

PARTITION OF BERYLLIUM AND SEVERAL OTHER TRACE ELEMENTS IN SURFACE WATERS

P. Skřivan¹, M. Šťastný², P. Kotková³, M. Burian¹

¹Geological Institute, Academy of Sciences of the Czech Republic, Prague, Czech Republic

²Institute of Rock Structure and Mechanics, Academy of Sciences of the Czech Republic, Prague, Czech Republic

³Czech University of Agriculture, Institute of Applied Ecology, Kostelec n. Č. lesy, Czech Republic

Changes in concentration of dissolved Be, together with As, Cd, Cu, Fe, Mn, Pb, and Zn, were studied in a system of acidified surface stream and its recipient, standing water of an artificial pond in central Bohemia. Samples of the pond sediment were analysed for the loosely bound fraction of these elements and the determined concentrations were correlated with the content of solid phases of the sediment which could be responsible for the fixation of studied elements. The most significant differences in the concentrations of elements of the two types of water were found in Be, Mn, and Fe, and they are ascribed to the changes in pH and oxidation state taking place in the system. Results of the correlation analysis suggest that the dissolved beryllium, which is of lithogenic origin in this region, is bound predominantly to the sediment organic matter, after the acidified stream water is mixed with the standing water of higher pH values. The studied system of surface waters with changing physical and chemical conditions can be therefore generally considered as an acid-base geochemical barrier in the exogenic cycle of beryllium.

beryllium; As; Cd; Cr; Cu; Fe; Mn; Pb; Zn; sediment; surface water; forms; pH; partition

INTRODUCTION

Impact of human activities on the biogeochemical cycle of beryllium has been studied above all with respect to the ecotoxicity of this trace element. The effects of coal burning on the atmospheric inputs of Be into the environment (Nriagu, Pacyna, 1988; Nriagu, 1990) are well known. Another important factor, however, strongly affects the intensity of Be cycling,

namely the acid atmospheric deposition. The influence of enhanced deposition rate of protons on the hydrolytic decomposition of bedrock was described by other authors (S k ř i v a n et al., 1989). In some cases it results in significantly elevated concentration of Be in acidified surface water (V e s e l ý et al., 1989), which introduces the question of the further fate of this toxic trace element in the aqueous environment.

The content of soluble forms of Be in surface water is determined by its bulk chemical composition, the concentration of F^- ions, and pH (playing the dominant role). Changing conditions in surface water, caused by various chemical and biological factors, may result in significant change of its pH, which should be immediately reflected in the distribution of beryllium between the liquid and solid phases. The place of the gradient of surface water pH could then be interpreted as a natural geochemical barrier of Be migration in this environment and elevated concentrations of this element should be found in the immobile phase of the system – in the corresponding fluvial sediments.

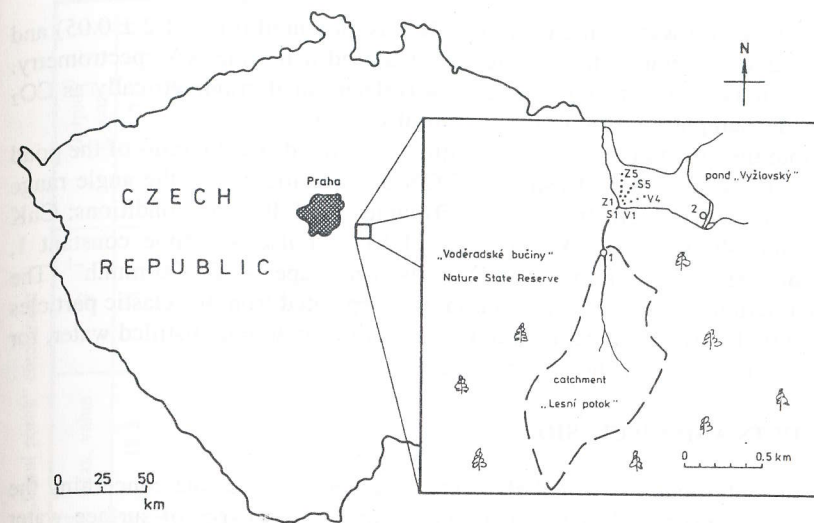
The aim of this work was to examine the mechanisms and effects of the geochemical barrier of the Be migration, which was supposed to occur in the mixing zone of a small acidified surface stream with more alkaline water of its recipient.

