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DISTRIBUTION, CYCLING AND IMPACT OF SELECTED INORGANIC CONTAMINANTS ON ECOSYSTEM OF THE LESNI POTOK CATCHMENT, THE CZECH REPUBLIC

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Abstract

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Biogeochemistry of the anthropogenic contaminants As, Be, Cd, Cu and Pb was studied in the experimental Lesni potok catchment in central Czech Republic. The completely forested landscape is underlined by syenogranite and monzogranite. Bedrock, as well as the soil cover, are enriched by As, Be and Pb. The enrichment of Cu and Pb in topmost layers of the soil profile are due to low mobility of elements, metabolic cycling by vegetation (Cu), and anthropogenic emissions (Pb). The content of As and Cd is more or less evenly distributed with depth, and in to a certain extent controlled by content of the soil clayey fraction. Concentration of mobile Be increases with depth of the soil profile. Atmospheric (mostly anthropogenic) inputs of As, Pb and Cu have been considerable. Bulk fluxes of all the studied contaminants in precipitation decreased in period 1994 - 1999 by approximately 80%. The distribution of elements between the solid and liquid phases depends on pH and Eh of system. Mobility of Pb and Cu is low, what results in their gradual accumulation in soils. Solid forms of As become mobile under reducing conditions. This is reflected in high concentration of As in shallow groundwater, which exceeds more than 50x that in surface water. Atmospheric inputs of Cd and Be are low (< 40 and < 20 ?g.m^{-2}.year^{-1}, respectively). The balance of atmospheric inputs and outputs through the surface water and shallow groundwater shows moderate accumulation of Cd. On the other hand, export of Be is more than 300 ?g.m^{-2}.year^{-1}.

Key words: As, Be, Cd, Cu, Pb, contaminants, cycling, catchment, mass balance.

Introduction

The region of central Czech Republic with the State Nature Reserve “Voděradské bučiny” forest was selected in late 80’s as a typical experimental landscape for the biogeochemical study of selected major, minor and trace elements (Minařík et al., 1998, 2000; Skřivan, Hladíková, 1987; Skřivan et al., 1993, 1996, 2000a,b). Detailed geochemical study of the granite bedrock and soils started in 1970's (Vejnar, 1973; Minařík et al., 1986; Němec, 1978). Study of the atmospheric inputs of inorganic contaminants began in 1989 and it was gradually supplemented by sampling of precipitation below the tree canopy (throughfall), and surface and shallow groundwater.

The routine monitoring spans of deep economic changes including the heavy industry reduction, gradual and (in 1999) complete desulphurization of large Czech power plants burning low quality brown coal.

This paper discusses the effects of lithology and deposition on the nature and composition of soils and water in the catchment. The major emphasis of this study was to evaluate the geochemical mass balances of As, Be, Cd, Cu and Pb in the catchment and to comprehend their temporal variations during the past decade.

Materials and methods

Study area – location and description

The completely forested Lesni potok (LP) catchment is located 30 km southeast of Prague in central Czech Republic (Fig. 1). A brief description of the area was presented in Minařík et al. (1998). The LP catchment is found on the area of Nature State Reserve "Voděradské bučiny". The geographical coordinates of the catchment are 49° 58' 35" lat. N, 14° 46' 40" long. E. and it covers an area of 0.765 km^2. Its south boundary reaches a maximum elevation of 500 m a.s.l. Thomson weir gauges runoff from the catchment in its northern part at 406

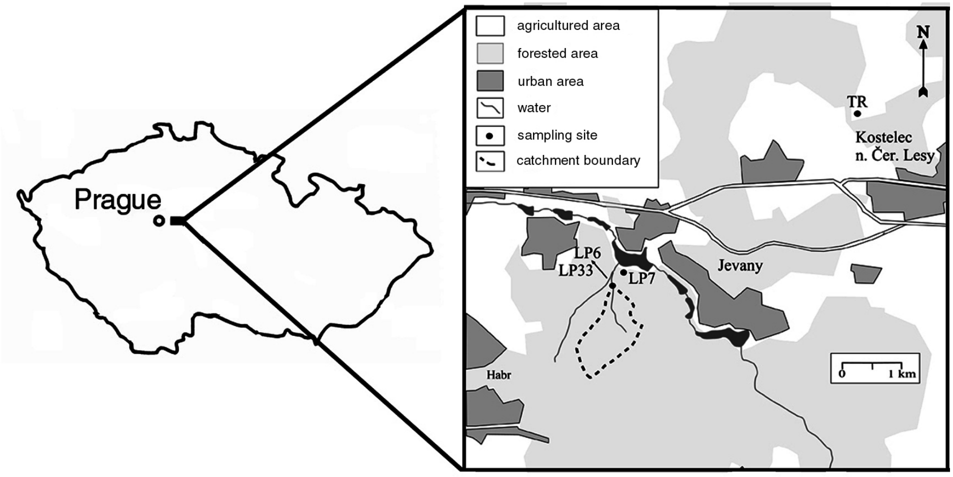

Fig. 1. Map of the studied region.

m a.s.l. The mean annual precipitation height is 635 mm, the mean annual temperature is 7.3 ^{o}C. Bulk chemistry of the precipitation and mixed forest throughfall have been monitored in a rural landscape (locality Truba - TR), approximately 4 km northeast from the catchment (Fig. 1). The beech and spruce throughfall has been collected inside the catchment (localities LP6 and LP7, respectively).

Methods of investigation

Bulk precipitation and mixed forest throughfall have been monitored monthly since 1993, throughfall below the canopy of beech (*Fagus sylvatica* L.) and Norway spruce (*Picea abies* L.) has been collected since 1997 (Skřivan et al., 2000a, b). At the end of each sampling period, sampling bottles were transported in sealed PE bags to the laboratory and weighed to determine the volume of the liquid. Parts of the samples were filtered using a 0.45 mm membrane filter and stabilized by diluted nitric acid. The filtrate was stored at +4 ^{o}C in a cooler until analysis for trace elements. The unfiltered part of samples was split for pH- and conductivity measurements and for the bulk chemistry determination.

