

## Biogeochemistry of Beryllium in an Experimental Forested Landscape of the Lesní potok Catchment in Central Bohemia, Czech Republic

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**ABSTRACT:** The geochemistry of beryllium (its concentration, speciation and fluxes) has been studied since 1985 in the catchment area of the "Lesní potok" (Černokostecko region, Central Bohemia), and in its surroundings. Results include the concentration and forms of Be (and other selected minor and trace elements) in the individual compartments of the system:

- The underlying bed, monzogranite of the Říčany type and two – mica Jevany syenogranite, is enriched in Be (with 12,7 mg.kg<sup>-1</sup> and 11,5 mg.kg<sup>-1</sup>, respectively).
- The total Be concentration increases in the individual soil horizons from 3,75 mg.kg<sup>-1</sup> in A-, to 7,38 mg.kg<sup>-1</sup> in Gr<sub>1</sub> horizon as a result of the Be-leaching by the acid precipitation. The acid- and ammonium nitrate leachable forms of Be in soil have similar patterns.
- Springs and acidified streams draining the forested area with bedrock of the Říčany granite (including the Lesní potok catchment) have considerably increased Be concentration (>1 to 10 µg.L<sup>-1</sup>), dependent on the pH-value of water. On the other hand, stagnant waters of the pond Výchlovský which receives Lesní potok stream water has a high pH and low (<0,5 µg.L<sup>-1</sup>) Be concentration.
- Mean concentration of beech- (*Fagus sylvatica* L.) and spruce- (*Picea abies* L. Karst) tissues (the dominant tree species of the forest) are 13,8 and 20,5 µgBe.kg<sup>-1</sup> in stem wood, 78,3 and 68,2 µgBe.kg<sup>-1</sup> in bark, respectively. Concentration of Be in beech leaves is 65 to 348 µgBe.kg<sup>-1</sup> d.wt., increasing in the course of growing season, and 310 µgBe.kg<sup>-1</sup> d.wt. in the litter of spruce needles.

Mean Be fluxes in bulk atmospheric precipitation are lower than 0,05 µg.m<sup>-2</sup>.day<sup>-1</sup>, whereas the fluxes in spruce- and beech throughfall are 0,04 to 0,1 µgBe.m<sup>-2</sup>.day<sup>-1</sup>. Mean Be output from the catchment markedly exceeds input, reaching 2,7 µgBe.m<sup>-2</sup>.day<sup>-1</sup>. No trends either in the Be-atmospheric input or in surface discharge were observed from 1985 to 1998.

**KEY WORDS:** beryllium, biogeochemistry, forest, catchment, monitoring, cycling.

### Introduction

Beryllium, metal with atomic number (4) and one stable isotope <sup>9</sup>Be, is the first element in the second column of the Periodic Table. It behaves, owing to its atomic parameters and properties, more like a transition metal than might be expected from the position of Be in the group of alkaline earth elements.

Some remarkable properties of metallic beryllium and its compounds determine the value of Be in modern industry.

Development of some special branches of technologies (atomic energy, nuclear reactors and weapons, space rockets, specialised electronics, fatigue-resistant alloys), however, results in higher exposure of selected human professions to beryllium.

Beryllium concentration in coal reaches values up to 100 mg Be.kg<sup>-1</sup>. The local atmosphere may become contaminated by coal combustion with Be-rich particulate matter, which can lead to health problems in mining regions. Deposition of Be could cause increased concentrations of Be in surface waters.

Views concerning the toxicity of Be are ambiguous. Higher concentrations of dissolved Be compounds in food and water could induce chronic health effects in humans. Nevertheless, contamination of drinking water with Be is essentially unknown, although the Be drinking water standard is very low (in the Czech Republic it is 0.2 µg Be.L<sup>-1</sup>). On the other hand, inhalation of solid aerosol with high concentration of beryllium leads to irritation of the respiratory tract and chronic exposure may develop berylliosis.

Total annual atmospheric emissions of beryllium in Europe are estimated at 50 metric tons. They are much lower than those

of most other toxic trace elements (Moore 1991). A small number of environmental studies devoted to Be have been conducted. Be is a typical lithophile trace element with enhanced content in felsic rocks, where it is bound predominantly in feldspars. Increased concentration of Be in coal is probably responsible for its main primary anthropogenic input into soils and surface water. Beryllium is highly mobile under acidic conditions in soils and weathering products of parent rocks. This behaviour of Be determines its sensitivity towards the acidic precipitation. Mobility of Be is higher in acidified surface waters. Uptake of Be by vegetation is low. Be may be toxic to vegetation.

The characteristics summarised above determine Be as an important object of study in the area of the Říčany granite massif. High concentrations of Be and their fluctuations in small surface streams draining the forested landscape of the Voděradské bučiny Nature State Reserve have been studied since 1985, when special attention was focused on the Lesní potok (LP) catchment. The study included monitoring of bulk atmospheric precipitation, beech- and spruce throughfall and stemflow, the distribution of Be throughout the soil profile and its uptake, and incorporation into the tissues of the forest trees. In 1998, we joined the international research Project "The dynamics of the biogeochemistry of beryllium". The Project involves laboratory- and field research of Be in two catchments in the Czech Republic (the other is in NW Bohemia) and two catchments in Maine, USA. This paper summarizes and assesses more than 1500 primary analytical values relating to the beryllium con-

centration and fluxes in the individual compartments of the Lesní potok catchment and its surroundings obtained up to the end of 1997, as a basis for further more detailed research.

## Materials and Methods

### Studied area

The Lesní potok (LP) catchment is 30 km southeast of Prague in Central Bohemia, the Czech Republic (Fig. 1). A brief description of the area was presented in Minařík et al. (1998). The LP catchment is in the Nature State Reserve Voděradské bučiny on the bedrock of the Říčany and Jevany granite. The geographical coordinates of the catchment are 49° 58' 35" lat. N, 14° 46' 40" long. E. The forested catchment covers an area of 0.765 km<sup>2</sup>. Its south boundary reaches maximum elevation of 500 m (above sea level). The Thomson weir (in the northern part of the catchment) is 406 m a.s.l. The mean annual precipitation is 635 mm and the mean annual temperature is 7.3 °C.

### Bedrock

Granitoids of the Říčany massif form the crystalline bedrock of the broader area and they extend approximately 20 to 35 km east of Prague (Fig. 2). They represent part of the Hercynian Central Bohemian Pluton. The massif is a typical small intrusion intruded near the Earth's surface. It occupies an area of about 80 km<sup>2</sup>. Its mineralogy is monotonous, but the body is structurally variable. It is concentrically zoned: the grain size of the equigranular medium-grained rock forming the core increases continuously toward the periphery, so that the rock gradually transforms into a porphyry with large K-feldspar phenocrystals of more than 1 cm in diameter. The average modal composition of the core- and peripheral rock types is almost identical (vol. %): quartz 26 and 29, K-feldspar 31 and 27, plagioclase (16% An) 36 and 35, biotite 6 and 7, respectively (Němec 1978); muscovite is a minor component. Monzogranite is the

rock type	monzogranite Říčany type 1)	syenogranite Jevany type 2)	dyke aplite 3)	marginal aplite 4)	sand- stone
oxide(wt.%)					
SiO <sub>2</sub>	69,64	70,62	70,43	74,59	91,750
TiO <sub>2</sub>	0,35	0,29	0,27	0,06	0,160
Al <sub>2</sub> O <sub>3</sub>	15,24	14,80	15,40	14,52	2,640
Fe <sub>2</sub> O <sub>3</sub>	0,72	0,57	1,42		2,650
FeO	1,48	1,28	0,83	0,59*	0,130
MnO	0,05	0,04	0,04	0,01	0,003
MgO	1,42	1,08	0,70	0,23	0,040
CaO	1,43	1,36	1,72	0,85	0,030
Na <sub>2</sub> O	3,50	3,92	3,80	3,77	0,040
K <sub>2</sub> O	5,40	5,09	4,48	3,52	0,140
P <sub>2</sub> O <sub>5</sub>	0,35	0,24	0,13	0,11	0,040
H <sub>2</sub> O*	0,43	0,41	0,52	0,65	
H <sub>2</sub> O*	0,27	0,23	0,27	0,12	
L.O.I.					1,950
ä	100,28	99,93	100,01	99,12	

1) mean value of 16 analyses (Holečková 1958, Vejnar 1973)

2) mean value of 11 analyses by Šmejkalová (1960)

3) mean value of 2 analyses by Palivcová et al. (1992)

4) mean value of 8 analyses by Němec (1978) and 2 according to Vejnar (1973)

\* total Fe as FeO

**Tab. 1.** Bulk chemical composition of the parent rocks underlying Lesní potok catchment and localities Truba and Arboretum.

predominant rock type of the Říčany body. In the area between Jevany and Černé Voděrady, the massif is transected by numerous aplite dykes whose average modal composition is (vol. %): quartz 37, K-feldspar 27, plagioclase (9% An) 31. Other constituents are muscovite, biotite, and tourmaline in variable amounts. In the southeastern part of the massif a rock of syenogranitic composition occurs, named the Jevany granite. Compared with the Říčany granite it is finer grained, poorer in mafic minerals and its plagioclase is more albitic (An 10-12 vol.%). The marginal aplite in the southern part of the massif is genetically related to the aplite dykes in the centre of the body. Numerous mafic biotite - rich dark enclaves are enclosed in the main granitic rock (Palivcová et al. 1992 for review).

The bulk chemical compositions of the rock types - the parent material of soils in the catchment, are given in the Tab. 1. Majority of granitic rocks of the massif are of the metaaluminous type with mol. % Al<sub>2</sub>O<sub>3</sub> ≤ alk + CaO and with Al<sub>2</sub>O<sub>3</sub> > alk, and some of the peraluminous type.