MATERIAL AND METHODS

Surface water

The geochemistry of Be in surface water was studied in a system of a small stream draining the „Lesní potok“ catchment, emptying into the pond „Vyžlovský“, adjacent to the Nature State Reserve „Voděradské bučiny“ region, approx. 30 km SE from the centre of Prague (S k ř i v a n et al., 1994). Sampling site of the stream is situated at the gauging station of the catchment, equipped with the Thomson weir and the staff gauge for the measurement of water level. Water of the pond was sampled at its sluice (see Fig. 1). The catchment „Lesní potok“ is completely forested (with prevailing beech and spruce), without any permanent inhabitants.

The surface water has been sampled since 1987 and the sampling procedure was adopted to its main purpose, which was the determination of dissolved forms of selected trace elements, including Be. The instant discharge, pH and temperature of water were measured together with water sampling. Collected water samples were immediately filtered through the nitrocellulose membrane filter (Sartorius, type 11306-47-N with pore size 0.45 μm), the filtrate was poured into the 100ml polyethylene bottle and stabilized with



1. Location of the study area

1 – sampling site of the surface stream, 2 – sampling site of the pond water V1–V4, S1–S5, Z1–Z5 – sites of the sediment sampling

diluted nitric acid (Fluka, analytical grade), to avoid the adsorption of studied cations on the walls of the sampling vessel. Temperature and pH of surface water were measured at the same time using the battery pH-meter (WTW, model pH-91). The samples were stored at 4 °C in a refrigerator until their analytical evaluation. Content of dissolved Be and other studied elements was determined by flame- and graphite furnace AA spectrometry (Varian, model SpectraAA 300).

Sediment

Samples of sediments were collected at the bottom of the pond Vyžlovský in an area adjacent to the mouth of the „Lesní potok“ brook (see Fig. 1). The material was sampled from the depth of 0–5 cm of the sediment. The samples were dried in a laboratory at room temperature in a flow box to avoid their contamination, crushed in an agate mortar, passed through the sieve (0.1 mm), and leached with diluted nitric acid (1 : 100, Fluka, analytical grade) at the ratio $V/m = 50$, and time of digestion $t = 40$ hours. The resulting suspension was then filtered through the membrane filter (the same parameters as in the

case of surface water), the resulting pH was measured ($\text{pH} = 1.2 \pm 0.05$) and the aliquot portion of the filtrate was analysed using the AA spectrometry. The content of organic carbon (C_{org}) was determined gravimetrically as CO_2 after the sample ignition in the stream of oxygene.

Both the qualitative and semiquantitative X-ray diffractograms of the pond sediments were obtained using a DRON 3 diffractograph in the angle range of $3\text{--}60^\circ 2\Theta$ (clay fraction $3\text{--}40^\circ 2\Theta$) under the following conditions: CuK radiation, 40 kV, 19 mA, sensitivity $1.10^3 \text{ impulses}\cdot\text{s}^{-1}$, time constant 1, goniometer shift $1^\circ\cdot\text{min}^{-1}$ for 2Θ , registering paper shift $600 \text{ mm}\cdot\text{h}^{-1}$. The clay fraction of the inorganic material was separated from the clastic particles of the rock forming minerals through the sedimentation in distilled water, for the detailed study of the clay minerals.

RESULTS AND DISCUSSION

Concentrations of studied elements, together with the data concerning the content of suspended matter, pH and the instant discharge of surface water at the weir closing the „Lesní potok“ catchment are summarized in Tab. I. Values of the annual output of the elements from the catchment, evaluated on the basis of data collected monthly at the Thomson weir, are presented, too. Systematical monitoring of chemical and physical parameters of the surface stream has been carried out since June 1993. Concentration of Pb was in all cases (with exception of one sample) below the detection limit of the employed analytical procedure (direct determination by graphite furnace AAS).