Surface water of a small brook draining the LP catchment was sampled monthly at the Thomson weir (location LP6, Fig. 1). Samples of surface water for the trace element analyses were filtered in the field through the membrane filter (pore size 0.45 mm), in a device Sartorius, SM 165 10, coupled with the manual vacuum piston pump. The filtrate was immediately stabilized by diluted nitric acid. Unfiltered and unstabilized samples of surface water were collected simultaneously for the determination of major analytes and for the pH and conductivity measurements.

Pumped fresh samples of groundwater were collected monthly from February 1999 untill September 2000 in a shallow well (depth 4.2 m, cased with inert material), which is located near the Thomson weir (Fig. 1). The samples were filtered immediately through the <0.45 mm filters and stabilized by diluted nitric acid.

Concentration of minor and trace elements was determined by AA spectrometry (VARIAN SpectrAA 300), by flame or graphite furnace techniques. Arsenic was determined by the hydride- generation technique, using the same AA Spectrometer. The major anions were determined by HPLC and in case of F^- by the ISE.

Results and discussion

Mineralogy and chemical composition of the bedrock

Two types of biotite granites form the bedrock in the studied area. Mostly porphyritic coarse to medium grained monzogranite (Říčany type) is developed in the southern part of the catchment. The light colored fine-grained syenogranite (Jevany type) forms bedrock in northern part of the catchment. The petrography and geochemistry of these granites was frequently studied (Palivcová et al., 1992). Modal analyses plotted in the Streckeisen's diagram (Fig. 2) modified by Kinnaird, Bowden (1991) show the position of the granite samples, which have been studied formerly in the Říčany massif (Palivcová et al., 1992) and those in the catchment area only. In Table 1 we present five new modal analyses. All these samples are slightly kaolinized.

Both types of granites exhibit similar mineralogy, but quartz and alkali feldspar megacrysts occur in the monzogranite only. The K-feldspar can be identified as an orthoclase - perthite to an intermediate microcline - perthite. Ground mass containing some quartz grains up to 5 mm in diameter, displays slightly zoned plagioclase of oligoclase to albite composition with rusty brown Mg rich biotite flakes. No other maffic minerals except for biotite were

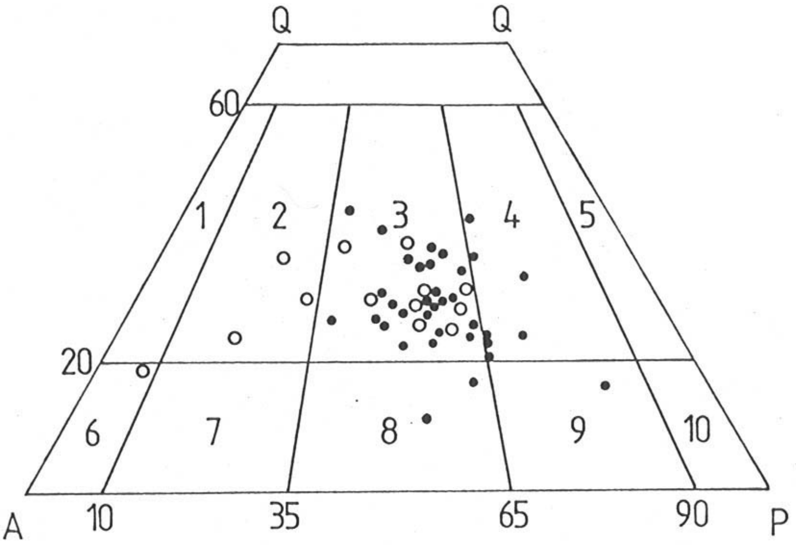

Fig. 2. Granitoids of the Říčany massif in the Q-A-P diagram. Dots designate the projection points of the rock samples from the whole granite stock (ca 80 km^2), circles designates those from the catchment area only. Legend: 1 – alkali granite, 2 – syenogranite, 3 – monzogranite, 4 – granodiorite, 5 – tonalite, 6 – alkali syenite, 7 – syenite, 8 – monzonite, 9 – monzogabbro, 10 – gabbro.

Table 1. Modal composition of the parent rocks in the Lesni Potok catchment and its near vicinity

Mineral	Sample No.				
	1	2	3	4	5
Quartz	29.16	14.41	20.64	26.42	27.57
K-feldspar	37.19	54.65	50.88	40.61	31.25
Plagioclase	13.24	4.03	13.74	20.05	23.22
Biotite	0.06	7.71	4.73	5.79	8.25
Muscovite	0.63	0.75	0.50	0.47	0.47
Kaolinite	19.33	17.85	9.20	6.22	8.92
Chlorite	–	0.10	–	0.18	0.07
Apatite, zircon	0.02	0.23	0.13	0.12	0.16
Ilmenite, titanite	0.17	0.21	0.06	0.06	–
Total (vol.%)	99.82	99.99	99.99	100.03	99.91

1 – kaolinized syenogranite (Jevany type). Outcrop near the road connecting Černé voderady and Zvánovice in the eastern margin of the catchment

2 – kaolinized syenogranite (Jevany type). Quarry „U rybníka“

3 – moderately kaolinized syenogranite (Jevany type). Quarry „Kamenka“

4 – moderately kaolinized syenogranite (Jevany type). Large boulders in the „Voderadské buciny“ Nature State Reserve

5 – moderately kaolinized monzogranite (Říčany type). Outcrop in the southern margin of the catchment area

found. The amount of muscovite is mostly less than 1 vol.%. The common accessory minerals are: apatite, sphene, zircon, ilmenite, rutile, magnetite, secondary chlorite and rare fluorite and tourmaline. Compared with the monzogranite, the syenogranite is poorer in biotite and its plagioclase is Na rich (An 10-12 vol.%). Recent analyses of the bedrock are given in Table 2.