Bulk precipitation- and average throughfall samplers (loc. Truba and Arboretum, see the Fig.1.) were located outside the northeastern rim of the Říčany massif, where the bedrock is Permian sediments, partly covered with Cenomanian sandstones. Modal composition of the sandstone is as follows (vol. %): quartz 88.6, muscovite 1.2, kaolinite 6.7, and goethite 3.7. Bulk chemical composition of the sandstone is given in the Tab. 1. The concentration of selected trace elements in the sandstone (including Be) is presented in the Tab. 2.

element	mg.kg <sup>-1</sup>	element	mg.kg <sup>-1</sup>
As	13,50	Cu	8,10
Be	0,90	Ni	3,60
Cd	0,04	Pb	9,90
Co	1,50	Zn	9,30
Cr	57,30		

**Tab. 2.** Concentration of selected trace elements in the sandstones of the Truba - Arboretum region.

Concentration of the 0,01M HNO<sub>3</sub> - leachable Be from the sandstone and the Říčany granite is given in the Tab. 3.

rock type	total Be mg.kg <sup>-1</sup>	Be extracted mg.kg <sup>-1</sup>	Be extracted %
monzogranite	12,70	0,0334	2,6
syenogranite	11,50	0,0053	0,5
sandstone	0,90	0,0128	14,2

**Tab. 3.** Concentration of the 0.01 M HNO<sub>3</sub> - leachable Be in the main rock types of the studied region.

### Vegetation cover of the catchment

The catchment is almost completely afforested with deciduous (53%) and coniferous (45%) trees with prevailing beech (*Fagus sylvatica* L.) and spruce (*Picea abies* L. Karst) (Sequens 1998; Russ 1998; Macek 1998). The beech dominates (91,2% of the deciduous catchment area). The mean area - weighted age of spruce is 84 years and of beech is 80 years. The overall timber supply (without bark) of the catchment is 18 454 m<sup>3</sup> coniferous timber, and 10 203 m<sup>3</sup> hardwood timber. The annual increase of timber (without bark) is 255 m<sup>3</sup> in spruce, and 174 m<sup>3</sup> in beech. Weight of the fresh biomass is as follows: 847 t in spruce needles, and 171 t in beech leaves.

### Methods of sampling and sample processing

#### Bulk precipitation, throughfall and stemflow

Bulk atmospheric precipitation in an open place occurred at the experimental station of the Faculty of Forestry, the Czech Agricultural University (locality "Truba") 5,5 km northeast from the catchment, at least 50 m away from trees (Skřivan et al. 1995). Samples of the mixed forest throughfall were collected from May until October 1996 at the locality Truba near the sampling plot of the bulk precipitation (Fig. 1), using nine sampling devices evenly distributed on a 20 m x 20 m square plot. The sampling plot involved beech (*Fagus sylvatica* L.), oak (*Quercus robur* L.), birch (*Betula pendula* L.), lime (*Tilia platyphyllos* L.), larch (*Larix deciduous* L.), spruce (*Picea abies* L. Karst), and pine (*Pinus sylvestris* L., *Pinus nigra* L.). Age of the forest growth is 95 years (1998). To obtain more precise information on the throughfall chemistry compatible with the published data, further samplers were installed in the beech (+ hornbeam) and in coniferous growth of spruce, which are the typical tree species of the Voděradské bučiny National State Reserve. Sampling of the beech throughfall has been in progress since April 1994, and of spruce throughfall since December 1996. The samples of beech- and spruce throughfall were

collected at the northern tip of the Lesní potok catchment into sets of sampling devices evenly distributed on a 20 m x 20 m square grids.

Procedures of the bulk precipitation and throughfall sampling were similar to those of Berg et al. (1994). Samples were collected monthly into polyethylene bottles (Skřivan and Vach 1993). The collectors of bulk precipitation consist of a 1L polyethylene bottle equipped with glass funnel 12 cm in diameter inserted into the cap of the bottle. The funnel is protected from birds by a casing made from another 5L polyethylene bottle turned upside down, with walls cut in a sawtooth pattern. The mouth of the glass funnel is protected from falling organic debris and insects by a small glass bubble (Fig. 3). The collectors are placed inside opaque plastic pipes (to avoid heating) which are attached to metallic rods approximately 1,5m above the ground (Fig. 4).

Samples of throughfall were originally collected in the VOSS collectors developed in the Czech Geological Survey, Prague. The device consists of a polyethylene (PE) funnel (11.8 cm in diameter) whose upper rim is again arranged in a sawtooth pattern to protect samples from contamination by birds. The lower mouth of the funnel is equipped with a nylon sieve and it is screwed up with the double PE screw to 1L PE sampling bottle

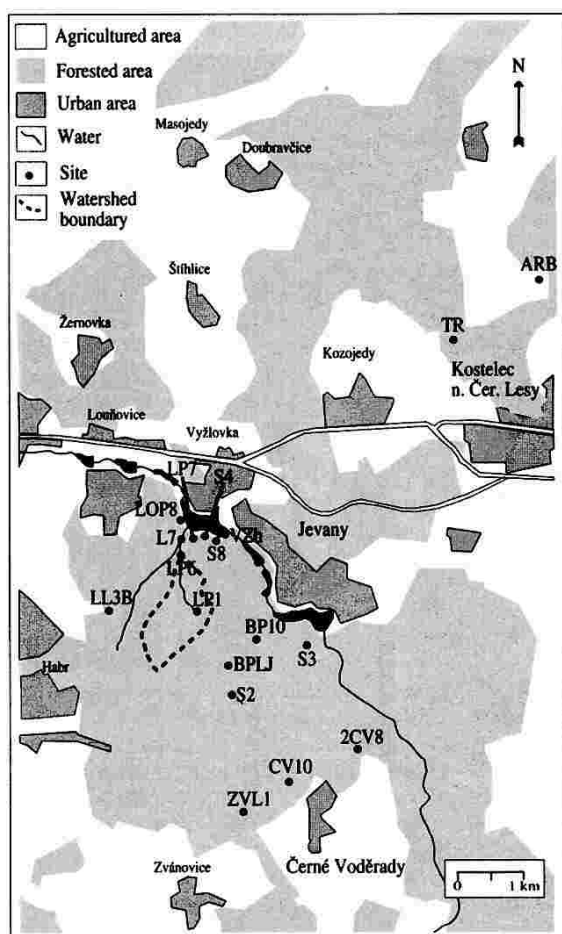


Fig. 1. Schematic map of the Černokostecko region, location of the sampling sites.

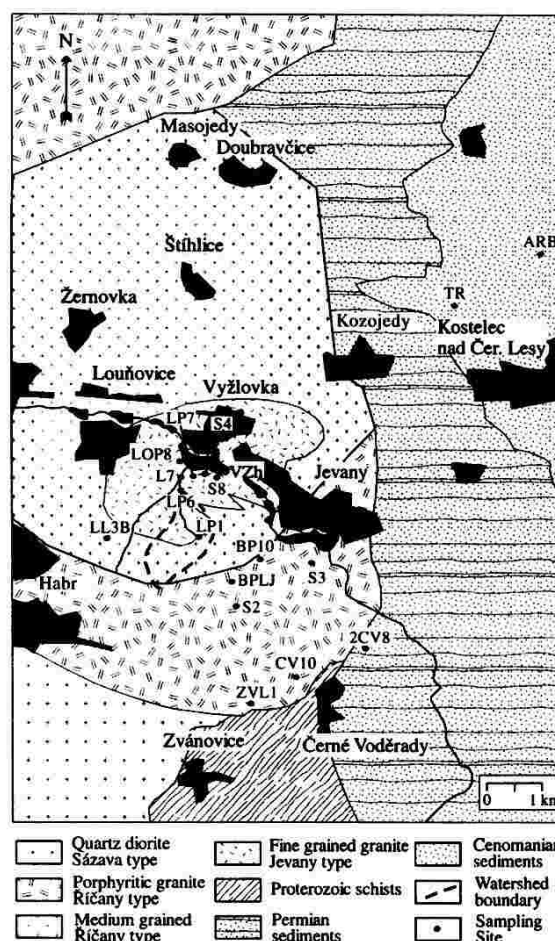
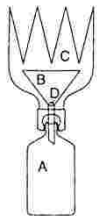


Fig. 2. Schematic geological map of the Černokostecko region.



**Fig. 3.** Glass funnel collector for the bulk precipitation sampling.  
A/ polyethylene collecting vessel  
B/ glass funnel  
C/ polyethylene protecting cover  
D/ closing glass ball



**Fig. 5.** Polyethylene collector for the throughfall sampling, type VOSS.

(Fig 5). The VOSS collectors possess several disadvantages that were discussed by Skřivan and Burian (1996). Solid organic debris may fall into the collecting funnel. The process of leaching increases concentration of the elements in the sample. Typical elements with positive error are the strongly metabolised metals such as Mg, Mn and K. On the other hand, the hydrophobic PE surface of the funnel attracts solid particles in atmospheric deposition, which represents an integral part of the cumulative samples of throughfall. The attached particles are then washed out at the end of the individual sampling period, which causes a negative error of the determination.

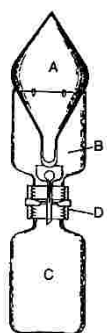
Since 1996 the samples of throughfall have been collected simultaneously in new GCTC (Glass Cone Throughfall Collector) devices shown in Fig. 6. Glass conical bulb A, serving as

an impact target of the throughfall drops, represents the main innovative element of the collector. The bulb is placed onto a cylindrical PE holder B where it is carried by eight small PE hooks turned down into the cylinder. Drops of throughfall caught on the conical part of the bulb flow down on its surface and enter the inner space of the holder through a narrow gap between the rim of the cylinder and the bulb. The liquid then flows down into the collecting 1L vessel C through the double PE screw cap D equipped with small glass funnel. The pipe of the funnel is sealed with a hollow glass ball, which automatically opens when liquid starts pouring in. The construction protects samples from leaves and other solids. The hydrophilic surface of the conical bulb, as well as the collecting funnel, minimizes also the losses of atmospheric aerosols. The GCTC col-

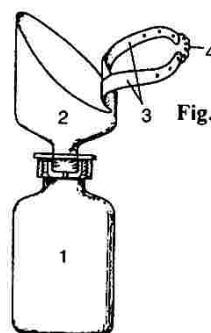


**Fig. 4.** Collector for the bulk precipitation sampling at Truba.





**Fig. 6.** Collector for the throughfall sampling, type GCTC.  
A/ glass conical bulb, serving as an impactor of wet precipitation  
B/ cylindrical polyethylene holder  
C/ polyethylene collecting vessel  
D/ polyethylene double screw cap



**Fig. 7.** Collector for sampling of stemflow.  
1/ polyethylene collecting vessel  
2/ polyethylene cylinder  
3/ polyethylene belts for the fastening of collector to the tree trunk  
4/ steel spring

lectors record only liquid throughfall events, as they do not sample snow. More than two years of experience with the GCTC collectors proved their suitability for the throughfall sampling (Skřivan and Burian 1996).

