CYCLING OF BERYLLIUM IN THE ENVIRONMENT UNDER ANTHROPOGENIC IMPACT

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Beryllium content and geochemical position in bedrock, surface water and atmospheric deposition was studied in an experimental catchment „Lesní potok" in the region with the Říčany granite as an underlying rock. Elevated content of Be was found in the rock samples, which will be employed for further study of the Be position in the rock-forming minerals and accessories. Study of the bulk chemistry of surface water of the catchment revealed significantly elevated concentrations of Be, caused by low pH values and high content of F^- ions in water. Low content of Be in the cumulative samples of atmospheric deposition confirmed the insignificance of this input for the Be cycling in the study area. The study of the trace element chemistry (including Be) of forest canopy throughfall has verified the role of physical and physiological mechanisms for the extention of their cycling.

beryllium; cycle; environment; catchment; deposition; surface stream; bedrock; mobilization

Beryllium is a typical lithophile trace element with average abundancy in the Earth's continental crust of 3.0 ppm (Krauskopf, 1979) with higher concentrations in acid igneous rocks. Data on the Be content in the sedimentary rocks are not so plentiful as they are for magmatic rocks (Wedepohl, 1969). Higher concentrations of Be (lower tens of ~~%~~) are found in clayey materials with higher content of iron. ppm

From the point of view of Be inputs into the environment, its high content is significant in some types of coal. According to Wedepohl (1969), majority of coals contain *x* . 1 to *x* . 10 ppm of Be, but Bouška (1981), on the other hand, reports Be concentrations in coal ash from the Most region (North Bohemian coal basin) in the range 0.7 to 990 ppm (with mean value 87 ppm), and in that of the Sokolov lignite basin 2 to 2 330 ppm (mean value 180 ppm).

In the course of weathering beryllium enters the surface and ground waters as one of their easily mobile chemical components. The dissolved forms of Be are highly sensitive to the pH of water - uncontaminated waters of neutral pH contain usually less than 0.1 ppb Be, while waters, pH of which is affected by the acid atmospheric deposition, exhibit Be content at least by one order higher (Veselý et al., 1989).

Speciation of Be in surface waters depends on their bulk chemical composition. In waters with low pH value it is associated with organic matter of MW 1 000 to 10 000. Dissolved Be in this case forms organic complexes or it is present as free Be^{2+} ions. Formation of the complex $[BeF^{+}]$ becomes significant in water with higher (neutral) pH, but it is (especially in acidified water) less stable than the complexes of aluminum, $[AlF^{2+}]$ and $[AlF_2^{+}]$ (Veselý et al., 1989). Beryllium migrates, according to Borovec (1993), in surface water of neutral pH, in the form of dissolved $[Be(OH)_2]$ or as $[Be(OH)^{+}]$.

Remarkable and unique input of beryllium into the environment - of its radio-nuclide ^{7}Be (with the decay half-time $T_{1/2} = 53.3$ d.) - is caused by the extraterrestrial sources of nuclei of mass 56 (Ni, Fe, Co) which absorb neutrons and protons of the primary component of cosmic-rays to liberate the nuclei of light elements with relatively long half-time. These nuclear reactions become more significant during extraordinary cosmologic events such as the supernova outburst, which occurred last on the 23rd Feb. 1987 (Supernova SN 1987 A) (Papastefanou, 1991).

Recent enhancement and acceleration of the Be cycle is promoted primarily by its additional anthropogenic inputs into the environment and through the secondary effect of the Be mobilization in the course of accelerated hydrolysis of bedrock by acid atmospheric deposition. The first mentioned mechanism is caused mostly by the burning of fossil fuels, resulting in vast emissions of fly ash with often high concentrations of toxic trace elements, including beryllium.

The acid atmospheric deposition resulting from the enhanced anthropogenic emissions of SO_2 and NO_x promotes the accelerated chemical weathering of rocks. Considerable portion of trace elements present as accessories in the rock-forming minerals, including beryllium, enters the resulting solutions and together with them the ground- and surface waters. The increase in Be concentrations in surface water is strongly dependent on its pH. In forested areas with the granitic bedrock (or another rocks high in SiO_2) of poor buffering capacity the pH of surface water often remains well below the neutral value and dissolved Be reaches concentrations exceeding the permitted limit for this kind of water. The mass-balance of input through total atmospheric deposition and output through surface water discharge performed in such type of forested catchment has excluded the possibility of the atmospheric Be as its main source (Skřivan et al., 1989; Skřivan, Jonášová, 1990).