Table 2. Recent silicate analyses of the parent rocks in the catchment [content in %]

Rock type	Monzogranite	Syenogranite
SiO_2	71.24	73.28
TiO_2	0.550	0.170
Al_2O_3	14.18	14.46
Fe_2O_3	0.463	0.350
FeO	0.762	0.252
MnO	0.024	0.011
MgO	0.760	0.240
CaO	1.170	0.930
SrO	0.039	0.030
BaO	0.166	0.129
Li_2O	0.02	0.007
Na_2O	3.72	4.01
K_2O	5.33	5.11
P_2O_5	0.183	0.060
CO2	0.010	0.010
C_{inorg}	0.049	0.014
F	0.146	0.059
S	<0.005	<0.005
ign. loss	0.636	0.383
$-H_2O$	0.190	0.110
$-F_{ekv}$	0.061	0.025
$-S_{ekv}$	<0.001	<0.001
Sum	99.28	99.59

Basic characteristics of soil

Soil types of the catchment were identified at 21 uniformly distributed sites. More detailed investigation was performed at three 1m deep pits. The soils developed on granites of the LP catchment are predominantly Cambisol type (approx. 70% of the catchment area), with Lithosol and Gleyic Cambisol subtypes. The average soil thickness is 67 cm in Cambisols, 7 cm in Lithosols and 87 cm in Gleyic Cambisols. The soil thickness is generally thinner over the topographic heights (Minařík et al., 1998; Skřivan et al., 2000b).

The mineralogy of the soil developed from the granite bedrock includes quartz, kaolinite, illite, K- feldspar and plagioclase and trace smectite (in order of the decreasing amount). The mineralogy was determined in all samples, collected near the Thomson weir. Substantial soil matter is X-ray amorphous. The SEM/EDAX study indicates that some of the soil minerals, especially the feldspars, are coated with the Fe- oxyhydroxides.

Atmospheric deposition

Dominant ions in the bulk precipitation are Ca and SO_4^{2-}. High fluxes of K in all types of throughfall are attributed to the leaching of the forest vegetation. Ca and Mg are derived from the canopy leaching and the near - surface atmospheric aerosol particles, intercepted by the tree crowns. Most Cl and Na (partly also Ca, Mg, SO_4^{2-}) originate from the oceanic spray. Correlation of the annual fluxes of the two elements both in the bulk precipitation and in throughfall is considerably strong ($R^2 = 0.77$, n = 19, Fig. 3). Excess of Cl is from the adsorption of gaseous HCl on the forest tree canopies. Emissions of HCl, SO_2 (SO_4^{2-}), and HF are probably derived largely in the Czech Republic from the fossil fuel combustion. Correlation of the deposition fluxes of the other two significant contaminants and acidifiers of the atmosphere, compounds of S (SO_4^{2-}) and F^-, is presented in Fig. 4 for all kinds of the throughfall. Strong correlation ($R^2 = 0.95$, n = 12) indicates the conjoint origin of the two atmospheric contaminants. SO_4^{2-} and F^- annual deposition fluxes (Table 3) are decreasing in bulk precipitation and in throughfall, resulting from the gradual desulfurization of the boilers of all Czech coal - fired power plants.

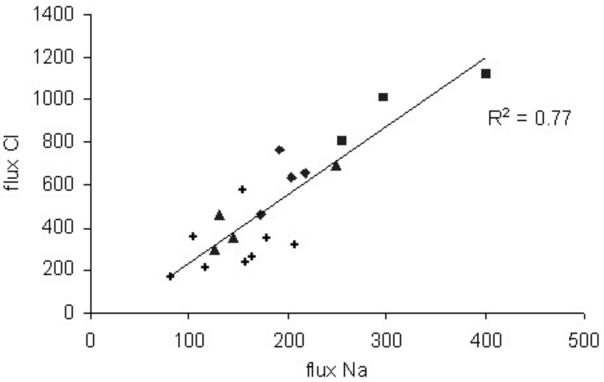

Fig. 3. Correlation of Na and Cl in bulk precipitation and in throughfall. Fluxes in $mg.m^{-2}.yr^{-1}$. Legend: ⧗ – bulk precipitation, ◆ – spruce throughfall, ■ – mixed throughfall, ♦ – beech throughfall.

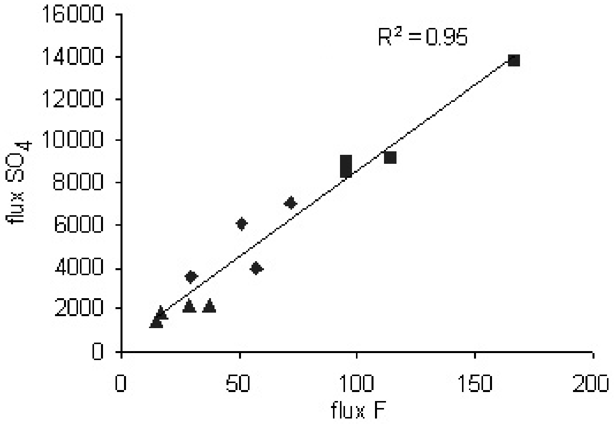

Fig. 4. Correlation of F^- and SO_4^{2-} in throughfall. Fluxes in $mg.m^{-2}.yr^{-1}$. Legend: ◆ - spruce throughfall, ■ – mixed throughfall, ♦ - beech throughfall.