Devices applied for the stemflow sampling (Fig. 7) are in principle similar to the VOSS collectors for the throughfall sampling, but they are adjustable to the tree trunks through the PE holder. They were used in 1994 for the beech stemflow sampling at locality LP6 in the proximity of the weir.

All the PE bottles were carefully washed (hot distilled water, 0.5%  $\text{HNO}_3$ , distilled and redistilled water). For the bulk precipitation sampling, 2.5 ml of diluted (22% v/v)  $\text{HNO}_3$  (Merck, Suprapur) were inserted in each sampling bottle to prevent the adsorption of dissolved elements onto the walls of the sampling bottle. On the other hand, the acid also dissolves part of the elements bound to the solid particles. The analysed liquid part of samples, obtained after their membrane filtration in a laboratory, represents the sum of dissolved elements in the precipitation together with the forms of the elements weakly bound to the solid particles in the deposition.

The bottles were transported in sealed PE bags to the laboratory. The bottles were weighed to determine the volume of the liquid. The samples were then filtered using a 0.45  $\mu\text{m}$  membrane filter (see above). The filtrate was stored at +4 °C in a cooler until the analysis. In the case of throughfall and stemflow, aliquots of samples prepared for the trace element determination were acidified (after the bulking of the average throughfall samples by volume), and after 1 day they were filtered through the membrane filters. Samples of bulk precipitation determined for the evaluation of bulk chemical composition, concentration, and for the laboratory pH measurements were collected separately.

Concentration of beryllium in most samples of the bulk precipitation, and in considerable number of samples of throughfall, was below the detection limit of the AA spectrometric determination (0.04  $\mu\text{g}\cdot\text{L}^{-1}$ ). To obtain information on the true concentration of Be in this medium, selected samples of the bulk precipitation and spruce- or beech throughfall were concentrated through evaporation prior to the final analysis. Unstabilised and unfiltered samples were evaporated at subboiling temperatures in quartz 800 ml beakers in a flow box. Volume of the samples was reduced down to 1/10 in throughfall and 1/70 in bulk precipitation, the concentrate was filtered through the 0.45  $\mu\text{m}$  membrane filters and then stabilised with diluted nitric acid as for the unconcentrated samples.

Values concerning the concentration and fluxes of beryllium in bulk atmospheric precipitation are summarised in Tables 9 and 10. Collecting of samples at the Truba (TR) started in May 1989. Methods of collecting the samples and their prepara-

tion for analyses have been the same since that time, but the samples were analysed in three various laboratories (in all cases by the AA Spectrometry, but with differing detection limits of the applied methods). This fact strongly complicates the assessment of values as a single data set. Analytical results have been fully compatible since September 1993 only, as all samples have been analysed by a single person (Dr. M. Burian, GI AS) in a single laboratory since that time.

#### Surface stream and springs

Surface water of a small brook draining the catchment Lesni potok was sampled at the Thomson weir (loc. LP6, Fig. 1) at least monthly (Skřivan et al. 1993). Small springs and streams of the broader area in the "Voděradské bučiny" Nature State Reserve (see the Fig. 1) were sampled mostly yearly in 1989, 90 and 91 (Skřivan and Artner 1989). All samples of surface water were either

- filtered in the field through the Filter Holder Sartorius SM 165 10 (BRD) furnished with the Cellulose Nitrate filter Sartorius 11306-47-N (pore size 0,45  $\mu\text{m}$ ), coupled with the manual vacuum piston pump Nalgene (USA). The filtrate was immediately stabilized with nitric acid (Merck, Suprapur, diluted 1:3 v/v with redistilled water), 1ml of diluted  $\text{HNO}_3$  per 100 ml of sample. Water samples of this type (signed pvf) contain the forms of elements which were dissolved at the moment of sampling, or
- acidified in the field with diluted (1:3 v/v) nitric acid (Merck, Suprapur, 1ml of diluted  $\text{HNO}_3$  per 100 ml of sample) and filtered after 24 hrs. in a laboratory in the same way as mentioned above. Liquid samples of this type (signed pvx) contain the dissolved plus acid soluble forms of elements, which are present in the suspended matter of the sampled stream.
- Unfiltered and unstabilized samples of surface water were collected simultaneously for the determination of bulk chemical composition and for the pH- measurements. Determination of pH was accomplished by the pH-meters HACH One (USA) and WTW pH 91 (Germany).

#### Stem wood, bark and assimilation organs of beech and spruce

Samples of the forest vegetation were collected from beech (*Fagus sylvatica* L.) and spruce (*Picea abies* L. Karst) trees inside the plots of the throughfall samplers (Fig. 1). Sampling of the stem wood and bark occurred in the autumn season (3. November 1997) from 3 trees of each species. A 1  $\text{cm}^2$  square of bark was cut approximately 1.3 m above ground and the stem wood was sampled from the most recent xylem rings into the pith of the stem with an increment steel borer coated with PTFE (Haglöf Sweden, length 40 cm, core diameter 0.5 cm). The auger

was rinsed with ethanol, diluted nitric acid and distilled water before the drilling, to prevent contamination of the wood cores. The samples were divided into three 3cm long subsamples, which represented inner- middle- and outer parts of the tree rings. Each subsample was then decomposed (see below) and analysed separately.

Assimilation organs of beech trees were sampled throughout a single growing season in 1997 from May till December. The leaves were sampled from one particular tree and branch. They were dried in flow box in a laboratory at room temperature and stored in sealed PE bags in a cooler until the analyses.

The spruce litter was sampled throughout one hydrological year (1997) in the plot of the throughfall collectors. Samples were collected in a 0.5 m<sup>2</sup> conical PE litter trap, which was emptied monthly. Samples were dried at room temperature in a flow box, the needles were separated from other debris, weighted and stored in the sealed plastic bags. A weighted mean single sample was then prepared from the monthly samples of the spruce needles at the end of the sampling period.

The sampled and dried assimilation organs were analysed without any cleaning to avoid losses of the soluble portion of analysed elements from the tissues. The applied procedure, on the other hand, did not clear away possible dust particles attached to the leaf surface, which were washed out by occasional precipitation events only.

#### Analyses of the liquid samples

Analyses of atmospheric precipitation, surface water, beech- and spruce throughfall and stemflow, as well as of the soil extracts (see below) were performed at the laboratory of the Geological Institute of AS CR. Concentration of Be was determined using atomic absorption spectrometry (VARIAN SpectrAA 300). The graphite furnace technique (ETA) was employed for the concentration level of 0, X - X,0 ppb Be. The precision of the determination was  $\pm 4,0$  % at the concentration level of 0,3 ppb Be.

#### Analyses of the solid samples

Solid rocks and organic matter were analyzed mostly in the laboratories of Analytika Ltd., Prague. The rock- and soil samples were crushed and pulverised in a mechanical agate mill. They were decomposed by a mixture of HF + HNO<sub>3</sub> or HF + HClO<sub>4</sub> acids. The organic material was decomposed with hot concentrated HNO<sub>3</sub> (Merck, Suprapur) under pressure. Decomposition of all types of samples was carried out in the microwave oven in a PTFE crucible. The concentration of Be and other trace elements was determined by ICP-MS spectrometry using the Varian UltraMass instrument.

#### Experimental acid leaching of the underlying rocks

The behavior of Be during the chemical weathering of the granite rocks was simulated with the acidic leaching of the crushed rocks using 0,01 M HNO<sub>3</sub> in a laboratory at 22°C and atmospheric pressure (see lower).

#### Determination of Be forms in soil

Beryllium concentration and speciation in the individual layers of the soil profile was studied in the soil fraction < 1mm. Total Be concentration was determined after the wet decomposition of soil samples (by a mixture of concentrated acids HF and HClO<sub>4</sub>) under pressure in PTFE crucibles, in a microwave oven. Acid-soluble forms of Be in the individual soil horizons were determined after the extraction of soil particles < 1mm in 0,1 M

nitric acid (Merck, Suprapur) for 24 hours at room temperature (V/m = 200, see also Minařík et al. 1998). Adsorbed beryllium in the soil horizons was determined after the extraction of soil particles < 1mm with 0,5 M NH<sub>4</sub>NO<sub>3</sub> for 24 hrs. at V/m = 200 and room temperature (see also Hornburg et al. 1995).

## Results and discussion

### Beryllium in the parent rock

Distribution of Be in both granitic types is shown in the Table 4.

monzogranite	syenogranite	author	method
average	range	average	range
12 (3)	-	-	-
13 (33)	<4-24	7 (5)	4-12
13 (1)	-	-	-
8,4 (11)	5-14	-	-
-	-	11 (1)	-
12,7 (1)	-	11,5 (1)	-

1 - fluorimetric determination with morin after sorption on silica gel from EDTA solution.

2 - optical emission spectrography

3 - flameless atomic absorption spectroscopy.

**Tab. 4.** Beryllium concentration in granitic rocks of the Říčany massif (analytical data in ppm, number of samples in brackets).

Both types of the parent granite are enriched in Be compared to typical granite (Rössler and Lange 1972), but the Be-concentration is higher in monzogranite than in syenogranite (12.7 mg.kg<sup>-1</sup>, and 11.5 mg.kg<sup>-1</sup>, respectively). Distribution of Be in the rock is not well known. Due to the size of Be<sup>2+</sup> it is believed that beryllium substitutes for Si in tetrahedral coordination in common rock-forming minerals such as micas and feldspars according to the scheme [Be<sup>2+</sup>Si<sup>4+</sup>]<sup>IV</sup>  $\leftrightarrow$  2 [Al<sup>3+</sup>]<sup>IV</sup>, but there is no direct evidence of this substitution. The presence of beryl occluded in feldspar is possible (Smith 1974). The data from Hörman in the Handbook of Geochemistry suggest that Be tends to favor plagioclase over coexisting K-feldspar and biotite. Ljachovic (1972), who studied numerous major rock-forming minerals which were separated from the intrusive granites, gives following average values for Be (the number of samples is in the brackets): biotite 4.9 mg.kg<sup>-1</sup> (137), muscovite 47.4 mg.kg<sup>-1</sup> (-), amphibole 8.3 mg.kg<sup>-1</sup> (22), plagioclase 11.8 mg.kg<sup>-1</sup> (199), K-feldspar 3.1 mg.kg<sup>-1</sup> (211), and quartz 0.76 mg.kg<sup>-1</sup> (203).

