees compared to those of conifers and to the fact that deciduous assimilatory organs cover the tree crowns for 7 to 8 months in a year only (Mn – PI in beech throughfall equals to 109, whereas in spruce throughfall it is 139; in case of Co it is 12.7 vs. 23.5). The enrichment of bulk precipitation by all the three compared elements, which is especially strong in Mn, can be hardly attributed only to its primary chemical composition. The comparison of PI's in bulk precipitation with those for beech leaves and needles rather indicates incidental sample impairment by the surrounding vegetation (pollen, organic debris etc.).

The PI's values for surface discharge reflect higher relative mobility of Ni>Mn>Co compared to Fe, which is in agreement with increasing affinity of the sequence of metals towards their oxidation. The mobility of Fe in aerated aquatic systems is limited by the spontaneous oxidation of Fe<sup>2+</sup> ions in presence of atmospheric oxygen to Fe<sup>3+</sup> ions, which form poorly soluble oxyhydroxides. Standard electrode potentials of oxidation of Co and Mn

in neutral solutions are close and considerably higher than that of Fe, whereas the Ni<sup>2+</sup> ion being stable at natural conditions [6]. On the other hand, the subsurface water collected approx. 2 m below the soil water level is characterized by low Eh and high concentrations of Fe<sup>2+</sup> (and Mn<sup>2+</sup>) ions, so that the calculated PI<sub>Ni</sub> is nearing that of iron, but PI<sub>Co</sub> (in agreement with its enrichment in soils) is the highest.

Mean PI's of Mn for both total and leachable concentrations in soils (and that of Ni in leachable forms) reach values close to 1 indicating that no important specific changes of concentrations of the elements, compared to those of Fe, occur in the soil cover. The higher PI values of total and leachable Co concentrations in soil (5.7 and 3.5 respectively) again indicate a moderate enrichment of the element in soils.

The values of PI's of Mn and Ni in bole wood (data for Co in beech haven't been yet available) indicate pronounced enrichment in both essential elements compared to Fe. Higher enrichment of Ni in beech than in spruce wood should be explained by differences in the depth of rooting

Table 3. Mean annual fluxes and compartment contents of Mn, Fe, Co, Ni together with the corresponding values of “proportional index” PI<sub>Me</sub>

medium	locality	Element	Mn	Fe	Co	Ni
Bulk precipitation	TR	flux (ug.m <sup>-2</sup> .yr <sup>-1</sup> )	13328	33902	22.2	285
		PI <sub>Me(precip)</sub>	14.6	1	5.1	10.3
Bulk precipitation	ARB	flux (ug.m <sup>-2</sup> .yr <sup>-1</sup> )	16478	29623	39.6	260
		PI <sub>Me(precip)</sub>	20.7	1	10.3	10.8
Beech throughfall	LP6	flux (ug.m <sup>-2</sup> .yr <sup>-1</sup> )	45511	15498	25.6	277
		PI <sub>Me(Bthrf)</sub>	109.3	1	12.7	21.9
Spruce throughfall	LP7	flux (ug.m <sup>-2</sup> .yr <sup>-1</sup> )	97986	26219	79.5	492
		PI <sub>Me(Sthrf)</sub>	139.2	1	23.5	23.1
Surface discharge	LP6	flux (ug.m <sup>-2</sup> .yr <sup>-1</sup> )	22119	16701	47.0	763
		PI <sub>Me(s.d.)</sub>	49.3	1	21.7	56.2
Subsurface discharge	LP6	flux (ug.m <sup>-2</sup> .yr <sup>-1</sup> )	13478	118354	119.5	125
		PI <sub>Me(ss.d.)</sub>	4.2	1	7.8	1.3
Soil content total		Me <sub>(soil tot.)</sub> mg.kg <sup>-1</sup>	127	4987	3.7	14
		PI <sub>Me(soil tot.)</sub>	0.9	1	5.7	3.5
Soil content leachable		Me <sub>(soil leach.)</sub> mg.kg <sup>-1</sup>	8.3	600	0.2	0.4
		PI <sub>Me(soil leach.)</sub>	0.5	1	2.6	0.8
Beech wood		Me <sub>(wood)</sub> mg.kg <sup>-1</sup>	48	65	N/A	1.82
		PI <sub>Me(beech wood)</sub>	27.5	1		34.4
Spruce wood		Me <sub>(wood)</sub> mg.kg <sup>-1</sup>	184	137	N/A	1.86
		PI <sub>Me(spruce wood)</sub>	50.0	1		16.7
Beech leaves		Me <sub>(leaves)</sub> mg.kg <sup>-1</sup>	889	92	0.14	1.209
		PI <sub>Me(beech leaves)</sub>		1	11.8	16.2
Spruce needles		Me <sub>(needles)</sub> mg.kg <sup>-1</sup>	435	33	0.12	0.877
		PI <sub>Me(spruce needles)</sub>	490.8	1	28.1	32.7
<b>Syenogranite</b>		<b>Me<sub>(rock)</sub> mg.kg<sup>-1</sup></b>	<b>346.75</b>	<b>12911.25</b>	<b>1.67</b>	<b>10.5</b>

systems and increased Ni availability (Table 1) in deeper soil horizons. The PI's of Mn, Co and Ni in assimilatory organs are high. They decrease in the order Mn>> Ni>Co and they correspond to the enrichment of the elements in throughfall. The highest PI's values for Mn in assimilatory organs, as well as in throughfall approve the enormous importance of the forest vegetation for the mobilization of this essential element, at least in ecosystems that developed on acidic bedrock like LP catchment.

## Conclusion

The content of the elements in the bedrock of LP catchment is generally low, except of Fe. Monzogranite rock type, compared to the syenogranite is enriched by the studied elements (two to three times). The content of the elements in soil indicates the relative mobility of the elements. The increased concentrations of the elements in the upper soil layer designate the excessive bounding to the organic matter.

The impact of vegetation on the element cycling in the environment is evident especially in the biogeochemical cycle of Mn. Manganese content in the vegetation tissues is very high and therefore throughfall is enriched by leaching and washout.

The input/output fluxes of the elements are compared too. Atmospheric inputs are strongly affected by the vegetation. In case of Mn, the altered concentration in the throughfall samples is fairly visible. The same applies for Ni and Co, which are also bound to the organic matter. The outputs, represented by surface and subsurface discharge, reflect the relative mobility of the elements decreasing in the order Mn>Ni>Co>Fe. Less mobile Fe is limited by the aerated conditions, where the soluble Fe<sup>2+</sup> ions are oxidized to almost insoluble Fe<sup>3+</sup> ions.

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