Water discharge

Chemistry of stream water collected at closing weir of the LP catchment (Fig. 1) has been studied since 1985. Since 1994, chemistry of monthly samples is available. Temporal variations, in the chemical composition of stream water and changes in the amount and properties of the principal dissolved substances, are associated mainly with the variations of the discharge, and consequently with its pH. The discharge of the Lesni potok varies from zero

T a b l e 3. Deposition fluxes of major constituents in bulk precipitation (loc. TR), mixed forest- (loc. TR), spruce (loc. LP7) and beech throughfall (loc. LP6) [fluxes are expressed in $mg.m^{-2}.yr^{-1}$]

Bulk precipitation, loc. TR										
Year	Na	K	Mg	Ca	F^-	Cl^-	SO_4^{2-}	NO_3^-	NH_4^+	N_{tot}
1993	*81*	*190*	*51.9*	*356*	*27.3*	*168*	*3554*	*1452*	*457*	*683*
1994	116	112	43.8	341	36.5	209	2776	1513	292	569
1995	178	198	42.4	231	34.1	353	2819	1656	612	850
1996	156	92	47.9	313	39.4	246	2883	1803	510	804
1997	207	147	45.9	289	27.4	326	2684	1966	552	874
1998	163	165	37.8	285	16.8	258	1837	1496	332	438
1999	153	91	31.9	186	6.3	579	575	1223	234	458
2000	104	79	32.9	187	7.5	358	1104	1333	249	495
mixed forest throughfall, loc. TR										
1993		*8221*	*725*	*3402*	*168*		*13758*	*5800*	*2319*	*3113*
1994	296	4376	384	1999	114	1012	9176	3154	944	1446
1995	401	2807	384	1466	96	1121	8946	3824	1232	1822
1996	255	3186	409	1538	96	807	8488	3179	972	1474
spruce throughfall, loc. LP7										
1997	204	1924	280	728	71.8	634	7033	2886	1140	1538
1998	191	2374	295	666	50.5	764	6077	2964	990	1439
1999	172	1315	171	487	29.0	459	3602	2885	935	1379
2000	217	1722	221	584	57.3	655	3956	3537	1018	1590
beech throughfall, loc. LP6										
1997	144	978	170	533	36.0	353	2252	1662	320	624
1998	248	1707	365	822	28.4	694	2234	1177	203	424
1999	126	794	114	451	14.8	295	1487	1714	399	697
2000	131	1495	197	548	16.7	459	1869	1727	281	608

values in italics were calculated from data of incomplete hydrological year

(in several years in August or September) to more than 20 $L.s^{-1}$ in spring. Mean annual discharge between 1994 and 2000 ranged between 0.5-3.6 $L.s^{-1}$. The H^+ concentration increased with discharge (Fig. 5).

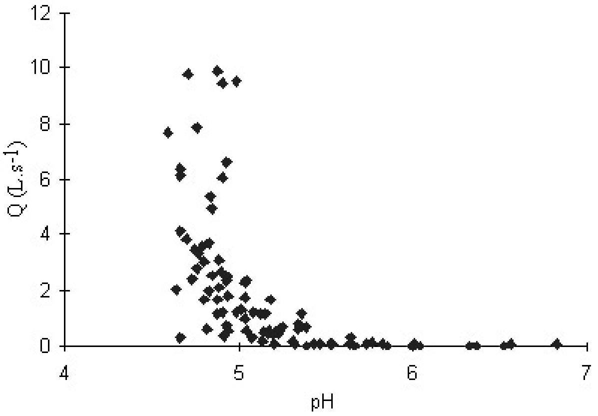

Fig. 5. Dependence of the pH-values of surface water on discharge.

Sulfate is the dominant anion, while the concentration of Cl^- and HCO_3^- is very low. Calcium, followed by Mg are the main cations of the surface water. Relations between the main ions of the stream water are presented in Fig. 6.

The annual shallow groundwater discharge from the catchment area, estimated from the balance of Cl^- fluxes and measured inputs and outputs of water, amounts approx. 0.37 $L.s^{-1}$. Mean concentrations of the studied toxic trace elements in surface and shallow groundwater of the catchment are presented in Table 4.

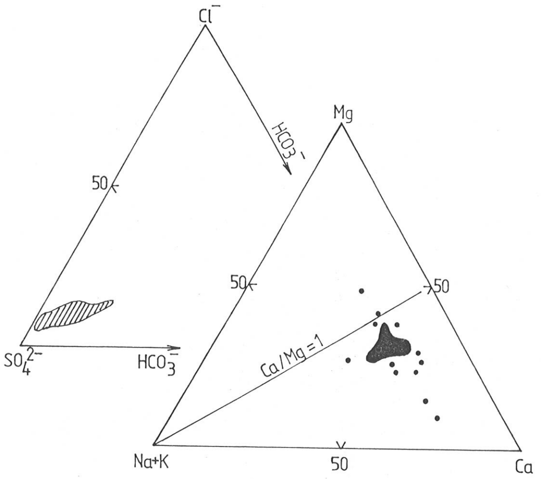

Fig. 6. Relation between the major ions in spring water of the Lesni potok (ternary diagrams were constructed from the values in millivals). Hatched area – all analyzed samples, black area – more than 80 samples).

T a b l e 4. pH, discharge weighted concentrations of studied contaminants, Fe and Mn in surface and subsurface water in 1999-2000 [in ppb]

Element	pH	As	Be	Cd	Cu	Pb	Fe	Mn
Surface water	4.98	0.26	4.72	0.28	0.53	0.17	130	134
Subsurface water	6.70	14.28	0.24	0.02	0.24	0.12	6976	838

Budgets any cycling of the contaminants

Arsenic

Arsenic is relatively abundant in both granite types, which form the crystalline bedrock of LP catchment. Especially the coarse-grained monzogranite is enriched in As. Typical content (13.4 ppm) is by one order higher than that in similar rock types (Wedepohl, 1969-78). Generally, ca. one half of the total As content in granitic rocks is assumed to be bound in feldspars. It substitutes Al^{3+} in their lattices in trivalent form (Ljachovič, 1972). Accessory sulfides and Fe or Ti oxides may represent additional source of As (Smith, 1974).

