

V. Koles -

Acta Universitatis Carolinae
Geologica 37 (1993): 111-122
Editum 7. 11. 1994

Secondary anthropogenic contamination of surface streams through lithogenic beryllium, mobilized by acid atmospheric deposition

PETR SKŘIVAN, PETR ARTNER, PAVLA KOTKOVÁ

Institute of Applied Ecology VŠZ, Kostelec n. Č. l., Czech Republic

Accepted September 3, 1993

Abstract: Study of the lithogenic beryllium mobilization in the experimental forested catchment "Lesní potok" and on adjacent localities in the Nature State Reserve "Voděradské bučiny" has revealed the significance of acid atmospheric deposition for the Be release into the corresponding surface streams.

Bedrock of the studied area, the Říčany granite, represents the parent material for Be, which is here predominantly bound in the Na-plagioclase and biotite.

Beryllium belongs to the group of elements with the highest migration ability. It is therefore questionable whether the high Be content in surface streams is not leading to its depletion in the weathered rock material or if the Be release from the continuously altering fresh bedrock is a steady-state process.

To answer this question, mass-balance of inputs (rock weathering, atmospheric deposition) and outputs (surface discharge, plant uptake) was performed for Be, K, Na, Ca, Mg, Sr, and Mn. The mobility coefficients of these elements were then evaluated from the mass-balance, together with the values of weathering rate determined from the elemental input by rock weathering.

Results of the mass-balance have shown that 0.1 mm of fresh rock succumbs to hydrolysis annually and that the loss of Be is proportional to the release of both the most mobile elements, Ca and Mg. This result confirms the idea of a steady-state process controlling the Be release from the altering rock.

INTRODUCTION

Direct anthropogenic contamination of the environment by toxic trace elements is well known and it is documented in a large number of papers. Mining and corresponding metallurgy, industrial processing technologies, burning of fossil fuel and agriculture are

main sources of environmental contamination by this type of chemical substances. Trace elements spoil the environment through atmospheric immissions and through direct contamination of surface water by solid and liquid wastes.

The secondary contamination is less obvious, especially that of surface waters, promoted by the enhanced input of these elements from rocks, representing their natural reservoirs. Mobilization of beryllium from parent rock and its weathering products may serve as typical example of such contamination.

This work presents the Be content of several selected small streams and springs in central Bohemia and discusses its entrance into the surface water through hydrolysis of the bedrock, accelerated by acid atmospheric deposition.