Chemical data presented in Tab. I show that the stream water contains in some cases considerable concentrations of minor and trace elements, above all of Be, Mn, and under some circumstances of Fe. High concentrations of Be reflect the elevated content of this element in the bedrock (Minařík, 1975; Vejnar, 1974). Beryllium is mobilized through the intensified hydrolytic alteration of the Říčany granite and through the leaching of the corresponding saprolite and soil, caused by the effect of the acid atmospheric deposition (Sklívan et al., 1989). Elevated concentration of Mn is typical in headwaters of the forested areas and it is caused to a certain extent by the metabolic activity of the tree vegetation (Kotková et al., 1996). Broad range of concentrations of dissolved Fe reflects the dominant influence of the instant redox-potential values of surface water.

Low content of suspended matter in the stream water, together with high concentrations of dissolved Be are the reason, why only 1% of beryllium is transported under such conditions in the solid form (Tab. I., cf. the output of dissolved Be with its output in the suspended matter).

I. Content of studied elements and further data concerning the surface discharge - „Lesní potok“ catchment

Parameter	Units	Element	Mean value	Min. value	Max. value	N	Output ¹⁾ g·year ⁻¹
Concentration	$\mu\text{g}\cdot\text{L}^{-1}$	As	3.13	<0.5	18.2	11	275
		Be	11.97	2.0	24.0	39	1 050
		Cd	0.36	<0.1	0.7	37	32
		Cr	0.83	<0.5	1.0	5	73
		Cu	1.35	<0.5	16.6	40	118
		Fe	494.9	40	5 900	30	43 430
		Mn	287.1	70	1 760	31	25 195
		Pb	<0.5	<0.5	(2.3)	27	<44
		Zn	25.3	12.0	100	31	2 220
		pH	units	pH	4.894 ²⁾	4.18	8.04
Discharge	$\text{L}\cdot\text{s}^{-1}$		2.67	0.02	8.99	13	$8.77 \times 10^7 \text{ L}\cdot\text{year}^{-1}$
Suspended matter	$\text{mg}\cdot\text{L}^{-1}$		5.3	0.9	16.7	11	$4.65 \times 10^5 \text{ g}\cdot\text{year}^{-1}$
Be in susp. ³⁾	ppm	Be	24.6	-	-	1	$11.4 \text{ g}\cdot\text{year}^{-1}$

¹⁾ since June 1993 till May 1994, evaluated on the basis of mean monthly values, taking into account the surface discharge

²⁾ evaluated as a mean value from the individual values for the concentration of H^+ ions

³⁾ analysis of the representative sample of biogenic/chemogenic sediment, collected at the weir closing the catchment, which reflects the chemistry of the suspended matter

Content of discussed elements in water of the recipient of the stream water from the catchment „Lesní potok“, in the pond Vyžlovský, is summarized in Tab. II (values for Cr, presented in Tab. I, were not available). Significantly lower concentrations were found in Be, Fe, and Mn (and to a certain extent also in Zn and Cd). The drop in Be (and possibly also Zn, Cd) concentration in the pond water is probably connected with the drastic change in pH of both the types of water (cf. Tabs. I and II). Under such conditions, the partition of these elements into the individual dissolved forms (complexes) is sharply changing (Veselý et al., 1989), resulting in changes of their adsorption characteristics towards the corresponding solid phase.

Considerably higher pH of the pond water (7.79) is evidently resulting from the different kind of land use (agriculture, urbanised areas) in the headwater area of the Jevanský brook (the main water resource of the pond Vyžlovský), and with the biological activities proceeding in the stagnant water of the artificial reservoir.

Lower concentrations of Fe and Mn reflect the redox equilibria in the standing pond water, whose surface layers are affected by the contact with the atmospheric oxygen. On the other hand, higher concentration of Cu and Pb (elements which are less susceptible to the changes in pH) in the pond water could reflect the direct anthropogenic impacts: In Cu the adjacent urbanised areas (villages of Louňovice and Vyžlovka), and in Pb the vehicular immissions from the neighbouring road Praha–Kutná Hora.