Our preliminary results were obtained on the basis of separation of the main minerals from monzogranite (locality Srbin) - vol. % of the mineral rock concentration in brackets:

biotite (8.4) - 8.3 mg.kg<sup>-1</sup>

K-feldspar (32.7) - 11.9 mg.kg<sup>-1</sup>

plagioclase<sup>II</sup> (27.5) - 14.8 mg.kg<sup>-1</sup>

quartz (24.8) - < 0.8 mg.kg<sup>-1</sup> (Navrátil 1999)

bulk rock (100) - 12.6 mg.kg<sup>-1</sup>

1/- analysed plagioclase sample contained admixture of quartz.

It is clear, that feldspars have to be the most important carriers of Be due to their considerable mass proportion in the granites. Beryllium concentration in sandstone underlying the sampling localities Truba and Arboretum is by one order lower than in

horizon	depth	percent of clay	total Be conc. mg.kg <sup>-1</sup>	acid-leachable Be mg.kg <sup>-1</sup> *	percent of leaching	NH <sub>4</sub> -leachable Be mg.kg <sup>-1</sup> **	percent of leaching
A	7,5	6,8	3,75	0,14	3,73	0,078	2,08
B <sub>w</sub>	24,0	20,5	5,43	0,60	11,05	0,112	2,06
Go	40,5	10,4	6,33	0,55	8,69	0,074	1,17
Gr <sub>1</sub>	57,5	32,2	6,21	1,11	17,87	0,510	8,21
Gr <sub>2</sub>	70,5	32,0	6,03	1,39	23,05	0,620	10,28
Gr <sub>3</sub>	85,5	9,0	6,30	0,60	9,52	0,240	3,81
Gr <sub>4</sub>	95,0	18,1	7,38	1,22	16,53	0,600	8,13

\* leaching with 0.1 M HNO<sub>3</sub> \*\* leaching with 0.5 M NH<sub>4</sub>NO<sub>3</sub>

Tab. 5. Distribution of total-, acid soluble- and exchangeable Be in the soil profile LP-33.

granites of the Říčaný massif (see the Table 4), but its leachability with slightly acid solutions (0.01 M HNO<sub>3</sub>) is much better, as it is shown in the Tab. 3.

**Behavior of Be during the rock weathering**

*a/ laboratory results*

Results of fourteen - day laboratory batch leaching of crushed rocks forming the bedrock of the catchment (0,16 - 0,25mm size fraction) show relatively strong bonding of Be both in monzo- and syenogranite. Out of the selected elements, Be is released into the reaction solution more readily than As and Fe, but less easily than Cd, Co, Cu, Mn, and Ni (Minařík et al. 1997a). Leaching experiments confirmed high mobility of Be during the hydrolysis of biotite (Minařík et al. 1997b).

*b/ field study*

The variations of Be- concentration during the weathering of monzogranite were studied in the vertical profile, which has developed in the central part of the catchment. The material ranging from unaltered rock to the residual soil has been sampled in an old quarry. The general field alteration scale is: fresh rock → slightly altered rock with several cracks, fractures filled with clay → strongly weathered rock broken into blocks → friable material with granular structure → brown forest soil with clasts. Mineralogy and bulk chemistry of the samples is given in Minařík et al. (1983). With increasing weathering, the concentration of Be continuously decreases from 13 to 8 ppm and is

the lowest in the residual soil. The Be- distribution in the profile is very similar to that of K.

**Beryllium in soil**

The distribution of Be in soil was studied in the vertical profile which has developed by the closing profile of the catchment (locality LP33, Fig. 1) from the syenogranite of the Jevany type. The material was sampled from a 1m deep pit near the weir of the catchment. The soil is classified (Spaargaren 1994) as a gleyic cambisol. Seven horizons were distinguished, and their mineralogy is identical: quartz, kaolinite, illite, orthoclase, plagioclase, and a small amount of smectite.

A (depth 0 - 15 cm) - very dark brown, moist, loamy sand, moderate coarse granular, very friable, abundant very fine and fine roots, abrupt, smooth boundary, density ρ = 0.78 g.cm<sup>-3</sup>.

AB (15 - 33 cm) - yellowish brown, moist, loamy, moderate medium angular, friable, abundant very fine roots, clear, smooth boundary, ρ = 1.23 g.cm<sup>-3</sup>.

Bw (33 - 48cm) - yellow, moist, loamy sand, structure-less, non-coherent, clear, smooth boundary, ρ = 1.80 g.cm<sup>-3</sup>.

Gr<sub>1-4</sub> (48 - 101cm) - light grey, moist, loamy, structure-less, plastic, small soft spherical reddish brown iron-rich nodules, ρ = 1.62 g.cm<sup>-3</sup>.

The horizons AB and Bw were described previously as Bw and Go, respectively (Minařík et al. 1998, Skřivan et al. 1997).

species locality		spruce LP7					beech LP6				
stem wood tree No.	content part	Be ppb	Cu ppm	Mg ppm	Mn ppm	Zn ppm	Be ppb	Cu ppm	Mg ppm	Mn ppm	Zn ppm
1	inner		0,93	118,00	197,00	10,70		1,11	178,00	50,00	3,70
	middle		0,81	107,00	183,00	9,20		1,24	148,00	41,00	5,50
	outer		0,95	98,00	171,00	9,20		1,54	160,00	32,00	3,90
	wt. mean	11,10	0,90	103,00	177,90	9,40	22,30	1,39	158,00	37,00	4,40
2	inner		0,94	120,00	230,00	10,40		1,13	226,00	54,00	7,50
	middle		0,80	89,00	180,00	9,50		1,31	106,00	15,00	7,20
	outer		1,25	85,00	159,00	7,60		1,66	129,00	42,00	5,00
	wt. mean	7,50	1,07	90,00	173,90	8,60	16,60	1,48	132,00	34,00	6,00
3	inner		0,90	108,00	304,00	12,40		1,11	319,00	156,00	5,20
	middle		0,70	83,00	202,00	9,80		1,00	435,00	100,00	3,50
	outer		1,80	122,00	177,00	106,00*		1,28	270,00	55,00	5,00
	wt. mean	22,70	1,33	107,00	199,40	10,50	22,70	1,17	330,00	81,00	4,50
mean		13,80	1,10	100,00	184,00	9,50	20,50	1,35	207,00	51,00	5,00
bark, mean		78,30	4,14	798,00	1383,00	160,20	68,20	3,48	586,00	364,00	15,00

\*/ the sample probably spoiled by contamination, not involved in calculations

Tab. 6. Concentration of Be, Cu, Mg, Mn, and Zn in stem wood of inner-, middle- and outer part of 3 stems of beech and spruce, mean concentration in bark (all in µg.kg<sup>-1</sup> d.wt.).

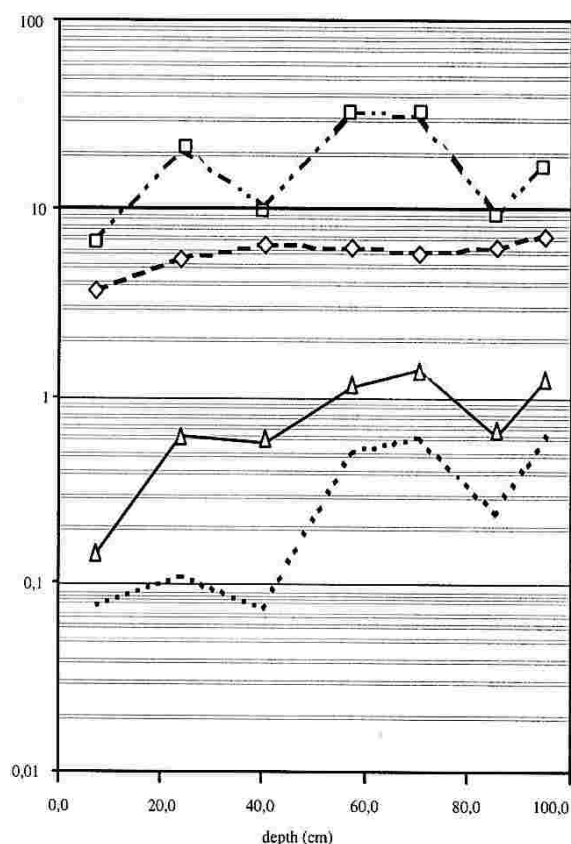


Fig. 8. Distribution pattern of beryllium throughout the soil profile: total Be (diamonds), acid leachable Be (triangles), ammonium nitrate leachable Be (crosses), concentration of physical clay (squares).

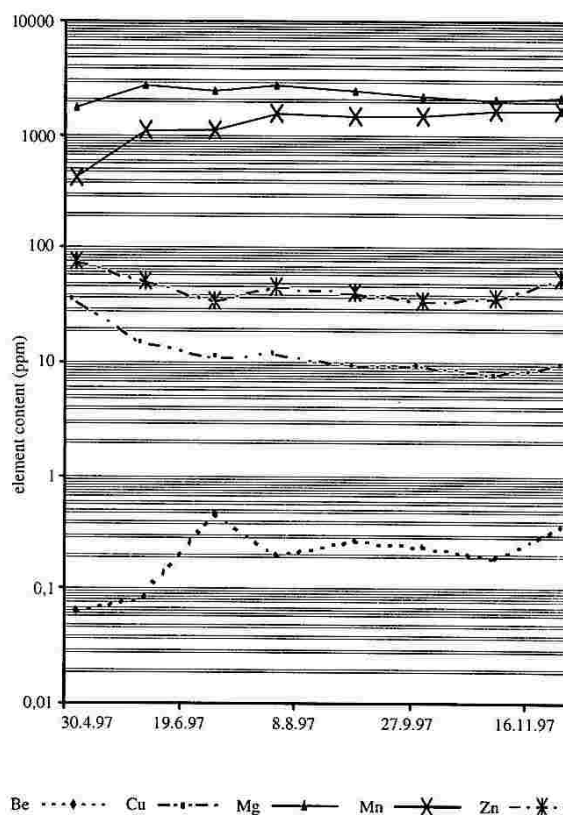


Fig. 9. Concentration of Be, Cu, Mg, Mn, Zn in leaves of beech (*Fagus sylvatica* L.) in dependence on their age (sampling date).