Beryllium in rocks and surface waters

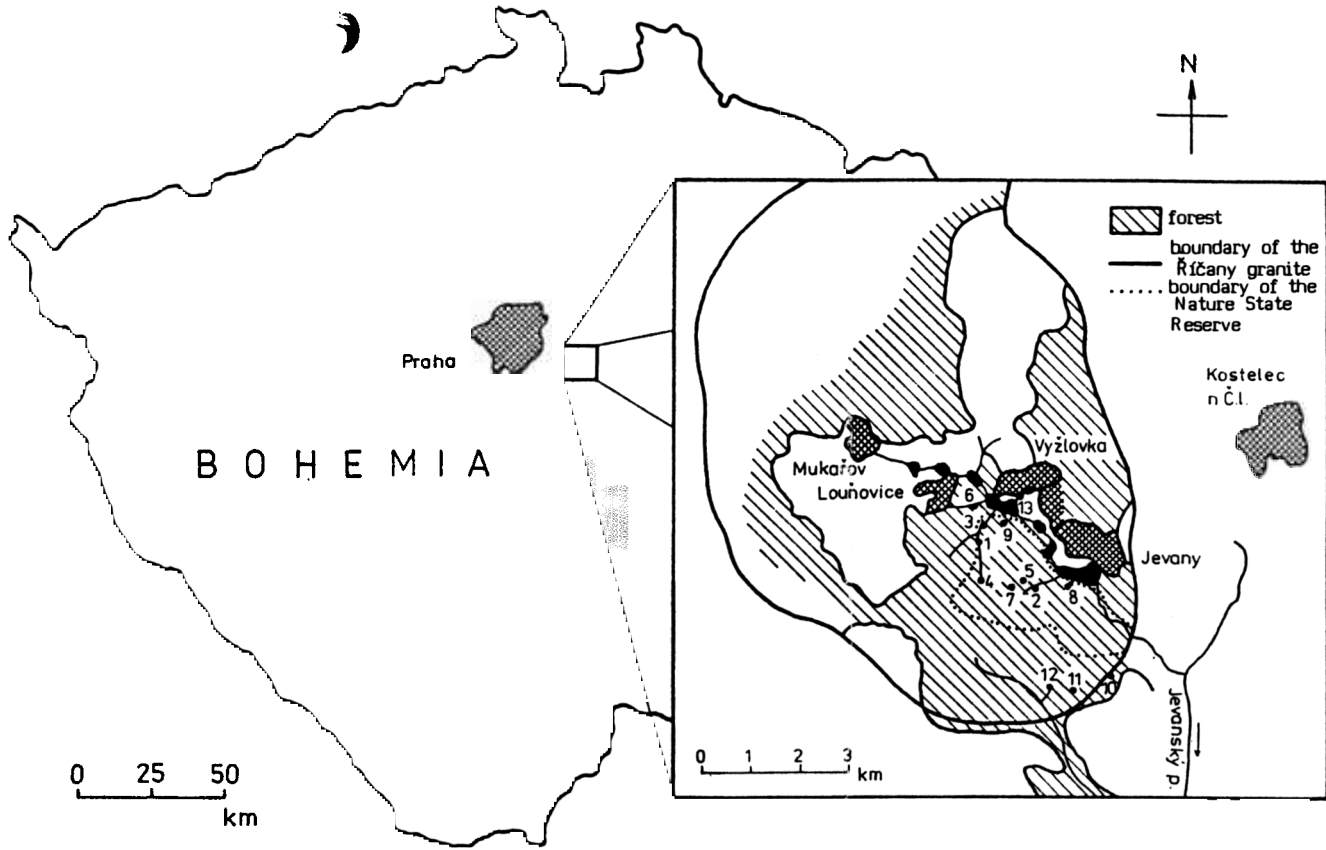
Mean Be content of igneous rocks is reported in the range from 0.2 to 5.5 ppm. The highest concentrations of Be are associated with potassium-rich acidic rocks (granites and syenites), lowest in ultrabazites (Rössler, Lange, 1972).

Several rocks of the Central Bohemian Pluton exhibit anomalous concentrations of Be. Porphyritic granite of the Říčany type contains according to Vejnar (1974) 12 ppm Be, Minařík and Houdková (1986) report contents 5-14 ppm, with mean concentration 8.4 ppm. Beryllium in granitoid rocks is accumulated in hornblende, biotite and orthoclase, the highest enrichment factor (in comparison with clark value), however, was found in Na-plagioclase (Minařík, 1975). On the other hand, Vejnar (1974) declares (comparing the chemical composition of rocks from the Central Bohemian Pluton) that more Be attain the K-rich magmatites, while in the leucocratic Na-rich types the Be-content is very low.

Beryllium content in surface waters was recently presented and discussed on the basis of large number of samples by Veselý *et al.* (1989). These authors reported significant correlation between the Be content and the concentrations of H^+ and F^- of the corresponding samples of water. They have reported the Be concentration range between 0.25 and 720 ppb, with geometric mean 0.59 ppb, evaluated from 2 421 samples, collected in Bohemia and Moravia in the years 1984 to 1987.

The data on Be speciation in fluvial sediments and suspended matter are essential for the understanding of its distribution and migration pattern in the supergene zone. Results of the sequential extraction procedure of fluvial sediments performed by using the modified Tessier *et al.* (1979) technique have shown that majority of labile Be is bound to iron and manganese hydrated oxides and to organic matter (Skřivan *et al.*, 1989).

Fig. 1. Study area with the sampling localities.



Study area

Content of Be and other ecologically important trace elements was studied in headwaters of small streams draining the Nature State Reserve "Voděradské bučiny" region, extending approx. 30 km SE from the centre of Prague, capital of the ČSFR. Sampling localities (streams and springs) are situated on the bedrock of Říčany porphyritic granite (Fig. 1.). The study was focused mainly on surface water of the completely forested (prevailing beech and spruce) catchment "Lesní potok", which is included in an integrated biogeochemical monitoring system GEOMON. Some of the sampling sites are affected by agricultural activities and by urbanization, which is reflected in the bulk chemical composition of corresponding water and in its pH.