Tab. III presents the content of forms of selected minor and trace elements of the sediment samples, which are soluble under the above mentioned ex-

II. Content of studied elements in the pond water (ppb), its pH (units)

Element	Concentration of dissolved forms ($\mu\text{g.L}^{-1}$)			
	mean	min.	max.	N
As	3.44	<1.0	10.0	6
Be	<0.5	<0.5	<0.5	6
Cd	0.12	<0.01	0.56	6
Cu	2.81	0.7	5.0	6
Fe	37.0	<10.0	69.0	6
Mn	90.4	<10.0	210.0	12
Pb	1.52	0.6	7.9	10
Zn	11.3	<6.0	47.0	9
pH	7.79	6.76	9.47	14

perimental conditions, together with the content of organic carbon in sediment. Total amount of organic matter, one of the possible phases responsible for the trace element fixation, can be simply evaluated according to Dean (1974), as a value of analytical concentration of C_{org} multiplied by a constant ≈ 2.13 . Elevated concentrations of soluble As, Be, Cd, together with Fe (and Mn) attest that a considerable portion of those elements is bound in recently formed solid phases of relatively low stability.

The data presented in Tab. III do not reflect in most cases the parameter of sample site position, with exception of the content of acid soluble Be, and the content of C_{org} . The significance of this parameter was assessed by means of the Spearman correlation coefficient (Anděl, 1978). Tested was the sequence of the individual quantities in the three sets of localities, V, S, and Z (see Fig 1).

III. Content of forms of studied elements leachable in diluted nitric acid, together with the content of organic matter, values of Spearman correlation coefficient (CC) and significance level (α) evaluating the significance of the position of sampling site

Locality	Content of acid soluble forms of elements in the sediment samples (ppm)									C_{org} (%)
	As	Be	Cd	Cr	Cu	Fe	Mn	Pb	Zn	
V1	4.15	6.2	1.29	1.05	4.2	2 828	309	25	38	7.19
V2	3.54	5.3	1.17	1.10	5.0	2 875	336	25	38	5.55
V3	8.08	5.5	1.83	1.25	6.6	4 278	429	30	55	5.79
V4	4.15	4.5	1.63	1.31	6.9	3 542	295	25	60	3.82
S1	4.88	8.8	1.45	1.46	6.2	3 165	306	33	49	7.25
S2	7.33	8.9	1.76	1.54	7.3	4 729	305	30	64	7.29
S3	3.28	4.9	1.59	1.26	4.0	3 197	263	24	51	4.17
S4	4.17	4.8	1.47	1.30	5.5	3 548	238	28	61	3.57
S5	3.55	4.5	1.63	1.39	6.2	3 570	254	21	61	2.75
Z1	4.86	5.2	1.18	0.75	4.1	2 226	250	19	35	5.84
Z2	5.00	8.0	1.82	1.27	8.5	3 915	379	33	52	7.67
Z3	3.86	4.5	1.12	0.99	6.3	3 196	757	23	35	6.19
Z4	1.96	2.1	0.46	0.88	5.3	2 404	430	11	25	2.88
Z5	1.87	1.5	0.23	0.86	3.9	2 092	259	7.9	19	1.44
CC %	-51	-84	-8	-5	-8	+21	-24	-58	+7	-76
α	0.0686	0.0025	0.7796	0.8692	0.7651	0.4488	0.3965	0.0359	0.7992	0.0064

The content of mineral phases in the studied sediment samples is presented in Tab. IV. The identified minerals represent the fraction of solid phase with developed crystal structures and their sum is valid for this inorganic portion of solid phase only. Major components in the form of clastic material represent the typical rock forming minerals of the bedrock (the Říčany granite). Presence of amphibole is rather surprising, but it corresponds to the rock type underlying the northern part of the Jevanský brook watershed, which is of tonalitic character. Surprisingly, no biotite (and/or muscovite), which are the typical rock forming minerals of the Říčany granite, were found. Both these minerals were evidently transformed under strongly acidic conditions of the forest soils into the layered secondary clay minerals. Content of these minerals, which are present in minor quantities only, was determined in the silt fraction of these minerals, separated by sedimentation.

No parameter involved in the Tab. IV exhibits any dependence on the position of its locality. The distribution of mineral phases in the sediment probably results from the morphology of the pond bottom and/or from the hydrodynamic situation at the individual sampling localities.

There are two ways to resolve the question of the speciation of trace elements in the sediment (to assess which solid phases of the sediment are responsible for the attachment of its trace elements):

- The sequential extraction procedure (Tessier et al., 1979), which employs selective extraction agents for the distinction of forms of elements bound through the ion exchange, in carbonates, onto the oxohydroxides of Fe and Mn, in the organic matter, in the crystal lattice of rock forming minerals or in the accessory minerals.
- The correlation analysis of the content of (soluble portion of) trace elements with the selected solid phases which could act as the fixing agents for these elements.