Soils in the catchment are unusually enriched in As. Average total concentration attains 36.3 ppm in 1 m deep profiles. Distribution of As throughout the soil profile follows that of the total Fe. The acid leachable portion of As (size fraction < 1 mm, 0.1 M HNO_3, V/m = 200, t = 24 hours, oxic conditions) in soil is very low (approx. 1% of the total As content, Table 6). Low mobility of As in soil could be explained by its bonding in Fe oxyhydroxides

Table 5. Total content and leachable forms of studied elements in soils of the LP33 profile [ppm d. wt.]

		Horizon						
Element	Depth [cm]	A	B_w	G_0	Gr_1	Gr_2	Gr_3	Gr_4
		0-15	15-30	33-48	48-67	67-74	84-87	90-100
As	total	35.31	43.10	30.55	39.55	42.15	28.13	35.14
	leachable	*0.68*	*0.18*	*0.22*	*0.27*	*0.32*	*0.34*	*0.52*
Be	total	3.75	5.43	6.33	6.21	6.03	6.30	7.38
	leachable	*0.14*	*0.60*	*0.55*	*1.11*	*1.39*	*0.60*	*1.22*
Cd	total	0.79	1.05	0.86	1.25	1.26	1.00	1.19
	leachable	*0.14*	*0.08*	*0.08*	*0.11*	*0.10*	*0.06*	*0.06*
Cu	total	26.77	28.49	10.77	37.91	35.56	13.44	24.49
	leachable	*1.23*	*0.55*	*0.34*	*0.92*	*1.45*	*0.51*	*0.98*
Pb	total	67.06	58.60	47.94	76.38	93.09	40.12	66.78
	leachable	*20.84*	*11.09*	*8.52*	*18.51*	*18.72*	*7.68*	*12.48*

Table 6. Mean annual deposition fluxes of elements (own results) compared with values of others (all in ug.m^{-2}.yr^{-1})

Bulk precipitation, loc. TR						
Water year	pH	As	Be	Cd	Cu	Pb
1993					1127	3237
1994	4.11	1384	33.4	78.7	1229	3414
1995	4.23	1717	39.9	103	1247	2459
1996	4.23	925	20.0	105	922	2832
1997	4.30	563	15.8	30.8	377	2279
1998	4.45	331	14.0	37.4	351	1598
1999	4.47	272	4.08	26.2	260	812
2000	4.42	436	3.32	42.5	254	1284
Year	Source					
1986-87	1	4000	42		4800	14200
1990-92	2	4200	90	470	4800	11000
1998	3			120		1560
?	4			130	3500	3300
1990	5	230	26	60	350	300
1990	6	44	7.7	32	310	230

1 – mean values in rural regions of the Czech Republic (Škoda et al., 1988), 2 – mean values for the C. R. (Beneš, 1994), 3 – median value for the C. R. (CHMI 1998), 4 – rural regions of England and Wales (Mott et al., 1998), 5/6 – lowest values in rural/remote regions of Norway (Berg et al., 1994)

(Rose et al., 1979 and others). No regular variations of the As distribution with depth have been observed.

Table 7. Mean annual discharge - weighted pH and concentrations of elements in LP surface water [in ppb]

Water year	pH	As	Be	Cd	Cu	Pb
1994	4.46	*0.466*	*10.96*	*0.499*	*0.266*	*0.250*
1995	4.48	2.061	9.62	0.593	0.772	0.259
1996	4.78	0.842	9.21	0.508	0.663	0.654
1997	4.89	0.659	6.00	0.287	0.250	0.250
1998	5.20	0.549	4.01	0.155	0.250	0.277
1999	5.07	0.316	4.69	0.280	0.272	0.251
2000	4.90	0.203	4.75	0.286	0.791	0.089

numbers in italics are valid for an incomplete year only

Table 6 shows gradual significant decrease of As deposition fluxes throughout the years 1994 - 1999. Worldwide anthropogenic emission sources of As result from the pyrometallurgical production of Cu, Ni, Pb and Zn, coal combustion and iron manufacturing (Nriagu, Pacyna, 1988). Coal burning power plants are probably the dominant source of As in the Czech Republic (Hokr, 1977). Steady decline of all As deposition fluxes in studied region between 1997-1999 (Skřivan et al., 2000a) reflects, therefore efficiency of the gradual desulfurization of flue gasses of the electric power stations burning low quality brown coal (Anon., 1999). Mean concentrations of As in surface water collected monthly vary in dependence on discharge and pH of stream, but the determinative physical quantity is the Eh of the system, with respect to As bonding to Fe oxyhydroxides (Skřivan, Hladíková, 1987). During the summer periods with low discharge of the LP, increased concentration of Fe in water is regularly accompanied by the increased concentration of As. Nevertheless, the annual discharge weighed mean As concentrations (Table 7) indicate certain irregular decline in period 1995–2000, reflecting probably the decreasing input of atmospheric As.

The presented balance of inputs and outputs (Table 8) supports rather conservative character of As in the environment with an access of atmospheric oxygen, even though the confidence of balance is embarrassed by high concentrations of As in shallow groundwater with low Eh (Table 4, see also values for Fe and Mn) and by the uncertainty of the precise amount of the subsurface discharge. Another uncertainty of the balance follows from unknown amount of As, which is volatilized in soil layers with low Eh by biomethylation (Andreae, 1980). High total As content in the bedrock and soil, low percentage of its loosely bound forms, together with relatively low atmospheric input indicate that majority of arsenic in soils is of lithogenic origin.