Further more detailed study of soil cover of the catchment has shown that the new description of soil horizons is more precise. The distribution of clay and Be in the soil profile is shown in Fig. 8. The variations in the total Be-concentration with depth are presented in the Tab. 5. The Be concentration increases, more or less regularly, from 3,75 ppm in the topsoil to 7,38 ppm in the deepest place of the profile. The concentration of acid-leachable Be (portion of the element soluble in 0.1 M HNO<sub>3</sub>) increases also from the umbric A horizon towards the bottom of the profile. Variations are in this case greater and more dependent on the amount of clayey fraction in the individual soil horizons. The dependence is even more evident in the 0,5 M NH<sub>4</sub>NO<sub>3</sub>-leachable forms of Be (Fig 8.). The concentration of exchangeable beryllium is proportional to the content and adsorption capacity of the secondary clay minerals in the soils. General decrease of the concentration of all determined Be forms towards the surface indicates that the mobile part of Be is leached and transported through the pores of the fine grained soil material to the lower horizons of the profile by soil water. Strong acids of anthropogenic origin which decrease the pH of precipitation (recent mean pH value in Central Bohemia is 4.3) accelerate this process, as the mobility of Be in soil rapidly increases under more acidic conditions. Organic acids also probably contribute to the translocation of Be.

#### Beryllium in stem wood, bark and assimilation organs of beech- and spruce trees

Concentration of Be in stem wood of three examined beech- and spruce trees, together with its mean concentration in bark, is presented in the Table 6. The table contains also figures for Cu, Mg, Mn, and Zn, to compare with values presented previously in the literature (Heinrichs and Mayer 1980; Hagemeyer and Schäfer 1995; Hagemeyer and Lohrie 1995). Comparison of the obtained data concerning the Be concentration in stem wood with the results of the others was not possible, as no published data for these species were found in the literature. Concentration of Cu, Mn and Zn in stem wood and bark of beech is considerably lower, compared with values presented by Heinrichs and Mayer (1980) for trees from the Solling Mountains in central Germany. Our values of spruce are lower again in Cu and Zn, but higher in Mn for both the stem wood and bark. Concentration of Zn in stem wood of beech trees from northern Germany (Hagemeyer and Schäfer 1995) is comparable with our values.

Concentration (d.wt.) of Be, Cu, Mg, Mn, and Zn and their gradual changes with time in leaves of beech (*Fagus sylvatica* L.) collected in 1997 at the locality LP6, are shown in the Table 7. The Table presents also values of the concentration of elements in the average sample of spruce needles collected throughout



the whole year 1997. Cu and Mn indicate marked seasonal variation of their concentration in leaves: trend of Mn is progressive, and that of Cu is decreasing. The remaining two essential elements, Mg and Zn, and also Be, do not exhibit any unambiguous trend and their concentration does not correlate with the precipitation intensity preceding the individual sampling events.

Physiological tasks of Mg and Zn in the tree tissues are significant and numerous. In case of Zn, however, there exists also considerable atmospheric input of aerosols from anthropogenic sources. Course in the concentration of the individual studied elements throughout the sampling time span is clearly shown in the Fig. 9. Distinct trends in Cu and Mn concentrations in leaves are evidently connected with their status in the metabolic processes of the living vegetation. Manganese is mainly important in the photosynthetic processes of the green parts of the vegetation and its uptake is high. Transport of copper in the tissues of the vegetation, on the other hand, is difficult and its uptake is very limited. The majority of Cu is concentrated in the chloroplasts, where it acts as a stabiliser of the chlorophyll.

year	sampling date	precipitation height <sup>1/</sup> m m	concentration of elements, d.wt.				
			Be µg.kg <sup>-1</sup>	Cu mg.kg <sup>-1</sup>	Mg mg.kg <sup>-1</sup>	Mn mg.kg <sup>-1</sup>	Zn mg.kg <sup>-1</sup>
1997	5.V.97	36,7	65,2	34,90	1716	414	77,6
	4.VI.97	18,3	84,4	15,10	2785	1072	51,6
	4.VII.97	72,6	460,3	11,20	2463	1128	33,9
	31.VII.97	71,2	198,4	12,20	2773	1505	46,6
	3.IX.97	53,0	262,8	9,20	2433	1495	41,0
	2.X.97	13,7	244,6	9,40	2182	1440	35,2
	3.XI.97	19,8	188,1	8,00	2026	1622	37,2
	1.XII.97	22,6	347,7	9,40	1662	1660	53,4
spruce needles <sup>2/</sup>	307,9	309,8	3,65	813	1771	26,6	

1 - monthly precipitation height of the beech throughfall (see the Tab. 13b) collected at the same place

2 - mean sample. Litter collected monthly throughout the year 1997

Tab. 7. Concentration of Be, Cu, Mg, Mn, and Zn in beech leaves as a function of growing season, mean concentration in spruce needles.

year	date	month	n (days)	P (mm) <sup>1/</sup>	pH	cBe	L/A <sup>2/</sup>
1989	31-Aug-89 to 30-Sep-89	8 to 9	64	123,90	n.d.	<0,20	1
	1-Nov-89 to 2-Jan-90	10 to 12	94	94,70	n.d.	<1,00	2
1990	1-Feb-90 to 3-Jan-91	1 to 12	366	450,02	n.d.	<1,00	2
1991	4-Feb-91 to 2-Sep-91	1 to 8	242	378,70	n.d.	<1,00	2
1992	30.X.92	10	30	43,81	n.d.	<0,50	3
1993	1-May-93 to 1-Sep-93	4 to 8	153	317,72	n.d.	<1,00	3
	1.X.93	9	30	59,30	n.d.	<0,04	4
	2.XI.93	10	32	50,45	n.d.	<0,04	4
	30.XI.93	11	28	63,72	n.d.	<0,04	4
	4.I.94	12	35	82,75	n.d.	<0,04	4
1994	2.II.94	1	29	23,45	n.d.	<0,04	4
	2.III.94	2	28	24,34	n.d.	0,08	4
	30.III.94	3	28	70,36	4,05	0,05	4
	3.V.94	4	34	57,53	3,42	0,05	4
	2.VI.94	5	30	66,38	4,10	<0,04	4
	30.VI.94	6	28	41,15	4,40	0,06	4
	28.VII.94	7	28	75,23	4,12	<0,04	4
	31.VIII.94	8	34	81,42	3,94	<0,04	4
	28.IX.94	9	28	48,23	4,28	<0,04	4
	1.XI.94	10	34	31,42	4,12	<0,04	4
	1.XII.94	11	30	33,19	4,18	<0,04	4
	10.I.95	12	40	81,86	4,36	<0,04	4
	1995	31.I.95	1	21	60,62	4,42	<0,04
1.III.95		2	29	38,06	4,37	<0,04	4
3.IV.95		3	33	56,20	4,26	0,03	4
2.V.95		4	29	55,67	4,01	<0,04	4
2.VI.95		5	31	132,04	4,40	<0,04	4
3.VII.95		6	31	80,45	3,97	<0,04	4
7.VIII.95		7	35	65,84	4,15	0,03	4
4.IX.95		8	28	97,35	6,15	<0,04	4
3.X.95		9	29	90,54	4,37	<0,04	4
2.XI.95		10	30	14,60	3,91	<0,04	4
7.XII.95		11	35	47,79	4,70	<0,04	4
9.I.96		12	33	46,55	4,33	0,06	4

/1: precipitation height (mm)

/2: (laboratory, author): 1 - Stavební geologie, Dr. Konopáčová  
2 - Geoindustria, Dr. Blahovec  
3 - Geoindustria, Dr. Manda  
4 - Geological Inst. AS, Dr. Burian

Tab. 8. Be concentration in bulk atmospheric precipitation (µg.L<sup>-1</sup>) at Truba (TR).

year	date	month	n (days)	P (mm) <sup>1)</sup>	pH	cBe	L/A <sup>2)</sup>
1996	6.II.96	1	28	5,13	4,21	<0,04	4
	1.III.96	2	24	30,53	4,19	<0,04	4
	2.IV.96	3	32	35,67	3,97	0,08	4
	3.V.96	4	31	44,60	4,06	0,05	4
	30.V.96	5	27	97,79	4,36	<0,04	4
	2.VII.96	6	33	98,68	4,19	0,05	4
	5.VIII.96	7	34	97,26	4,27	<0,04	4
	3.IX.96	8	29	70,09	4,43	<0,04	4
	3.X.96	9	30	56,46	4,21	<0,04	4
	4.XI.96	10	32	40,27	4,22	<0,04	4
	2.XII.96	11	28	33,36	4,40	<0,04	4
	9.I.97	12	38	48,14	4,22	0,04	4
1997	4.II.97	1	26	4,96	4,02	0,07	4
	5.III.97	2	29	44,16	4,37	0,05	4
	2.IV.97	3	28	65,84	4,23	<0,04	4
	5.V.97	4	33	49,83	4,27	<0,04	4
	4.VI.97	5	30	40,53	4,24	<0,04	4
	4.VII.97	6	30	145,23	4,78	<0,04	4
	31.VII.97	7	27	112,93	4,11	<0,04	4
	3.IX.97	8	34	112,75	4,15	<0,04	4
	2.X.97	9	29	30,89	5,80	<0,04	4
	3.XI.97	10	32	36,90	4,48	<0,04	4
	1.XII.97	11	28	35,93	4,13	<0,04	4
	9.I.98	12	39	56,73	4,37	<0,04	4

/1: precipitation height (mm)

/2: (laboratory, author): 1 - Stavební geologie, Dr. Konopáčová  
2 - Geoindustria, Dr. Blahovec  
3 - Geoindustria, Dr. Manda  
4 - Geological Inst. AS, Dr. Burian

Tab. 8. Be concentration in bulk atmospheric precipitation ( $\mu\text{g}\cdot\text{L}^{-1}$ ) at Truba (TR), *continued*.