The previous frequently applied method was elaborated to a number of varieties, but it has several disadvantages: 1) it is rather time-consuming; 2) in comparison with the latter method - expensive; 3) it provides in some cases distorted results.

The latter method, as a rule, enables to distinguish a limited number of forms of the studied elements only, and it is not effective in the determination of ratios in which are the studied elements distributed between the individual forms.

In spite of its limitations, correlation analysis was applied in our study to assess the possible active phases responsible for the fixation of studied trace elements and to evaluate the mechanisms which could be involved in this process.

Tab. V presents the statistically significant results of the correlation analysis of the leachable portion of studied elements with selected solid phases.

Respecting the low number of data available and breaking the assumption of normality, the Spearman correlation coefficient was employed for the correlation analysis. All phases which could be responsible for the fixation of the dissolved forms of elements were examined: organic matter (C_{org}), Fe and Mn hydroxides, clay minerals kaolinite, illite, and smectite, and the secondary crystalline ferric phase, the mineral lepidocrocite. The content of active Fe-hydroxides, which are of amorphous character and are supposed to be formed recently in the mixing zone of the two types of surface water, is represented by the data presented for Fe in Tab. III.

To discuss the results of correlation analysis, it is necessary to assess the possible meaningful relations between the studied elements and the solid phases which could have been responsible for their retention and fixation. The determined amount of dissolved elements (Tab. III) represents their forms which entered the solution through dissolution, desorption, and ion-exchange processes, mediated by the diluted nitric acid. On the other hand, the portion of elements present in the crystal lattice of the mineral phases deter-

IV. Semiquantitative phase analysis of the inorganic portion of the material

Locality	Mineral content (%)							
	Q	plg	ort	amp	I	K	S	lep
V1	38	31	23	0.80	1.60	0.80		3.15
V2	41	35	17	0.85	2.50	0.85		3.30
V3	55	27	13		2.20	1.60		1.10
V4	59	19	17		2.40	1.20		1.70
S1	55	14	21	3.30	3.30	1.10	1.10	1.00
S2	63	14	14	3.80	1.30	0.75	0.75	2.50
S3	39	31	27		0.80		0.80	1.60
S4	44	26	25	0.90		0.30		2.65
S5	54	25	15	1.05	3.25	0.65	0.45	1.05
Z1	48	34	14					0.40
Z2	51	33	9		1.45	1.45	1.45	2.05
Z3	39	33	22		2.35	0.80		3.10
Z4	37	30	30	0.50	0.90			1.45
Z5	43	35	18		1.70	0.90		1.70

Q - quartz, plg - plagioclase, ort - orthoclase (K-feldspar), amp - amphibole, I - illite, K - kaolinite, S - smectite, lep - lepidocrocite

mined in the sediment, which are not attacked by the applied extractant solution, is without any significance in the correlation analysis.

Amorphous oxohydroxides of Fe and Mn, organic matter, and layered clay minerals are probably the only phases which could act as adsorbent or, more generally, as agents promoting the fixation of the studied trace elements which enter the system originally in their dissolved forms.

It is also necessary to distinguish the true primary correlations between the carrier phase and the trace element from the secondary dependent correlations between the individual trace elements.

Data presented in the Tab. V can be divided into three groups, according to the value of the significance level:

- the best correlations with significance level $\alpha < 0.01$
- good ones with significance level $0.05 > \alpha > 0.01$
- acceptable correlations with $0.1 > \alpha > 0.05$.

Two groups of parameters with the best correlation level can be selected from the Tab. V:

1. Correlation of dissolved Fe with dissolved Zn, Cd, and Cr.
2. Correlation of C_{org} with dissolved Be (and As).

The first group can be supplied with other fair correlations of Fe with As and Pb, and the second one of C_{org} with Pb. Other pairs with a high correlation level, Zn-Cd, Cr-Zn, As-Be, Be-Pb, As-Pb, are not independent, as they can be derived from the two above mentioned main groups of correlation.

On the other hand, no correlation, at least on acceptable level, was found in any examined parameter with the dissolved Mn, and with the determined concentrations of the minerals lepidocrocite and illite. Surprisingly, poor results in the correlation analysis were obtained also for the dissolved forms of Cu.