Beryllium

Granitic rocks of the Říčany massif, which form the crystalline bedrock of the catchment, are enriched in Be. The highest Be concentrations were found in the monzogranite (13 ppm is the average of 3 samples – Němec, 1978). Analyses of slightly kaolinized rocks sampled directly in the catchment area show 10.2 ppm in monzogranite and 7.15 ppm Be in syenogranite.

Table 8. Balance of input (through bulk precipitation) and outputs (through surface- and subsurface discharge) in LP catchment, values in [ug.m^{-2}.yr^{-1}]

Water year	Flux	As	Be	Cd	Cu	Pb
1995	input - bulk precip.	1717	39.9	103	1247	2459
	output - surface w.	251	1172	72.2	94.1	31.6
	output - subsurface w.	254	5.25	0.35	4.24	0.62
	balance	1212	-1138	31	1148	2427
1996	input - bulk precip.	925	20.0	105	922	2832
	output - surface w.	124	1361	75.0	98.0	96.6
	output - subsurface w.	308	6.37	0.35	5.14	0.75
	balance	492	-1347	29.8	819	2735
1997	input - bulk precip.	563	15.8	30.8	377	2279
	output - surface w.	64.2	585	28.0	24.4	24.4
	output - subsurface w.	203	4.20	0.43	3.39	0.50
	balance	295	-573	2.45	350	2254
1998	input - bulk precip.	331	14.0	37.4	351	1598
	output - surface w.	19.0	138	5.4	8.6	*9.6*
	output - subsurface w.	43.2	0.89	0.28	0.72	0.11
	balance	269	-125	31.7	341	1588
1999	input - bulk precip.	272	4.08	26.2	260	812
	output - surface w.	23.0	341	20.4	19.8	*18.3*
	output - subsurface w.	198	4.09	0.27	3.30	0.48
	balance	51.5	-341	5.54	236	793
2000	input - bulk precip.	436	3.32	42.5	254	1284
	output - surface w.	13.6	319	19.2	53.3	*6.0*
	output - subsurface w.	216	4.46	0.30	3.60	0.53
	balance	207	-321	22.9	197	1277

Fluxes of subsurface output were estimated from the annual water discharge and concentrations of elements determined in 1999

Geochemical position of Be in the host rock was determined by means of the laser ablation - mass spectrometer (LA-ICP-MS). The results indicate that majority of Be is bound in plagioclase (Table 9). This mineral is the major source of Be in soil developed above the granite bedrock during its weathering.

Table 9. Content of Be in the parent rock [ppm] (Navratil et al., 2002)

Element/mineral	Orthoclase	Plagioclase	Biotite	Quartz
Number of analyses	37	37	8	7
Be content (ppm)	0.8	18.1	7.1	0.3

Experimental acid leaching of the main rock-forming minerals performed at room temperature and atmospheric pressure (Minařík et al., 1997) revealed rapid release of Be from biotite, whereas the release of Be from both feldspars was less rapid.

Mean values of the total Be concentration in soil (5.9 ppm) are lower than those in the underlying rocks and they depend on the position of the particular sampling locality in the catchment (on the depth of the water table, slope of the terrain, etc.). The Be distribution throughout the soil profile is strongly dependent on the depth: the deeper it is, the higher is its total content, as well as its acid - leachable (0.1 M HNO_3) portion. Variations are in the latter case more dependent on the amount of the clayey fraction in the individual soil horizons. Decrease of Be concentration in soil towards the surface indicates that mobile portion of the element is gradually leached out of the soil profile by acid atmospheric precipitation and it eventually enters the surface water.

Mean values of the Be concentration in bulk atmospheric precipitation have been gradually decreasing throughout the past 6 years. Strong correlation ($R^2 = 0.95$, n = 7) of the Be deposition fluxes with those of As (Fig. 7) denotes the coal burning as a dominant emission source of atmospheric Be. In year 2000, mean annual concentration of Be reached 0.005 ?g.L^{-1} Be as a result of gradual desulfurization Czech coal power plants.

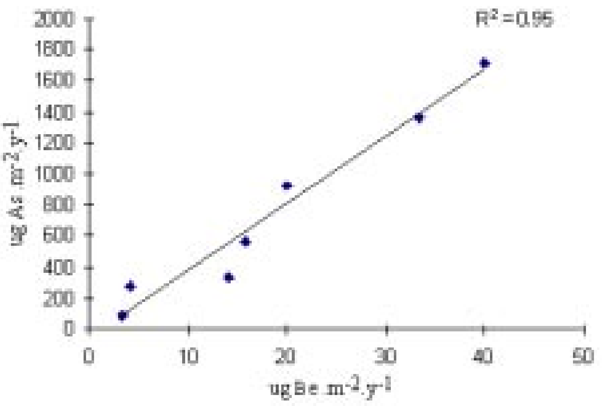

Fig. 7. Correlation of fluxes of Be and As in bulk precipitation. Fluxes in mg.m^{-2}.yr^{-1}.

Instant concentration of the dissolved Be in stream water varies strongly in dependence on its pH and the discharge the LP stream. It increases as the pH declines and there is also a weak increase of the Be concentration with increased discharge. Content of the dominant Be species in water, Be^{2+} and BeF^{+}, is also pH dependent (Navrátil, 2000). The mean annual discharge weighted Be concentration in the stream declined from 11.0 ?g.L^{-1} in 1994 to 4.75 ?g.L^{-1} in 2000 (Table 7), as a result of the decreasing input of protons in precipitation and gradual exhaustion of the Be- pool in soil.