MATERIALS AND METHODS

Sampling procedure was adopted to the main purpose, which was the determination of dissolved forms of studied elements. Samples were collected from the surface streams using the polystyrene shovel and then they were immediately filtered using the polycarbonate filtration device Sartorius SM 165 10 and the manual vacuum piston pump Nalgene, through nitrocellulose membrane filters (Sartorius, Type 11306-47-N, pore size 0.45 μm). The filtrate was immediately poured into the 100 ml polyethylene bottle and stabilized by adding of 2 ml 22 % nitric acid (Fluka, pp.) to avoid adsorption of studied cations on the walls of the sampling flask. Temperature and pH of surface water were measured at the same time using the battery pH-meter (WTW, type pH 91). Until their analyses the samples were held at 4 °C in a refrigerator. The content of dissolved Be and other discussed elements was determined by flame- and graphite furnace AA spectrometry.

RESULTS AND DISCUSSION

Table 1 presents data on the content of Be in surface streams and springs shown in Fig.1. Majority of sampling sites is characterized by low pH value of water, resulting from poor buffering capacity of the bedrock. Sampling site No. 6 is slightly affected by agricultural activities, as part of this catchment is covered by arable land. Surface water from the sampling site No. 13 serves as an example of material from prevailing agricultural and urban area, with extremely high pH value.

Beryllium content in samples of surface water from larger region, including material collected on other geological formations were subjected to the regression analysis. Parameters of the dependence of Be concentration in surface water samples on their pH are summarized in Table 2. Graphical expression of the dependence of variables

presented in Fig. 2 shows fair degree of correlation, which is in agreement with the results of Veselý *et al.* (1989).

Table 1. Content of beryllium in surface water of selected localities.

Sampling site			content of Be (ppb)				pH		
No.	code	n	min.	max.	average	std.dev.	min.	max.	average
1	LP6	20	3.00	10.50	5.785	1.769	4.63	5.83	5.01 ^{x/}
2	BP10	7	2.00	4.60	3.514	1.096	5.14	5.79	5.50
3	L7	3	2.00	4.00	3.00	1.000	5.45	5.81	5.65
4	LP1	3	3.00	5.00	4.333	1.155	4.87	5.06	4.93
5	BPLJ	1	—	—	2.00	—	—	—	5.93
6	LOP8	1	—	—	2.00	—	—	—	6.26
7	S2	1	—	—	4.00	—	—	—	4.76
8	S3	1	—	—	6.00	—	—	—	4.70
9	S4	1	—	—	7.00	—	—	—	4.51
10	2CV8	1	—	—	4.00	—	—	—	6.70
11	CV10	1	—	—	11.00	—	—	—	4.51
12	ZVL1	1	—	—	8.00	—	—	—	5.24
13	VZM5	1	—	—	—	—	—	—	10.50

^{x/}average pH was evaluated from the av. values of [H⁺]

Mobilization of Be, which is predominantly bound in soil and weathered rock by adsorption forces to Mn and Fe hydroxides and to organic matter (supposedly through complexation with humic and fulvic acids), has to be influenced in both cases by the concentration of protons present in the system. Hydrogen ions act as potential-determining species for the solid surfaces of Mn and Fe hydrated oxides (Parks, 1967), strongly affecting their surface charge on the solid/water interface and substituting other cations, bound there by ion exchange. Concentration of hydrogen ions determines also the organic complexing acids dissociation, which necessarily affects their bonding with cations. The mobilization principles of Be are thus far understandable. Much more complicated, however, is the quantitative evaluation of this phenomenon.