The main objective of this work was to obtain more precise data about the Be concentrations in principal components and fluxes of the environment - in rocks, surface water and atmospheric deposition. The study has been focused on the following problems:

- to evaluate the amount and forms of Be in surface water and in cumulative samples of atmospheric deposition
- to evaluate the content of Be in the underlying rock and in its main rock forming minerals
- to find out the correlation of dissolved forms of Be in surface water with its pH and with concentrations of significant complexing anions.

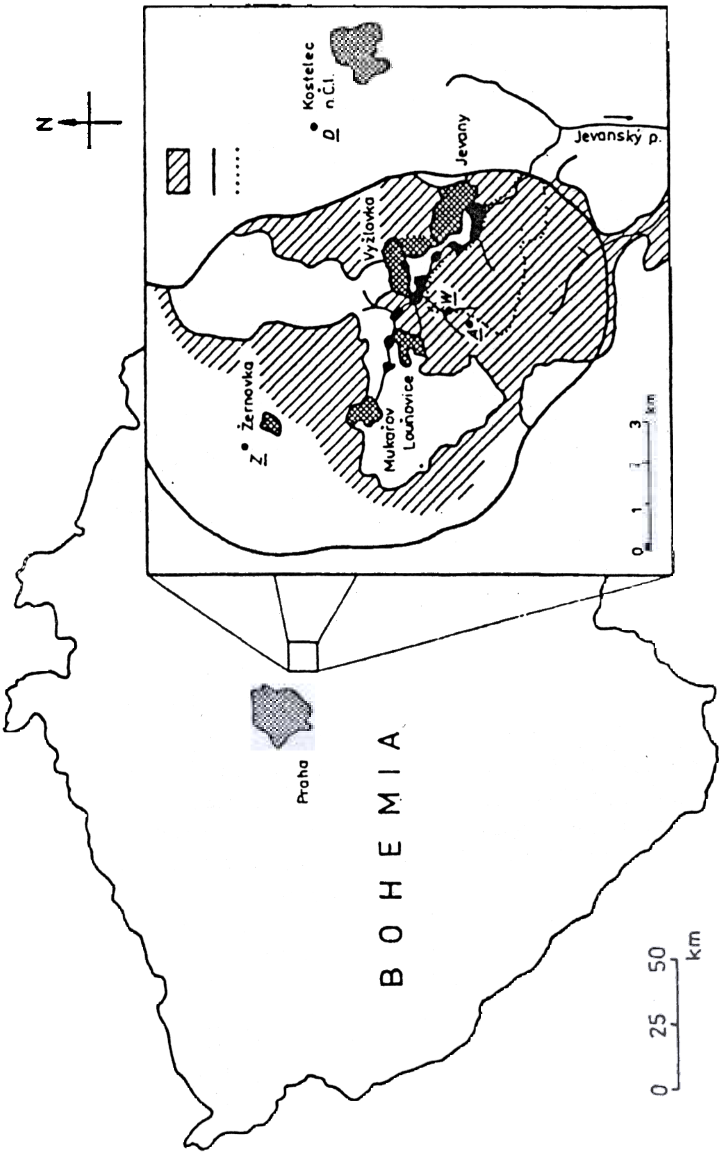
EXPERIMENTAL

The complex study of geochemistry of beryllium in the environment has been performed in the upper part of the Jevanský brook watershed with the underlying rock of Říčany granite. Majority of the field work was performed in the experimental catchment „Lesní potok" brook (Minařík, Houdková, 1986; Skřivan et al., 1988, 1989; Skřivan, Jonášová, 1990).

Rock samples were collected in a small abandoned quarry *W* from the watershed (see loc. <u>*A*</u> on Fig. 1) and in a large quarry which was in operation up to the last year, NW from the village Žernovka (loc. <u>*Z*</u> on Fig. 1), as the material from locality <u>*A*</u> was moderately weathered. Both samples, in weight cca. 10 kg, were collected for the evaluation of bulk chemical composition and for the separation of main mineral components, their chemical analyses and for further laboratory leaching experiments.