Mobility of beryllium is extremely high in an acidified environment. This is the case of the LP catchment, where high input of deposited protons is only partly buffered by the acid bedrock. Sign of the balance of Be inputs and outputs (Table 8) is therefore negative through the whole studied time span. Owing to low weathering rate of the granite bedrock, strong output of Be is then supplied in particular from its inventory in the mineral soil. More comprehensive studies on the distribution of Be in the LP catchment were recently presented by Navrátil et al. (2002) and Skřivan et al. (1993, 1996 and 2000b).

Cadmium

Scarce data are available concerning the distribution of Cd in bedrock of the catchment. It seems that Cd is not abundant in neither of the bedrock types. The mean values calculated from 6 analyses show 0.21 ppm for the monzogranite and 0.07 ppm for syenogranite. Preliminary results obtained on the basis of the rock-forming minerals separation from fresh monzogranite indicate considerable enrichment of Cd in biotite, the only maffic phase. There is no direct evidence for isomorphous substitution of Cd in this mineral. Presence of some inclusions of the extraneous phase such as sulfides is possible. Exchangeable Cd in mica seems to be very labile. More than 60% of the total Cd content has been released into the solution during acid leaching of biotite at laboratory conditions (size fraction 0.16-0.25 mm, 0.01 M HNO_3, V/m = 10, duration 14 days, room temperature and atmospheric pressure, batch leaching). The total loss of Cd has been the highest among all the tested heavy metals (Minařík et al., 1997).

Contrary, the soils covering the granite in LP catchment are enriched in Cd approx. 10 times in comparison with the parent rock. It is obvious that this enrichment cannot result from the natural rock weathering. The soil contamination from external anthropogenic sources is the most probable explanation. Typical value of the total Cd content in the soil horizons into a depth of 1 m is approximately 1 ppm. On the other hand, both the total, and the acid leachable portion of Cd in soil are the highest in surface zone, which is rich in organic matter. This result indicates that the mobile part of Cd accumulates predominantly in the humic A horizon. This is in agreement with Levi-Minazi et al. (1976) and Anderson (1977), who found the Cd sorption in soils to be correlated with the soil organic matter content.

Recent mean annual Cd concentrations in the atmospheric precipitation on an open place are lower than those in stream water. The deposition fluxes of Cd have considerably decreased during the last four years (Table 6). It is well known that the anthropogenic flux of Cd into the global atmosphere exceeds the emissions from natural sources by almost one order (Nriagu, 1980). The contamination of atmosphere by Cd has a regional character. Coal combustion and, to a lesser extent, nonferrous metals smelting and refining are the major specific sources of Cd in the Czech Republic. The deposited Cd rich industrial aerosols, together with metabolic cycling by forest vegetation, are then the most probable reason for the enhanced concentrations of Cd in the topsoil.

The concentration of Cd in the surface water of the LP has been varying between 0.02-0.6 ?g.L^{-1} during the last 7 years. The total concentration of Cd significantly depends on pH changes and its concentration increases with increasing pH value of the streamwater water. The course of variations in the discharge- weighed mean annual concentrations of Cd throughout the past decade depend on the annual water discharge and consequently on its pH value.

Cadmium is more mobile than Pb, As or Cu (Table 8) and its balance in catchment depends on the amount of its atmospheric input and on the hydrological parameters of individual year. The higher the precipitation height of the year, the greater will be the output of Cd and the balance may then become negative.

Copper

Content of Cu is relatively low in bedrock of the catchment. The average concentration 9 ppm is identical for both main granite types. Partitioning of Cu between the individual rock-forming minerals indicates that nearly 50% of the total Cu content is associated with the biotite and more than 20% with accessories (Minařík et al., 2000). Copper in igneous rocks tends to form disseminated sulfide grains rather than to occur as a substituent in the lattices of main and accessory minerals (Wedepohl, 1963). Weak binding of Cu in parent rock, as well as in the biotite, has been confirmed by the experimental acid leaching (Minařík et al., 1997).

Soils in the catchment are abundant in Cu. Total Cu content throughout the soil profile varies from 11 to 38 ppm with average value around 25 ppm, in dependence on the amount of fine soil fraction and of organic matter. Content of the leachable Cu is the highest in uppermost humic A horizon. Combined effect of enhanced atmospheric input of Cu (originating in anthropogenic emissions), metabolic cycling of the essential Cu through literfall and throughfall, and formation of stable Cu complexes with organic matter are perhaps responsible for the Cu enrichment in the topsoil. The forms of Cu in soil are still far from being clearly understood. Strong evidences were observed, that most of the available copper is bound to organic matter (mainly with substances of low molecular weight). To a lesser extent it is adsorbed on clays and Fe- or Mn- oxyhydroxides (Mortensen, 1963; McLaren, Crawford, 1973; Jenne, 1977 etc.).

The mean annual deposition fluxes of Cu in the atmospheric deposition in an open place (Table 6) decreased (similarly to the fluxes of As, Be and Cd) between 1994 and 2000 from 1230 to 250 ug.m^{-2}.yr^{-1}. This trend repeatedly indicates the large Czech coal powerplants as substantial regional atmospheric pollution sources in the central Czech republic. The mostly anthropogenic origin of Cu in the atmosphere is again in agreement with Nriagu (1989), who estimated that 75% of the Cu emissions into the atmosphere originates from the anthropogenic sources such as smelters, power plants and incinerators.

Concentration of Cu in surface water of the LP has been varying in wide range from < 0.25 to 2.1 ug.L^{-1} during the period from 1994 to 2000. The gradual decrease of Cu in stream water is proportional to the increase of its pH values and to the decrease of Cu deposition fluxes. Temporal variations of the mean annual discharge- weighted Cu outputs depend mainly on the amount of the water discharge.