Table 2. Results of regression analysis – dependence of Be concentration on pH in surface water samples.	
dependent variable:	C_{Be} (concentration of Be - ppb)
independent variable:	pH of corresponding samples
number of samples:	41
regression analysis model:	$C_{Be} = a \cdot pH^b$
	$\log a = 11.4769$
	$b = -6.09205$
	$F_{1,40} = 384.3019$
probability level:	0.00000
corr. coefficient:	-0.951697
	$R^2 = 90.57 \%$

as a measure for considering their migration ability. The coefficient is defined as follows (Marchand 1974):

$$Mc_x = \frac{[x]_w}{[x]_r}, \quad (1)$$

where

$[x]_w$ is the concentration of an element x in water which is in contact with studied rock (in ppb),

$[x]_r$ is the concentration of this element in the rock (in ppm).

valuation of Mc is aggravated by the fact that the chemical composition of surface water cannot be directly used for the value $[x]_w$, as it reflects to a certain extent the composition of wet atmospheric deposition and that it is affected also by the biological activity, especially by vegetation growth. In order to obtain valid and applicable values of $[x]_w$, it is hence necessary to balance at least the four main natural fluxes of matter, namely the inputs through deposition and weathering, and the outputs through surface water discharge and by vegetation uptake, in a defined area (catchment). The value of $[x]_w$ can be then determined from the following equation:

$$[x]_w = \frac{W_x}{O} = \frac{O_x - D_x + U_x}{O} = [x]_{sw} - \frac{[x]_d \cdot D}{O} + \frac{U_x}{O}, \quad (2)$$

where

O is the specific water discharge from the catchment [$m^3 \cdot m^{-2} \cdot yr^{-1}$]

W_x , D_x , and U_x are the specific inputs to/uptake from surface water by rock weathering, deposition, and vegetation uptake respectively, in $[\text{mg} \cdot \text{m}^{-2} \cdot \text{yr}^{-1}]$,

O_x is the total specific discharge of an element x through surface water $[\text{mg} \cdot \text{m}^{-2} \cdot \text{yr}^{-1}]$,

$[x]_{\text{sw}}$ is the determined concentration of an element in surface water,

$[x]_d$ is the concentration of dissolved species of an element in wet atmospheric deposition,

and D is the annual precipitation height $[\text{m} \cdot \text{yr}^{-1}]$.

Two necessary conditions have to be met so that the result of the mass-balance might be satisfactory and meaningful: No volatile or very poorly soluble compounds may result within the limits of pH and Eh naturally existing in the environment, or by biological activity, from the dissolved species of the balanced element.

The quantity W_x representing the rate, in which the element x is liberated from the rock through its hydrolysis, can serve for the evaluation of the weathering rate, WR, according to the following equation:

$$\text{WR} [\text{m} \cdot \text{yr}^{-1}] = \frac{W_x}{S \cdot [x]_r}, \quad (3)$$

where S is the specific gravity of the rock $[\text{kg} \cdot \text{m}^{-3}]$.

Table 3. presents values of the mobility coefficient Mc_x evaluated from the equations (1) and (2) for Be, K, Na, Ca, Mg, Sr, and Mn, and the corresponding values of weathering rate WR, obtained from the equation (3). Values of U_x can seriously affect the resulting magnitude of $[x]_w$ and it is therefore useful to apply experimental data for the growth rate of trees and for the content of elements in wood obtained directly in the particular catchment. These data were not available and we were referred to the literature. Values of Mc_x and WR in Table 3. nevertheless are in good agreement with commonly accepted migration characteristics of the discussed elements and with the relative stability of their mineral carriers.

Modal analysis of the Říčany granite (Minařík *et al.*, 1983) revealed following composition: 25.3 % quartz, 44,4 % K-feldspars (orthoclase + microcline), 22.1 % plagioclase, 8.1% biotite, 0.1 % muscovite. According to another paper of this author (Minařík, 1975) and of Vejnar (1974) Be is concentrated in the main rock-forming minerals present in the Říčany granite in following order: Na-plagioclase > biotite >

> orthoclase > quartz. Other elements presented in the Table 3. are distributed in these minerals as follows:

Na – plagioclase ➤ orthoclase > biotite, muscovite > quartz

K – orthoclase, muscovite, biotite ➤ plagioclase > quartz

Ca – plagioclase > orthoclase, biotite > muscovite > quartz

Mg – biotite ➤ muscovite, plagioclase, orthoclase > quartz

Sr – orthoclase > plagioclase > biotite > quartz

Mn – biotite ➤ plagioclase, orthoclase > quartz

Table 3. Values of the mobility coefficient M_c for selected elements and of the weathering rate WR for Říčany granite together with essential data for the calculations.