Samples of surface water were collected at the closing profile (see <u>*W*</u> on Fig. 1) equipped with a limnigraph and a Thomson overflow. The samples were immediately filtered through a membrane filter (-0.45 μm) and stabilized with diluted HNO_3, so that they represent the sum of the dissolved forms of Be. The sampling and stabilisation of water are described in detail elsewhere (Skřivan et al., 1988).

The extent of the inputs of Be and other elements through atmospheric deposition was studied by sampling both the total atmospheric deposition (wet and dry, which represents the gravitational deposition and the washing-out effect of the precipitation), and the throughfall, which provides informa-



1. Map of the study area with sampling localities depicted

tion about the influence of the content of pollutants in the near-surface layer of the atmosphere.

Cumulative samples of both the atmospheric deposition and the forest canopy throughfall were collected monthly at the locality Truba (see *D* on Fig. 1.) using modified Voss samplers. Small amount of diluted HNO_3 was inserted into the bottle for sampling total atmospheric deposition to avoid adsorption of ionic forms of trace elements onto its walls. At the end of the sampling period the aliquot of the throughfall water was acidified with diluted HNO_3 and after 24 hrs. both types of samples were membrane filtered (-0.45 µm) so that the concentrations of elements in the solution represent the sum of their dissolved forms and the forms weakly bound to the solid particles of the deposition. The procedures of collecting the samples and their further processing were described by Skřivan and Vach (in press).

RESULTS AND DISCUSSION

The bulk chemical composition of the rock samples, together with the data published previously by Minařík and Houdková (1986) are summarized in Tab. I. Tab. II shows the contents of selected minor and trace elements.

The parent rock material is formed by the Říčany granite. It represents a massive rock of light grey colour of porphyric texture, with equigranular groundmass of average grain size 3 mm. According to the results of numerous planimetric analyses (Palivcová, 1965) the average modal composition is as follows: quartz 28%, K-feldspar 29%, plagioclase (16% An) 35%, and biotite 7%. As minor components are present muscovite and sometimes tourmaline. Apatite, zircon, sphene, rutile and (scarsely) cassiterite are present as accessories only.

Geochemically, it is a typical tin-bearing granite containing a considerable share of volatiles. It displays elevated content of Sn, Pb, Be, F, B, W, and Nb. No lateral variation of Be content was observed in this rock material. Average contents of beryllium in 33 samples were 13 ppm, ranging < 4 to 24 ppm (Němec, 1978).

The contents of selected trace elements in both types of the atmospheric deposition are presented in Tab. III. Samples collected in open landscape (abbreviated here as CAD) can serve for the evaluation of the atmospheric input of studied elements into the catchment. In previous work (Skřivan, Jonášová, 1990) data from the sampling station at Sojovice of the Czech Hydrometeorological Institute were mostly employed for the rough balance of inputs and outputs. This station is situated approx. 30 km NW

I. Bulk chemical composition (oxides) of the Říčany granite. Mean values according to Mинařík and Houdková (1986), numbers in columns A and Z represent material sampled in 1993

Element (oxide)	Contents (%)				
	min.	max.	arithmetical mean	A	Z
SiO_2	67.85	71.80	69.59	70.37	71.50
TiO_2	0.08	0.44	0.25	0.28	0.52
Al_2O_3	14.21	15.98	15.09	16.49	14.54
Fe_2O_3	1.15^x	2.98^x	1.83^x	1.27	2.23
FeO	-	-	-	0.81	1.78
MnO	0.02	0.09	0.05	-	-
MgO	0.54	1.66	0.91	0.61	1.37
CaO	0.82	1.76	1.16	0.74	0.94
Na_2O	3.51	4.98	4.01	4.72	3.24
K_2O	4.32	5.86	4.89	4.02	4.14
SO_3	-	-	-	<0.01	0.03
P_2O_5	0.15	0.41	0.24	-	-

^{x}) total Fe content presented as Fe_2O_3

from the experimental catchment „Lesní potok", which may cause uncertainties about the validity of the employed data.