Balance of inputs and outputs of Cu in the catchment (Table 8) reveals copper as a conservative element and shows that up to 1999 approx. 90% of deposited Cu was retained in the catchment.

Lead

Lead is considerably enriched in parent rocks of the LP catchment. The arithmetical mean in monzogranite is nearly identical to that in syenogranite, 50 and 49 ppm, respectively. Analyses of the major rock - forming minerals separated from the monzogranite show the highest Pb content in K-feldspar. The other common silicate minerals found in this rock, in descending order of the lead content, are plagioclase, biotite and quartz. Contribution of quartz and accessory minerals to the total Pb content of the rock is negligible. It may be assumed, on the basis of mass balance of main constituents of the given rock, that approx. 80% of the total Pb in the rock matter is bound in K-feldspar and plagioclase. It seems that the release of Pb from feldspars is very slow during the rock weathering, as indicated by the acid leaching experiments (Minařík et al., 1997).

Due to increased content of Pb in parent rocks, soils are also enriched in Pb. Mean value of the total Pb content is 64 ppm in soil profile to the depth of 1 m, with maxima in clay abundant horizons. Approx. 20% of the total Pb content in soil is released by the acid leaching. Extractable amount of Pb is the highest in the humic A-horizon. Higher surface concentrations of the labile Pb species probably result from the atmospheric deposition of solid lead aerosol of vehicular origin.

General trend of the Pb deposition fluxes shows considerable decrease throughout the monitored time span (Table 6). This affirmative feature correlates with the sales of leaded gasoline in the Czech Republic (Skřivan et al., 2000a). On the other hand, the older data by Škoda et al. (1988) and Beneš (1994) show even higher values for the Czech Republic in the years preceding this study. The figures (Škoda et al. (1988) and Beneš (1994)) indicate that up to 500 mg of anthropogenic lead has been deposited onto each square meter of LP catchment since the beginning of the usage of the tetraalkyl lead compounds in vehicular traffic.

The lead concentration in the surface stream of the LP catchment is low. In fact, most of the primary data concerning Pb have been below the detection limit of analytical determination (0.5 ?g.L^{-1}) even in 2000, when the sample preconcentration was introduced (see the Table 7). Numbers in the Table 8 show strong retention of lead in soils of the catchment. Many others have repeatedly observed this feature. It is worthwhile to notice the paper of Johnson et al. (1995) who warns that the mobile anthropogenic Pb is being gradually transported downward through the soil profile into the mineral soil and that the potential for Pb pollution in drainage waters may be, therefore, greater than previously suspected.

Conclusions

Syenogranite and monzogranite were identified as the parent rocks in the experimental Lesni potok catchment. The bedrock represents the only natural source of studied trace contaminants (As, Be, Bd, Cu, and Pb) in the ecosystem. The rocks can be chemically classified as granites with low content of Ca. The bedrock is enriched in several trace elements, in the monzogranite are especially abundant As, B, Be, F, Pb, Sn and W. Geochemical reactivity of both the rock types is low. Due to its low buffering capacity, the bedrock is capable to neutralize the acid atmospheric deposition only incompletely. Soils developed on the granite bedrock are predominantly of a cambisol type. Their essential mineralogy includes quartz, kaolinite, illite, K-feldspar and plagioclase. Iron oxyhydroxides are forming within the soils only in minor amount. As a whole, soils contain enhanced amount of the same trace elements as the parent rocks. Distribution of studied contaminants throughout the soil profile reflects their dominant source and mobility under given conditions. Cu and Pb are enriched in the uppermost horizons, As and Cd are more or less evenly distributed in dependence on the content of clayey fraction and the content of highly mobile Be is increasing with depth.

Surface water draining the area is predominantly of a Ca-SO_4 type. Mean annual pH values of the surface stream varied from 4.8 to 5.5, mostly in dependence on the discharge. Moderate increase of the average pH values was observed throughout the study, in accordance with the increasing pH of the precipitation. Increasing mean pH value of the surface water is also causing gradual decrease of Be outputs. Shallow groundwater of the catchment with higher pH and extremely high Fe and Mn concentrations, confirming its low Eh, contains also high concentrations of As, but lower concentrations of the other contaminants.

Gradual decrease of the annual deposition fluxes of studied trace elements reflects the effects of coal burning power plants desulfurization in Czech Republic. Improving quality of the atmosphere is also reflected in growing mean annual pH values of the precipitation, from 4.1 in 1994 to 4.4 in 2000.

Mass balance of studied contaminants in the catchment shows decreasing anthropogenic atmospheric input of As, Cu and Pb. Inputs of Cd, and especially Be through atmospheric deposition are small. Beryllium is the only contaminant, which - owing to its high mobility in acidified environment - has strong and negative balance in the catchment. Loss of Be in the system is compensated at the expense of its inventory in soils.

Translated by T. Navrátil

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Minařík L., Skřivan P., Novák J.K., Fottová D., Navrátil T.: **Distribuce, cykly a vlivy vybraných anorganických kontaminantů na ekosystém povodí Lesního potoka v České republice.**

Biogeochemie některých antropogenních kontaminantů byla studována v povodí Lesního potoka ve středních Čechách.

Granitické horniny, které tvoří krystalické podloží v oblasti povodí jsou obohaceny arzénem, beryliem a olovem. Rovněž půda nad granitem (převážně kambisolového typu) má zvýšený obsah těchto prvků.

Atmosférický vstup As, Cu a Pb do povodí je značný na rozdíl od vstupu Be a Cd. Látkové bilance ukazují systematický pokles obsahu anorganických kontaminantů v atmosférických srážkách během sledovaného období 1994-2000. Je to především důsledkem snižováním emisí ze spalování uhlí a přechodu na bezolovnatý benzín v Čechách koncem 90. let dvacátého století.