The secondary mineral lepidocrocite (FeOOH), with developed crystalline structure, supposedly remained intact during the acid extraction of the sediment samples, so that no trace elements which could be present in its structure were leached. Origin of the dissolved iron, determined in the solution after the acid digestion of the sediment, have to be found in the amorphous surface - active oxohydroxides which are forming as a chemogenic solid products of the oxidation of dissolved Fe(II).

Correlations with clay minerals, as the possible phases with the ability to bond the dissolved species through adsorption and/or ion-exchange, are generally of poor quality, probably owing to the low content of these minerals in the studied bottom sediment. The best results were obtained surprisingly in smectites, which are the clay minerals with the lowest content in the

V. Results of the correlation analysis using the Spearman correlation coefficient. Upper values represent the individual correlations (%), lower ones depict the significance level α . Empty fields represent low correlation of the parameters (with significance level > 0.1).

Parameter														
	As													
Be	77 0.0059	Be												
			Cd											
Cd	71 0.0102	54 0.0528		Cd										
					Cr									
Cr				70 0.0116		Cr								
							Cu							
Cu	67 0.0161			68 0.0137	62 0.0253			Cu						
									Fe					
Fe	62 0.0243			90 0.0012	75 0.0066	79 0.0043				Fe				
											Mn			
Mn												Mn		
													Pb	
Pb	79 0.0044	82 0.0030	69 0.0124	68 0.0140	66 0.0179	66 0.0167								Pb
Zn	55 0.0462		85 0.0021	87 0.0018	62 0.0261	89 0.0013					61 0.0289			Zn
C _{org}	72 0.0099	87 0.0019											69 0.0300	
														C _{org}
illite														
														I
kaolinite					52 0.0631						55 0.0467			60 0.0300
smectite		53 0.0572	50 0.0700	63 0.0237							51 0.0684			
lepidocrocite														

examined material. This finding may correspond to the high sorption capacity of this group of clay minerals, caused by their expanding three-layer structures. From this point of view, also their ability to accept organic compounds of polar or ionic character between their unit layers is significant.

Respective the explanation of changes in the speciation of studied elements, proceeding as a result of changing physico-chemical conditions of the system after the stream water is mixed with that of the pond, only Be, Fe, and Mn are in the focus of our interest, as the others do not change so significantly their distribution between the solid and liquid phases. (Incidentally, source of the major part of all the three elements has to be found in the bedrock.) The decrease in the concentration of Fe and Mn evidently follows from the oxidation of their bivalent forms and the loss of solubility of the higher oxidation state of these metals or from their intensified adsorption in more alkaline environment.

The importance of the hydrated metal oxide (Fe, Mn, Al) coatings and of organic matter in the surface water particulates for bonding the trace elements (including Be) is well known and discussed in many papers and monographs (Stumm, Morgan, 1981; Salomons, Förstner, 1984; Eisma 1993; and others), even though the dissolved organic matter is also important in the solubility control of the trace elements through the complexation reactions (Stumm, Morgan, 1981; Bourg, Darmendrail, 1992).

Results from the sequential extraction procedures performed with fluvial sediments confirm the significance of Fe and Mn hydrated oxides and of organic matter in binding the complex dissolved compounds of Zn, Co, Ni, Cu, Cr in this material. Borovec (1993) discusses the geochemical position of Ag, Be, and Mo in the silt fraction of sediments of the Labe river on the basis of the six-step sequential extraction procedure. This author found that Be was bound in all the determined phases (carbonaceous, reducible, oxidizable sulfidic/organic, residual), with exception of the form bonded through the ion-exchange. Another paper of this author (Borovec et al., 1994) describes the results of the sequential extraction of Be and other more elements (Co, Ni, Cr, Zn) in material of the same type. These results indicate that Co, Cr, Ni, and Be are bonded predominantly in the reducible and oxidizable phases (which do not include the humic material, resistant to the attack of diluted nitric acid combined with 30% H₂O₂). Surprisingly, Zn was found to be primarily concentrated in the adsorbed and/or carbonaceous forms.