Samples of the forest canopy throughfall contain strikingly higher concentrations of Mn, Zn, and probably also Cu and Be. It is well known that the bulk chemical composition of throughfall differs significantly from that collected in open landscape. Throughfall consists of three components: precipitation deposited on the canopy, dry deposition washed from it by rain, and internal canopy biological sources. The chemistry of throughfall itself is influenced significantly by rainfall characteristics, canopy age and type, dry deposition load and by soil chemistry of the sampling locality (Lindberg, 1989). The differences observed in the chemical composition of the two types of atmospheric deposition may be then attributed to the scavenging effect of the canopy, causing the impact capture of the near-surface aerosol rich in anthropogenic pollutants, and to the metabolic activity of the vegetation. The latter mechanism is probably much more significant, as the three above mentioned elements are essential for plants. Their elevated concentrations in throughfall should be a result of foliar leaching of matter originating in the internal tree tissues.

II. Contents of selected minor and trace elements in the Říčany granite. According to Minařík and Houdková (1986), numbers in columns A and Z represent material sampled in 1993

Element	Contents (ppm)					
	min.	max.	arithmetical mean	n^x	A	Z
As	1.1	11.0	5.3	13		
B	13	330	74	11		
Be	5.0	14.0	8.4	11	9.50	7.75
Co	2.75	32.0	8.1	15		
Cr	20.6	140.0	83.1	16		
Cu					2.5	2.5
F	700	1 900	1 390	11		
Ni	11	59	31	16		
Pb	37	140	56	21		
Sn	3.6	44.0	15.1	11		
Sr	183	475	332	21	470.0	247.5
Th	9.0	40.5	22.4	12		
U	6.25	21.0	7.3	12		
W	0.75	3.10	-	17		
Zn	18.0	82.5	41.0	21	39.8	62.0

number of samples

Tab. IV shows main data concerning bulk chemical composition of water representing the surface discharge of the experimental catchment. Low concentrations of main cations are typical for surface waters from areas with bedrock of poor buffering capacity, such as the Říčany granite. Analysed samples are also low in NO_3^- which is typical for surface water from forested areas. Relatively low concentration of Cl^- ions has its origin in the atmospheric deposition, mainly from the oceanic spray. On the other hand, the concentration of SO_4^{2-} is fairly high. Its origin is, with respect to low amount of sulphur in the granite, also chiefly in the atmospheric deposition of SO_4^{2-} ions in solution of $(NH_4)_2SO_4$ aerosol and of the absorption of gaseous SO_2. Resulting low pH of the precipitation (pH = approx. 4.3) is reflected in acid character of the surface water, which is the more acid, the higher is the precipitation volume. Relatively high concentration of F^- ions is caused mainly by elevated content of fluorine in the parent rock (see the Tab. II), and it is significant for the complexation of dissolved Al and Be (see above). High content of Be, exceeding the maximum permitted values, is typical for

III. Contents of selected trace elements (in ppb) in the cumulative samples of total atmospheric deposition and of throughfall, sampling site D

Element	Type of sample	Contents (ppb)				*n*
		arithmetical mean	min.	max.	standard deviation	
Be	CAD[x]	<0.20	-	-	-	33
	TH[x]	0.34	<0.1	1.0	0.32	6
Cu	CAD	3.20	<1	22	4.31	46
	TH	9.30	7.2	15.5	3.22	6
Mn	CAD	35.60	<10	310	54.70	46
	TH	1 957	870	4 670	1 267	6
Pb	CAD	5.66	1	15	3.29	53
	TH	1.76	<0.5	2.9	0.90	6
Sr	CAD	8.55	<5	25	4.68	31
	TH	-	-	-	-	0
Zn	CAD	85.10	9	370	75.60	41
	TH	272.5	51	870	294.7	6