It also specifically activates several oxidases, such as cytochromoxidase, polyfenyloxidase, or oxidase of the ascorbic acid. The role of beryllium in the metabolism of trees is unknown, but its concentration in various tree tissues does not exclude the possibility of Be root uptake and physiological cycling together with some of the important essential elements.

## Fluxes

### Concentration, fluxes and trends of beryllium in the bulk atmospheric precipitation.

Table 8 contains the whole set of results of the bulk atmospheric precipitation, for a review. It presents results from various analytical laboratories with differing detection limits of the Be-determination. Tables 9 and 10 are arranged in the same way and they involve values of the concentration of Be (cBe, in  $\mu\text{g}\cdot\text{L}^{-1}$ ) and fluxes of Be, Al, Fe, Mn (fMe, in  $\mu\text{g}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$ ), together with volume and pH of the collected samples. Al and Fe were chosen as typical major lithogenic elements, and Mn represents a group of minor- or trace essential elements with strong internal cycling caused by metabolic processes of the vegetation.

Mean annual pH values, which were calculated from the mean volume – weighted concentrations of  $\text{H}^+$  ions vary between 4.25 and 4.30. Results of the bulk precipitation monitored at the ARB are not so plentiful, because they cover only (up to the end of 1997) 20 months. Nevertheless, values of the fBe and other presented elements, as well as the volume weighted mean pH, are close to the corresponding values of the TR.

Mean values of the fluxes of elements were employed for the evaluation of relative enrichment factors of the selected el-

ements in bulk precipitation ( $\text{EF}_{\text{Me}}$ ) with respect to their concentration in the bedrock of the sampling localities. Concentration of Be and other elements were normalised to Fe as a reference element. The relative enrichment factor was calculated according to the following equation:

$$\text{EF}_{\text{Me}} = \frac{\text{fMe} \cdot c_{\text{Fe}}(\text{rock})}{\text{fFe} \cdot c_{\text{Me}}(\text{rock})}$$

where fMe, fFe represent the mean annual flux of the examined element and iron in bulk precipitation, and  $c_{\text{Fe}}(\text{rock})$ ,  $c_{\text{Me}}(\text{rock})$  indicate the concentration of the element and Fe in the bedrock.

The mean value of  $\text{EF}_{\text{Al}}$  in both sampling sites is close to 1, which documents its comparable character and sources with the reference element. High values of  $\text{EF}_{\text{Mn}}$  are strongly affected by the extreme Mn concentrations in bulk precipitation in the late autumn months, which suggests "contamination" of the precipitation with throughfall.

This phenomenon follows from strong metabolic uptake and release of Mn by the tree vegetation, as described previously (Skřivan et al. 1997).

Increased mean values of  $\text{EF}_{\text{Be}}$  (12.8, and 18.2, respectively,) most probably originate in the insufficient detection limit of the applied analytical method, as majority of the determined Be values is below this limit ( $0.04 \mu\text{g}\cdot\text{L}^{-1}$ ). Values of the computed Be-fluxes (fBe), where one half of the detection limit was used in this case, had to be therefore overestimated.

The uncertainty of true analytical concentrations of Be in the bulk precipitation has been recently solved by pre-concentration of samples (see the Chapter Bulk precipitation, throughfall and stemflow). Tab. 11 presents the first results of

year	date	month	n days	P (mm)	pH	cBe	fBe	fAl	fFe	fMn	fBe/fFe	fAl/fFe	fMn/fFe
1993	1.X.93	9	30	59,30	n.d.	0,020	0,040	n.d.	112,70	15,4	0,00035		0,13684
	2.XI.93	10	32	50,45	n.d.	0,020	0,032	n.d.	129,30	31,1	0,00024		0,24024
	30.XI.93	11	28	63,72	n.d.	0,020	0,046	n.d.	111,50	111,5	0,00041		1,00000
	4.I.94	12	35	82,75	n.d.	0,020	0,047	n.d.	63,80	125,3	0,00074		1,96296
sum			<b>256,21</b>										
mean			<b>64,05</b>			<b>0,041</b>		<b>104,30</b>	<b>70,8</b>				
1994	2.II.94	1	29	23,45	n.d.	0,020	0,016	n.d.	49,30	8,9	0,00033		0,18033
	2.III.94	2	28	24,34	n.d.	0,080	0,070	n.d.	86,90	12,5	0,00080		0,14400
	30.III.94	3	28	70,36	4,050	0,050	0,126	n.d.	115,60	18,6	0,00109		0,16087
	3.V.94	4	34	57,53	3,420	0,050	0,085	n.d.	169,20	27,9	0,00050		0,16500
	2.VI.94	5	30	66,38	4,100	0,020	0,044	n.d.	214,60	32,7	0,00021		0,15258
	30.VI.94	6	28	41,15	4,400	0,060	0,088	n.d.	161,70	20,6	0,00055		0,19272
	28.VII.94	7	28	75,23	4,120	0,020	0,054	n.d.	239,10	18,8	0,00022		0,07865
	31.VIII.94	8	34	81,42	3,940	0,020	0,048	n.d.	205,90	27,8	0,00023		0,13488
	28.IX.94	9	28	48,23	4,280	0,020	0,034	n.d.	89,60	37,2	0,00038		0,41538
	1.XI.94	10	34	31,42	4,120	0,020	0,018	n.d.	60,10	10,0	0,00031		0,16615
	1.XII.94	11	30	33,19	4,180	0,020	0,022	n.d.	69,70	254,4	0,00032		3,65079
	10.I.95	12	40	81,86	4,360	0,020	0,041	n.d.	30,70	4,7	0,00133		0,15333
sum			<b>634,55</b>										
mean			<b>52,88</b>	<b>4,019</b>		<b>0,054</b>		<b>124,40</b>	<b>39,5</b>				
1995	31.I.95	1	21	60,62	4,420	0,020	0,058	n.d.	161,70	13,3	0,00036		0,08214
	1.III.95	2	29	38,06	4,370	0,020	0,026	n.d.	64,30	4,3	0,00041		0,06735
	3.IV.95	3	33	56,20	4,260	0,030	0,051	n.d.	122,60	32,4	0,00042		0,26389
	2.V.95	4	29	55,67	4,010	0,020	0,038	n.d.	172,80	27,6	0,00022		0,16000
	2.VI.95	5	31	132,04	4,400	0,020	0,085	n.d.	208,70	40,9	0,00041		0,19592
	3.VII.95	6	31	80,45	3,970	0,020	0,052	80,40	80,40	9,1	0,00065	1,00000	0,11290
	7.VIII.95	7	35	65,84	4,150	0,030	0,056	90,70	99,70	11,3	0,00057	0,90943	0,11321
	4.IX.95	8	28	97,35	6,150	0,020	0,070	140,80	146,00	18,1	0,00048	0,96429	0,12381
	3.X.95	9	29	90,54	4,370	0,020	0,062	69,90	46,80	8,7	0,00133	1,49333	0,18667
	2.XI.95	10	30	14,60	3,910	0,020	0,010	73,00	248,20	10,0	0,00004	0,29412	0,04020
	7.XII.95	11	35	47,79	4,700	0,020	0,027	71,50	91,50	204,8	0,00030	0,78209	2,23881
	9.I.96	12	33	46,55	4,330	0,060	0,085	75,50	69,10	27,1	0,00122	1,09184	0,39184
sum			<b>785,70</b>										
mean			<b>65,48</b>	<b>4,295</b>		<b>0,052</b>	<b>86,00</b>	<b>126,00</b>	<b>34,0</b>				
1996	6.II.96	1	28	5,13	4,210	0,020	0,004	133,80	82,50	7,3	0,00004	1,62222	0,08889
	1.III.96	2	24	30,53	4,190	0,020	0,025	152,70	122,10	17,7	0,00021	1,25000	0,14479
	2.IV.96	3	32	35,67	3,970	0,080	0,089	200,60	167,20	15,0	0,00053	1,20000	0,09000
	3.V.96	4	31	44,60	4,060	0,050	0,072	259,00	215,80	18,7	0,00033	1,20000	0,08667
	30.V.96	5	27	97,79	4,360	0,020	0,072	345,50	148,50	242,7	0,00049	2,32683	1,63415
	2.VII.96	6	33	98,68	4,190	0,050	0,150	93,60	122,60	19,1	0,00122	0,76341	0,15610
	5.VIII.96	7	34	97,26	4,270	0,020	0,057	48,60	85,80	7,7	0,00067	0,56667	0,09000
	3.IX.96	8	29	70,09	4,430	0,020	0,048	64,30	103,90	9,2	0,00047	0,61860	0,08837
	3.X.96	9	30	56,46	4,210	0,020	0,038	78,30	28,20	9,0	0,00133	2,77333	0,32000
	4.XI.96	10	32	40,27	4,220	0,020	0,025	31,50	39,00	16,7	0,00065	0,80645	0,42903
	2.XII.96	11	28	33,36	4,400	0,020	0,024	52,50	54,80	98,9	0,00043	0,95870	1,80435
	9.I.97	12	38	48,14	4,220	0,040	0,051	190,00	81,10	44,3	0,00063	2,34375	0,54688
sum			<b>658,00</b>										
mean			<b>54,83</b>	<b>4,232</b>		<b>0,055</b>	<b>137,50</b>	<b>104,30</b>	<b>42,2</b>				
1997	4.II.97	1	26	4,96	4,020	0,070	0,013	59,10	26,70	4,7	0,00050	2,21429	0,17500
	5.III.97	2	29	44,16	4,370	0,050	0,076	467,50	53,30	7,8	0,00143	8,77143	0,14571
	2.IV.97	3	28	65,84	4,230	0,020	0,047	120,60	108,20	15,5	0,00043	1,11522	0,14348
	5.V.97	4	33	49,83	4,270	0,020	0,030	151,00	226,50	81,5	0,00013	0,66667	0,36000
	4.VI.97	5	30	40,53	4,240	0,020	0,027	148,60	83,80	28,2	0,00032	1,77419	0,33710
	4.VII.97	6	30	145,23	4,780	0,020	0,097	138,00	217,80	31,0	0,00044	0,63333	0,14222
	31.VII.97	7	27	112,93	4,110	0,020	0,084	91,20	62,70	15,5	0,00133	1,45333	0,24667
	3.IX.97	8	34	112,75	4,150	0,020	0,066	295,10	202,30	22,5	0,00033	1,45902	0,11148
	2.X.97	9	29	30,89	5,800	0,020	0,021	106,50	91,60	11,6	0,00023	1,16279	0,12674
	3.XI.97	10	32	36,90	4,480	0,020	0,023	47,20	63,40	28,5	0,00036	0,74364	0,44909
	1.XII.97	11	28	35,93	4,130	0,020	0,026	34,30	19,20	43,6	0,00133	1,78000	2,26667
	9.I.98	12	39	56,73	4,370	0,020	0,029	39,70	21,80	16,7	0,00133	1,82000	0,76667
sum			<b>736,67</b>										
mean			<b>61,39</b>	<b>4,300</b>		<b>0,028</b>	<b>0,045</b>	<b>141,57</b>	<b>98,10</b>	<b>25,6</b>	<b>0,00084</b>	<b>1,50190</b>	<b>0,45377</b>
						EF <sub>Me</sub>	<b>18,200</b>	<b>2,10</b>	<b>1,00</b>	<b>195,0</b>			

/I: precipitation height (mm)

Values of cBe = 0.02 represent one half of the detection limit of the determination.