Conclusions of these authors generally confirm our results of the correlation analysis, in spite that the overall character and mineral composition of both the studied sediments may differ with respect to differing bedrock and to the extent and types of anthropogenic impacts. Beryllium, which is trans-

ported in the acidified surface waters of the forested areas into the pond water almost exclusively in the dissolved forms, as BeF⁺ or Be(OH)₂ (Veselý et al., 1989; Borovec, 1993), appears to become in the standing water loosely bound to organic matter, which promotes – through its hydrophilic functional groups – the adsorption onto the newly formed and reactive voluminous inorganic coatings of Fe and Mn oxohydroxides with high specific surface which are formed in the more alkaline and oxidized water of the pond.

CONCLUSIONS

Distribution of beryllium between the liquid and solid phases in surface water is significantly affected by its pH value. Acidified surface stream draining the forested area with granitic bedrock, with mean pH = 4.894 and mean concentration of dissolved Be = 11.7 µg.L⁻¹, transports 99% of this element in soluble forms. After the stream water is mixed with the standing water of the pond with water of mean pH = 7.79, dissolved Be becomes bound to the particulate matter and enters the sediments. Concentration of residual dissolved Be drops to values <0.5 µg.L⁻¹. Results of the correlation analysis indicate that particularly the organic matter is responsible for beryllium binding with the solid phase. Distribution of other studied trace elements (As, Cd, Cu, Pb, Zn) between the solid and liquid phases is not so strongly affected by the changes in the water pH, which is indicated by the similar concentrations of these elements in both types of water of the studied system.

Acknowledgments

This study was funded by the Grants No. 204/93/0276 and 205/93/0717 of the Grant Agency of the Czech Republic. Assistance in the field was provided by Marek Vach from the Institute of Applied Ecology, Czech Agricultural University, in the laboratory by Jana Sychrovská. We wish to thank to Eva Melichárková from the Inst. of Structure and Mechanics of Rocks, AS CR, for the analyses of C_{org}.

References

- ANDĚL, J.: Mathematical Statistics. Praha, SNTL 1979 (in Czech).
- BOROVEC, Z.: Partitioning of silver, beryllium and molybdenum among chemical fractions in the sediments from the Labe (Elbe) river in central Bohemia, Czech Republic. *GeoJournal*, 29, 1993: 359-364.
- BOROVEC, Z. – TOLAR, V. – MRÁZ, L.: The state of accumulation and source relations of Co, Ni, Cr, Be, and Zn in silt-clay sediments of the Labe river. *Geol. Carp. – Ser. Clays*, 45, 1994: 3-9.

- BOURG, A. C. M. – DARMENDRAIL, D.: Effect of dissolved organic matter and pH on the migration of zinc through river bank sediments. *Environ. Technol.*, 13, 1992: 695–700.
- DEAN, W. E., Jr.: Determination of carbonate and organic matter in calcareous sediments and sedimentary rocks by loss on ignition: Comparison with other methods. *J. Sedim. Petrol.*, 44, 1974: 242–248.
- EISMA, D.: *Suspended matter in the aquatic environment*. Berlin, Springer 1993.
- KOTKOVÁ, P. – SKŘIVAN, P. – BURIAN, M.: Fluxes of selected trace elements in a natural beech forest – a comparison of atmospheric deposition with throughfall. *Environ. Ecol. Statist.*, 1996 (in press).
- MINAŘÍK, L.: Distribution of elements in the main rock-forming plutonic minerals. *Čas. Mineral. Geol.*, 20, 1975: 185–199.
- NRIAGU, J. O.: Global metal pollution. *Environment*, 32, 1990: 7–33.
- NRIAGU, J. O. – PACYNA, J. M.: Quantitative assessment of worldwide contamination of air, water, and soils by trace metals. *Nature*, 333, 1988: 134–139.
- SALOMONS, W. – FÖRSTNER, U.: *Metals in the hydrocycle*. Berlin, Springer 1984.
- SKŘIVAN, P. – ARTNER, P. – MARTIŠ, M.: Trace elements in stream sediments of two small forested catchments. *Proc. Int. Conf. Headwater Control*, Prague, 1989: 262–266.
- SKŘIVAN, P. – MINAŘÍK, L. – BURIAN, M. – VACH, M.: Cycling of beryllium in the environment under anthropogenic impact. *Scientia Agric. Bohem.*, 25, 1994: 69–79.
- STUMM, W. – MORGAN, J. J.: *Aquatic chemistry*. New York, J. Wiley 1981.
- TESSIER, A. – CAMPBELL, P. G. C. – BISSON, M.: Sequential extraction procedure for the speciation of particulate trace metals. *Anal. Chem.*, 51, 1979: 844–851.
- VEJNAR, Z.: Trace elements in rocks of the Central Bohemian Pluton. *Věstník ÚÚG Praha*, 49, 1974: 159–165.
- VESELÝ, J. – BENEŠ, P. – ŠEVČÍK, K.: Occurrence and speciation of beryllium in acidified freshwaters. *Water Res.*, 23, 1989: 711–717.