$O = 0.132 \text{ m.yr}^{-1}$ $D = 0.635 \text{ m.yr}^{-1}$
 $S = 2667 \text{ kg.m}^{-3}$ *porfir* *depozice* *uplate* *vyhled* *rozd* *rod* *rod*

element	$[x]_{sw}$	$[x]_d$	U_x	$[x]_w$	$[x]_r$	M_{c_x}	WR
Be	5,785	0.156 ^{1/}	0.5	8.82	8.4 ^{3/}	1.05	$5.20 \cdot 10^{-5}$
Na	6 560 ^{1/}	290 ^{1/}	100 ^{2/}	5 923	29 800 ^{3/}	0.20	$0.98 \cdot 10^{-5}$
K	1 010 ^{1/}	280 ^{1/}	400 ^{2/}	2 693	40 600 ^{3/}	0.07	$0.33 \cdot 10^{-5}$
Ca	23 100 ^{1/}	1 850 ^{1/}	500 ^{2/}	17 988	8 290 ^{3/}	2.17	$10.70 \cdot 10^{-5}$
Mg	8 150 ^{1/}	360 ^{1/}	90 ^{2/}	7 100	5 490 ^{3/}	1.29	$6.40 \cdot 10^{-5}$
Sr	186	5	— ^{4/}	162	332 ^{3/}	0.49	$2.42 \cdot 10^{-5}$
Mn	292 ^{1/}	36 ^{1/}	— ^{4/}	119	387 ^{3/}	0.31	$1.52 \cdot 10^{-5}$

^{1/}values from Skřivan, Jonášová (1990)

^{2/}values from Lelong *et al.*(1990)

^{3/}values from Minařík, Houdková (1986)

^{4/}no values available

Relative alteration rate of minerals as possible bearers of these elements, beginning with the most stable mineral, can be depicted in the order orthoclase > (muscovite) > > plagioclase, biotite. The last two minerals, which are preferably apt to decompose, liberate all the studied elements into the liquid phase during the weathering process, potassium only is largely retained in the secondary clay minerals. Manganese can, under suitable conditions, form poorly soluble products of Mn(IV), which could affect its balance and resulting values of $M_{c_{Mn}}$ and WR . This was, however, not confirmed.

The sequence of the weathering rates of studied elements is in good agreement with results of Minařík (1983), who studied the mobility of several minor and trace elements in the course of weathering and related their behaviour to the bulk chemistry and mineralogy of rock and its weathering products in a vertical profile.

The results of mass-balance, expressed as a vertical loss of the solid rock determined from the mobilization of chemical component with the highest migration ability, show that 0.1 mm of unaltered Říčany granite succumbs annually to hydrolysis, which has been promoted in the past several decades by the acid atmospheric deposition. The loss of Be is proportional to the liberation of both the most mobile elements, Ca and Mg. All these three elements probably originate from Na-plagioclase and biotite, representing almost one third of the mass of this type granite. This result confirms the idea that the solid rock weathering products in this case are not the main source of Be in surface water and that it is supplemented in an adequate amount directly from the parent rock:

CONCLUSIONS

Study of the lithogenic beryllium mobilization in the experimental forested catchment "Lesní potok" and on adjacent localities in the Nature State Reserve "Voděradské bučiny" has revealed the significance of acid atmospheric deposition for the process. Bedrock of this area, the Říčany granite, represents the parent material for Be, which is mobilized simultaneously with other products of the rock-forming mineral hydrolysis. The hydrolysis is accelerated by enhanced input of protons from the acid atmospheric deposition. This was documented by strong correlation of Be content in surface water with its pH. Beryllium, together with Ca and Mg, are the most mobile elements in this environment and they enter the liquid phase mainly through hydrolysis of Na-plagioclase and biotite. Weathering rate of the Říčany granite, determined by the hydrolysis of the most unstable mineral, was established to be 0.1 mm.yr⁻¹. The value was evaluated on the basis of input and output mass-balance in a hydrologically defined region (catchment).

REFERENCES

- Lelong F., Dupraz C., Durand P., Didon-Lescot J. F., 1990: Effects of vegetation type on the biogeochemistry of small catchments (Mont Lozere, France). Jour. Hydrol. 116, 125-145.
- Marchand D. E., 1974: Geol. Survey Profess. Paper 352-J, Washington D. C., pp. 379-424.
- Minařík L., 1975: Distribuce prvků v hlavních horninotvorných minerálech plutonitů. Čas. pro min. a geol., 20 (2), 185-199.