[x]) CAD = cumulative atmospheric deposition,
TH = throughfall

IV. Bulk chemical composition, contents of Be and pH in samples of surface water from sampling site W

Element/ion (units)	Contents				*n*
	arithmetical mean	min.	max.	standard deviation	
Na (ppm)	7.569	6.2	8.9	0.758	21
K (ppm)	1.077	0.8	1.7	0.230	21
Ca (ppm)	18.942	10.02	30.06	4.894	21
Mg (ppm)	7.696	2.43	10.21	2.111	21
HCO_3 (ppm)	8.970	4.21	22.58	5.488	21
Cl (ppm)	6.347	2.84	8.51	1.397	21
SO_4 (ppm)	74.683	51.85	98.32	13.669	21
NO_3 (ppm)	6.826	1.31	11.38	2.676	17
F (ppm)	0.491	0.37	0.60	0.097	21
Be (ppb)	7.755	2.0	24.0	5.271	31
pH	5.070	4.63	5.85	0.299	56

this type of surface water. Its main source represents the parent rock with elevated content of Be, which is mobilized through the accelerated hydrolysis of aluminosilicates, caused by the anthropogenic input of atmospheric protons (Skřivan, Jonášová, 1990). Nevertheless, the pH of water is the main factor limiting the resulting concentration of dissolved Be. Other streams from the Říčany granite bedrock, which exhibit higher pH values as a result of anthropogenic activities (agriculture, urbanization), are significantly lower in Be (Skřivan et al., in press).

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Cyklus berylia v prostředí pod antropogenními vlivy.

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V modelovém povodí „Lesní potok“ na horním toku Jevanského potoka na Černokostelecku byla studována geochemická pozice stopového toxického prvku berylia a její antropogenní ovlivnění. Jako podklad posloužily údaje o obsahu a základních formách Be v podložní hornině, povrchové vodě, celkové atmosférické depozici a v podkorunových srážkách.

Podloží širší oblasti tvoří Říčanský granit, kyselá hornina s nízkou pufrační schopností vůči kyselým atmosférickým srážkám, obsahující zvýšené koncentrace řady stopových prvků včetně Be. Vzorky hornin byly odebrány v opuštěném lomku v těsné blízkosti modelového povodí (mírně navětralý materiál) a v donedávna těženém lomu u obce Žernovka (zcela čerstvý materiál). Chemické složení horniny, včetně 15 stopových prvků, ukazují tab. I. a II. Výsledky potvrzují, že jde o typický cínonosný granit s vyšším podílem těkavých komponent a zvýšeným obsahem Sn, Pb, Be, F, B, Y W a Nb.

Nejvýznamnější geochemickou charakteristikou berylia ve studované oblasti jsou zvýšené koncentrace rozpuštěných forem Be v povrchových tocích, způsobené urychleným zvětráváním podložní horniny v důsledku chemického působení kyselé atmosférické depozice. Systematický monitoring obsahu stopových prvků v atmosférické depozici vyloučil možnost výrazného ovlivnění obsahu Be v povrchových tocích tímto vstupem (obsah Be, Cu, Mn, Pb, Sr a Zn v kumulativních vzorcích celkové atmosférické depozice je uveden v tab. III).

Celkové chemické složení, obsah Be, F^- a pH povrchového toku, vzorkovaného v místě koncového profilu modelového povodí, ukazuje tab. IV. Základní složení povrchové vody, zejména nízký obsah NO_3^-, alkálií a alkalických zemin odráží způsob využití povodí (zalesněná oblast bez osídlení) a málo reaktivní horninové podloží. Naopak vysoký obsah SO_4^{2-} svědčí o vlivu kyselé atmosférické depozice, což se rovněž projevuje nízkými hodnotami pH. Tato charakteristika toku společně s vyšším obsahem horninového fluóru způsobují vysoké koncentrace Be v povrchové vodě.

Poslední ze sledovaných charakteristik, podkorunové srážky (tab. III), odrážejí význam impaktního záchytu aerosolu z přízemních vrstev atmosféry a zejména (v případě esenciálních prvků) fyziologických mechanismů mobilizace elementů z půdního a zvětralinového prostředí.

Prezentované výsledky potvrzují význam procesu druhotné (nepřímé) antropogenní kontaminace prostředí toxickým beryliem v důsledku intenzifikace chemického zvětrávání hornin působením kyselých atmosférických srážek. Současně vytvářejí předpoklady pro orientaci dalšího detailnějšího výzkumu pozice Be v supergenní zóně.

berylium; cyklus; prostředí; povodí; depozice; povrchová voda; podloží; mobilizace

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