Tab. 9. Content of Be ( $\mu\text{g}\cdot\text{L}^{-1}$ ), and flux of Be, Al, Mn, Fe ( $\mu\text{g}\cdot\text{m}^{-2}\cdot\text{day}^{-1}$ ) in bulk atmospheric precipitation, sampling site Truba (TR).

year	date	month	n (days)	P (mm) <sup>1</sup>	pH	cBe	fBe	fAl	fFe	fMn	fBe/fFe	fAl/fFe	fMn/fFe
1996	30.V.96	5	27	105,57	4,36	0,02	0,078	145,50	164,200	21,50	0,00048	0,88611	0,13094
	2.VII.96	6	33	92,45	4,19	0,05	0,056	195,30	254,900	19,10	0,00022	0,76618	0,07493
	5.VIII.96	7	34	106,03	4,27	0,02	0,056	66,90	41,700	12,40	0,00134	1,60432	0,29736
	3.IX.96	8	29	65,39	4,43	0,02	0,045	68,30	72,200	10,60	0,00062	0,94598	0,14681
	3.X.96	9	30	58,41	4,21	0,02	0,039	0,00	29,200	15,80	0,00134	0,00000	0,54110
	4.XI.96	10	32	37,02	5,04	0,02	0,023	0,00	38,200	67,40	0,00060	0,00000	1,76440
	2.XII.96	11	28	34,79	4,40	0,02	0,025	65,40	58,400	68,30	0,00043	1,11986	1,16952
	9.I.97	12	38	38,32	4,22	0,03	0,030	131,10	78,700	19,80	0,00038	1,66582	0,25159
	sum			537,97									
mean			67,25	4,31		0,044	84,06	92,190	29,36				
EF <sub>Me</sub>							8,120	1,00	0,780	210,00			
1997	4.II.97	1	26	5,67	4,02	0,08	0,017	76,40	39,300	4,80	0,00043	1,94402	0,12214
	5.III.97	2	29	36,65	4,37	0,02	0,025	43,50	46,800	8,00	0,00053	0,92949	0,17094
	2.IV.97	3	28	44,74	4,23	0,02	0,032	87,90	81,500	12,50	0,00039	1,07853	0,15337
	5.V.97	4	33	33,76	4,27	0,02	0,020	133,00	143,200	21,70	0,00014	0,92877	0,15154
	4.VI.97	5	30	37,67	4,24	0,02	0,025	163,20	84,100	91,70	0,00030	1,94055	1,09037
	4.VII.97	6	30	105,47	4,78	0,02	0,070	120,90	140,600	19,70	0,00050	0,85989	0,14011
	31.VII.97	7	27	99,99	4,11	0,02	0,074	86,70	55,600	12,60	0,00133	1,55935	0,22662
	3.IX.97	8	34	90,78	4,15	0,02	0,053	293,70	173,600	15,80	0,00031	1,69182	0,09101
	2.X.97	9	29	29,02	5,90	0,02	0,020	240,20	83,100	9,60	0,00024	2,89049	0,11552
	3.XI.97	10	32	30,79	4,48	0,02	0,019	40,40	47,100	8,50	0,00040	0,85775	0,18047
	1.XII.97	11	28	34,51	4,13	0,02	0,025	38,70	44,400	123,20	0,00056	0,87162	2,77477
	9.I.98	12	39	46,78	4,37	0,02	0,024	39,60	18,000	14,60	0,00133	2,20000	0,81111
	sum			595,82									
mean			49,65	4,29		0,036	113,70	79,775	28,56	0,00059	1,23703	0,52023	
EF <sub>Me</sub>							12,800	1,73	1,000	224,00			

<sup>1</sup>: precipitation height (mm).

Values of cBe = 0.02 represent one half of the detection limit of the determination.

Tab. 10. Concentration of Be ( $\mu\text{g}\cdot\text{L}^{-1}$ ), and flux of Be, Al, Mn, Fe ( $\mu\text{g}\cdot\text{m}^{-2}\cdot\text{day}^{-1}$ ) in bulk atmospheric precipitation at the Arboretum (ARB).

the procedure, which has been applied for selected samples of the bulk precipitation and throughfall.

Tab. 11 shows that the sample volume of the bulk precipitation must be reduced at least 50 times and throughfall 10 times, to obtain values above the detection limit of the ETA AA Spectrometry.

The probable overestimation of the fBe values in the Tables 9 and 10 was verified by the actual values of the Be concentration in bulk precipitation (Table 11), where the mean value  $0.005 \mu\text{g Be}\cdot\text{L}^{-1}$  is more likely. This value is considerably

sample type	locality	month, year	concentration factor	Be concentration, ppb found	Be concentration, ppb calculated
bulk precipitation	TR	6/98	5,47	<0,04	<0,00773
		7/98	6,21	<0,04	<0,00644
		10/98	70,00	0,15	0,00214
bulk precipitation	ARB	5-10/98	45,00	0,28	0,00622
		6/98	7,46	0,25	0,03351
		7/98	7,25	0,19	0,02621
		12/98-1/99	15,20	0,35	0,02300
-spruce throughfall	LP7	6/98	8,16	0,18	0,02206
		7/98	4,72	<0,04	<0,00847
		12/98-1/99	19,44	1,60	0,08230

Tab. 11. Be concentration ( $\mu\text{g}\cdot\text{L}^{-1}$ ) in concentrated samples of the bulk precipitation and throughfall (GCTC collectors).

lower than that published by Krám et al. (1998) who found the volume-weighted annual Be concentration  $0,040 \mu\text{g}\cdot\text{L}^{-1}$  for the Lysina catchment in western Bohemia in 1992. That region, however, is probably more affected by emissions from the power plants burning the low-quality Be-rich brown coal from north-western Bohemian coal basins. The annual Be- flux in bulk precipitation of the Černokostelecko region (Truba, Arboretum) in the years 1993 to 1997 was 13 to  $20 \mu\text{g}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$ , compared with  $45 \mu\text{g}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$  in the Lysina catchment.

Estimated value of  $f\text{Be}_p/f\text{Fe}_p = 0.00015$ , derived from the actual values of cBe in the Tab. 11, gives then more probable mean value of the Be enrichment factor in bulk precipitation, which equals to  $\text{EF}_{\text{Be}} = 3.36$ . This value is only slightly higher than the mean value of  $\text{EF}_{\text{Al}}$ .

### Concentration and fluxes of beryllium in the mixed-, beech-, and spruce -throughfall

Chemistry of the throughfall has a complex character resulting from numerous processes which determine its chemical composition (Heinrichs and Mayer 1980; Norden 1991; Skřivan et al. 1995).

Chemical composition of the wet atmospheric precipitation entering the tree canopy, is further enriched by its interaction with the above – ground parts of the trees through several ways:

- by wash-out of solid atmospheric aerosol, which was caught by interception on the surface of the vegetation (Atteia et al. 1993; Novo et al. 1992; Hantschel et al. 1990).

- by dissolution of gaseous substances, which are adsorbed on the above – ground parts of the vegetation from



year	date	month	n (days)	P (mm) <sup>1)</sup>	n	pH	cBe	f/Be	f/Al	f/Fe	f/Mn	fBe/fFe	fAl/fFe	fMn/fFe
1993	1.VI.93	5	31	44,15	9	4,27	1,00	1,424	n.d.	384,49	6650	0,00370		17,29630
	1.VII.93	6	30	50,60	9	3,97	0,40	0,675	n.d.	202,39	3272	0,00333		16,16667
	27.VII.93	7	26	64,87	9	4,26	0,20	0,499	n.d.	274,46	2171	0,00182		7,90909
	1.IX.93	8	36	25,60	9	4,76	0,30	0,213	n.d.	184,91	1266	0,00115		6,84615
	1.X.93	9	30	27,23	9	5,56	0,10	0,091	n.d.	87,13	1026	0,00104		11,77083
	2.XI.93	10	32	41,55	9	5,21	0,02	0,026	n.d.	38,96	1753	0,00067		45,00000
	30.XI.93	11	28	39,37	9	4,98	0,10	0,141	n.d.	108,27	4415	0,00130		40,77922
	4.I.94	12	35	61,77	9	4,98	0,09	0,159	n.d.	100,60	3918	0,00158		38,94737
sum				<b>355,14</b>										
mean				<b>44,39</b>		<b>4,43</b>		<b>0,403</b>		<b>172,65</b>	<b>3059</b>			
1994	2.II.94	1	29	14,53	9	4,98	0,04	0,020	n.d.	13,53	596	0,00148		44,07407
	2.III.94	2	28	14,63	9	4,98	0,40	0,209	n.d.	125,40	1144	0,00167		9,12500
	30.III.94	3	28	48,06	9	3,59	0,09	0,154	n.d.	149,32	1322	0,00103		8,85057
	3.V.94	4	34	41,81	9	3,50	0,06	0,074	n.d.	135,26	984	0,00055		7,27273
	2.VI.94	5	30	33,02	9	5,61	0,06	0,066	n.d.	154,09	1398	0,00043		9,07143
	30.VI.94	6	28	20,22	9	5,14	0,02	0,014	n.d.	10,83	498	0,00133		46,00000
	28.VII.94	7	28	52,68	9	4,70	0,02	0,038	n.d.	127,94	1242	0,00029		9,70588
	31.VIII.94	8	34	48,51	9	4,68	0,04	0,057	n.d.	102,74	1227	0,00056		11,94444
	28.IX.94	9	28	22,76	9	4,60	0,07	0,057	n.d.	43,08	821	0,00132		19,05660
	1.XI.94	10	34	15,04	9	5,21	0,09	0,040	n.d.	26,54	946	0,00150		35,66667
	1.XII.94	11	30	17,07	9	5,87	0,09	0,051	n.d.	44,95	3408	0,00114		75,82278
	10.I.95	12	40	52,43	9	3,94	0,06	0,079	n.d.	82,57	1533	0,00095		18,57143
	sum				<b>380,75</b>									
mean				<b>31,73</b>		<b>4,04</b>		<b>0,072</b>		<b>84,69</b>	<b>1260</b>			