Received for publication on February 15, 1996

SKŘIVAN, P. – ŠTASTNÝ, M. – KOTKOVÁ, P. – BURIAN, M. (Geologický ústav AV ČR, Praha; Ústav struktury a mechaniky hornin AV ČR, Praha; Česká zemědělská univerzita, Institut aplikované ekologie, Kostelec n. Č. lesy, Česká republika):

Distribuce berylia a několika dalších stopových prvků v povrchových vodách. *Scientia Agric. Bohem.*, 27, 1996 (2): 131–145.

V práci jsou prezentovány a diskutovány výsledky studia změn v distribuci vybraných minoritních a stopových prvků (MSP) – Be, As, Cd, Cu, Fe, Mn, Pb, Zn – mezi kapalnou a tuhou fází (povrchovou vodou a korespondujícím sedimentem) v systému acidifikovaný povrchový tok – umělá vodní nádrž (rybník). Ke studiu posloužil drobný vodní tok (Lesní potok v SPR „Voděradské bučiny“) na Černokostecku, ústící do Vyžlovského rybníka (obr. 1). Vzorky sedimentů tohoto rybníka, odebrané v době jeho vypuštění v roce 1993, byly podrobeny loužení zředěnou kyselinou dusičnou pro stanovení obsahu labilně vázaných forem studovaných prvků. Zjištěné hodnoty

byly korelovány s obsahem tuhých fází, potenciálně způsobujících fixaci těchto prvků v sedimentu.

Výsledky korelační analýzy ukázaly, že beryllium je v rybničním sedimentu přednostně vázáno v organické hmotě. Primárním zdrojem tohoto toxického stopového prvku jsou lokální podložní horniny (říčanský granit), z nichž je Be mobilizováno působením kyselé atmosférické depozice (Skřivan et al., 1989). Výsledky studia ukázaly, že 99 % Be je v tomto povrchovém toku transportováno v rozpustných formách o průměrné koncentraci 11,7 $\mu\text{g Be}\cdot\text{L}^{-1}$. K následné fixaci Be v sedimentu dochází po smísení kyselá vody povrchového toku (průměrné pH = 4.894) se stagnující vodou o vyšším pH (7,79), kde koncentrace rozpuštěného Be klesají na hodnotu menší než 0.5 $\mu\text{g Be}\cdot\text{L}^{-1}$. Studovaný systém povrchových vod proto může být považován za příklad působení acidobázické geochemické bariéry v exogenním cyklu berylia.

Nejvýraznější rozdíly v koncentraci rozpuštěných forem sledovaných MSP v obou typech vody (acidifikovaný povrchový tok – stagnující rybniční voda) byly nalezeny u Be, Mn a Fe, významné rozdíly byly nalezeny také u Zn, Cd, Cu a Pb. Nižší koncentrace v rybniční vodě jsou přičítány rozdílným hodnotám pH (Be, Zn, Cd) a Eh (Mn, Fe) u obou typů vod. Vyšší koncentrace (u Cu, Pb) jsou vysvětlovány přímou antropogenní kontaminací z urbanizovaných oblastí (Cu) a vehikulárními imisemi (Pb) z frekventované silnice 3. třídy Praha–Kutná Hora.

beryllium; As; Cd; Cr; Cu; Fe; Mn; Pb; Zn; sediment; povrchová voda; formy; pH; distribuce

Contact Address:

Doc. Ing. Petr Skřivan, CSc., Geologický ústav AV ČR, Rozvojová 135, 165 00 Praha, Česká republika, tel.: 02/24 31 14 21, fax: 02/24 31 15 78