Minařík L., Absolon K., Köllnerová Z., Klečka M., 1983: Chemical changes of granite during its weathering. Leaching and diffusion in rocks and their weathering products. Theophrastus Publ., Ed.: S.S. Augustitis, Univ. Athens, Greece, pp. 293-306.

Minařík L., Houdková Z., 1986: Distribuce prvků při zvětrávání granitických hornin a tvorbě půd v oblasti říčanského masívu. Acta Mont. 74, 59-78.

Parks G. A., 1967: Aqueous surface chemistry of oxides and complex oxide minerals. In: Equilibrium concepts in natural water systems, Advan. Chem. Ser., pp. 121-160.

Rössler H. J., Lange H., 1972: Geochemical Tables. Leipzig, 468 pp.

Skřivan P., Absolon K., Letovská N., Houdková Z., 1989: Speciace některých minoritních a stopových prvků v recentních sedimentech povrchových toků. Proc. II. Natl. Conf. "Geochemistry of geological processes and the environment", Smolenice, ČSFR, 265-270. Ed. GÚDŠ Bratislava.

Skřivan P., Jonášová M., 1990: K otázce litogenního a antropogenního původu Be a některých dalších stopových prvků v povrchových vodách na Černokostecku. Proc. II. Natl. Conf. "Heavy Metals in the Environment", Č. Budějovice 14.-18. 5. 1990, pp. 29-34.

Tessier A., Campbell P. G. C., Bisson M., 1979: Sequential extraction procedure for the speciation of particulate trace metals. Anal. Chem. 51 (7), 844-851.

Vejnar Z., 1974: Trace elements in rocks of the Central Bohemian Pluton. Věstník ÚÚG Praha, 49, 159-165.

Veselý J., Beneš P., Ševčík K., 1989: Occurrence and speciation of beryllium in acidified freshwaters. Wat. Res. 23 (6), 711-717.

Druhotná antropogenní kontaminace povrchových vod litogenním beryliem, mobilizovaným kyselou atmosférickou depozicí

P. SKŘIVAN, P. ARTNER, P. KOTKOVÁ

Studium chemického složení vod drobných vodních toků v povodí Jevanského potoka ukázalo výrazně zvýšené koncentrace rozpustných forem berylia. V soulase s literárními údaji bylo zjištěno, že obsah Be koreluje s hodnotou pH studovaných vod.

Geologické podloží studované oblasti je tvořeno říčanským granitem, který představuje zdrojový materiál tohoto prvku. Jde současně o horninu s malou pufrací schopností vůči kyselé atmosférické depozici, jejímž důsledkem je urychlení procesů hydrolyzy horninotvorných minerálů a zvýšená mobilizace berylia, vázaného zde především v Na-plagioklasu a biotitu.

Beryllium patří mezi prvky s relativně vysokou migrační schopností. Naskytá se proto otázka, zda jeho zvýšená mobilizace kyselou atmosférickou depozicí vede k postupnému ochuzení zvětralinového regolitu o tento prvek, nebo zda je Be uvolňováno přímo v procesu hydrolyzy horninotvorných minerálů více méně rovnoměrně s ostatními mobilními prvky.

V užší oblasti, vymezené povodím Lesního potoka (drobný vodní tok v SPR Voděradské bučiny) byla proto provedena bilance hlavních vstupů (zvětráváním podloží, atmosférickou depozicí) a výstupů (odtokem z povodí, odnímáním vegetací) u Be, K, Na, Ca, Mg, Sr a Mn. Z bilancovaných veličin byla potom stanovena hodnota *koeficientu mobility* daného elementu a z vypočteného vstupu zvětráváním horniny byla určena pro každý z uvedených prvků *rychlost zvětrávání* podložní horniny.

Výsledky bilance ukázaly, že za daných podmínek podléhá ročně 0.1 mm nezávětralé horniny hydrolyze a že ztráta Be je úměrná rychlosti uvolňování obou dalších nejmobilnějších prvků, Ca a Mg. Tento výsledek potvrzuje domněnku, že obsah Be v povrchových vodách přímo odráží rozsah jeho uvolňování z matečné horniny.