Tab. 12. Concentration of Be ( $\mu\text{g}\cdot\text{L}^{-1}$ ), and flux of Be, Al, Mn, Fe ( $\mu\text{g}\cdot\text{m}^{-2}\cdot\text{day}^{-1}$ ) in mixed forest throughfall, at Truba (TR), VOSS samplers.

the atmosphere (Joslin and Wolfe 1992; Kaupenjohann et al. 1988).

- by leaching and/or ion exchange of the metabolites which are excluded out from the trees on their assimilation organs (Arthur and Fahey 1993).
- Net concentration of chemical compounds in throughfall increases also by evaporation of the aqueous phase on the above – ground part of the vegetation.

On the other hand, part of the chemical constituents of the wet precipitation gets lost through uptake by the foliage. The concentration of most chemical substances in throughfall exceeds that in the bulk precipitation on an open place (Erisman 1993). Increase in their concentration depends on the intensity of interaction between the aqueous phase and the surface of the vegetation or, in other words, on the density of the individual tree crowns (Ford and Deans 1978; Robson et al. 1994; Kostelnik et al. 1989). Our study was designed to install a small number of throughfall samplers under different canopies and to draw conclusions from the evaluated relative increase of concentration of elements.

Krám et al. (1998) found only moderately higher concentration of Be in throughfall ( $0.060 \mu\text{g}\cdot\text{L}^{-1}$  vs.  $0.040 \mu\text{g}\cdot\text{L}^{-1}$  in bulk precipitation), and the calculated annual throughfall flux of Be ( $42 \mu\text{g}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$ ) was lower than that in bulk precipitation. They consider thus the dry deposition of Be as negligible.

Results of sampling of the mixed forest- beech-, and spruce throughfall, with respect to the Be concentration, are summarised in Tables 12, 13a,b, 14a,b, and 15.

Concentrations and fluxes of Be in the throughfall vary according to the location of sampling sites, the type of collector, and the vegetation type. The highest concentrations and fluxes were found at Truba (using the VOSS collectors) with mean annual Be- flux reaching 60 and  $76 \mu\text{g}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$  in the mixed-, and beech stands, respectively. Values of beech-, and spruce throughfall sampled in the Lesní potok catchment are considerably lower, especially those in samples collected in the GCTC

devices. Mean annual Be- flux in beech throughfall (VOSS collectors) is  $29 \mu\text{g}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$ , whereas in the GCTC collectors it is  $12 \mu\text{g}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$ . Values for spruce throughfall are similar. Elevated values of Be- flux in throughfall sampled at Truba, which are comparable with values presented by Krám et al. (1998), may result from local emission sources (proximity of heating equipment in several local residence houses, local road). Lower values of both concentration and flux of Be calculated from throughfall sampled into the GCTC collectors have to be attributed to their function, which seems to eliminate, to a certain extent, the deposition of particulate matter. A considerable portion of the solid aerosol, which settles on the glass cones of the collectors in the rainless periods, may slide away and is thus eliminated from the bulk samples.

Role of the forest vegetation in the biogeochemical cycling of beryllium remains to a considerable degree unknown up to now. To bring new pieces of information to solve this problem, data concerning the Be concentration and fluxes presented in the Tables 9 to 15 were examined to assess the possible sources of the element in throughfall. The evaluation was based on the introduction of an auxiliary denomination, the *throughfall mobilisation factor* ( $\text{MF}_{\text{Th}}$ ) which was defined according to the following presumptions:

1. Ratios of fluxes of an examined- and a major terrigenous element (serving as a reference substance) in bulk precipitation and in throughfall are equal, if the solid aerosol is the only source of both elements in the atmosphere and hence in both the deposition fluxes.
2. Concentrations of both the examined- and reference elements in throughfall are proportionally higher, as the above – ground parts of trees intercept the fine solid particles from the near-surface layers of the atmosphere.
3. If there exist other additional sources of the examined element in throughfall, then the ratio of fluxes of the compared elements in throughfall, normalised to their ratio in bulk atmospheric precipitation would be higher than one.

year	date	month	n (days)	P (mm) <sup>1)</sup>	n	pH	cBe	f/Be	f/Al	f/Fe	f/Mn	fBe/fFe	fAl/fFe	fMn/fFe	
1995	31.I.95	1	21	38,00	9	3,76	0,10	0,1810	n.d.	137,52	2045	0,00132		14,86842	
	1.III.95	2	29	22,97	9	3,88	0,02	0,0160	n.d.	66,54	753	0,00024		11,30952	
	3.IV.95	3	33	32,44	9	3,98	0,08	0,0790	n.d.	76,68	767	0,00103		10,00000	
	2.V.95	4	29	31,21	8	3,69	0,10	0,1210	n.d.	161,44	1453	0,00075		9,00000	
	2.VI.95	5	31	101,60	9	4,88	0,04	0,1310	n.d.	140,93	2098	0,00093		14,88372	
	3.VII.95	6	31	46,33	9	4,41	0,04	0,0600	167,2	71,74	1450	0,00083	2,33125	20,20833	
	7.VIII.95	7	35	46,98	9	6,10	0,05	0,0670	97,0	63,09	859	0,00106	1,53830	13,61702	
	4.IX.95	8	28	81,28	9	4,56	0,05	0,1450	243,0	119,02	2555	0,00122	2,04146	21,46341	
	3.X.95	9	29	44,84	8	4,59	0,02	0,0350	156,9	146,88	1722	0,00024	1,06817	11,72368	
	2.XI.95	10	30	6,89	9	5,85	0,20	0,0460	66,6	25,26	1304	0,00182	2,63636	51,63636	
	7.XII.95	11	35	15,72	9	5,35	0,06	0,0270	121,2	30,99	1805	0,00087	3,91304	58,26087	
	9.I.96	12	33	21,55	9	3,56	0,20	0,1310	202,4	97,95	3030	0,00133	2,06667	30,93333	
sum				<b>489,80</b>											
mean				<b>40,82</b>		<b>4,19</b>		<b>0,0860</b>	<b>150,6</b>	<b>94,83</b>	<b>1653</b>				
1996	6.II.96	1	28	3,73	9	4,30	0,20	0,0270	49,3	18,64	76	0,00143	2,64286	4,07143	
	1.III.96	2	24	11,99	9	3,56	0,20	0,1000	199,8	94,91	919	0,00105	2,10526	9,68421	
	2.IV.96	3	32	18,99	9	3,64	0,20	0,1190	308,6	130,55	765	0,00091	2,36364	5,86364	
	3.V.96	4	31	26,27	9	3,64	0,30	0,2540	364,4	177,98	1543	0,00143	2,04762	8,66667	
	30.V.96	5	27	72,02	9	4,09	0,07	0,1870	426,8	245,42	3174	0,00076	1,73913	12,93478	
	2.VII.96	6	33	54,72	9	5,32	0,02	0,0330	447,7	61,35	1592	0,00054	7,29730	25,94595	
	5.VIII.96	7	34	75,03	9	5,50	0,02	0,0440	64,0	70,62	1501	0,00063	0,90625	21,25000	
	3.IX.96	8	29	46,26	9	5,30	0,02	0,0320	39,9	23,93	1053	0,00133	1,66667	44,00000	
	3.X.96	9	30	25,19	9	4,82	0,02	0,0170	84,0	36,10	1813	0,00047	2,32558	50,23256	
	4.XI.96	10	32	21,56	9	5,98	0,20	0,1347	101,1	38,40	2702	0,00351	2,63158	70,35088	
	sum				<b>355,76</b>										
	mean				<b>35,58</b>		<b>4,23</b>		<b>0,0950</b>	<b>208,6</b>	<b>89,79</b>	<b>1514</b>	<b>0,00120</b>	<b>2,43066</b>	<b>23,82814</b>
											<b>MF<sub>TR</sub></b>	<b>8,00000</b>	<b>1,70000</b>	<b>49,60000</b>	

1): precipitation height (mm)

Tab. 12. Concentration of Be ( $\mu\text{g}\cdot\text{L}^{-1}$ ), and flux of Be, Al, Mn, Fe ( $\mu\text{g}\cdot\text{m}^{-2}\cdot\text{day}^{-1}$ ) in mixed forest throughfall, at Truba (TR), VOSS samplers, *continued*.

year	date	month	n (days)	P (mm) <sup>1)</sup>	pH	cBe	f/Be	f/Al	f/Mn	f/Fe	fBe/fFe	fAl/fFe	fMn/fFe	
1996	3.V.96	4	31	16,33	n.d.	0,05	0,028		42,9	167,0	0,00017		0,25683	
	30.V.96	5	27	71,68	n.d.	0,02	0,053	241,4	99,5	242,3	0,00053	2,42488	2,43412	
	2.VII.96	6	33	66,37	n.d.	0,02	0,040		238,5	80,1	0,00050		2,97742	
	5.VIII.96	7	34	69,93	n.d.	0,02	0,041	76,6	207,2	38,9	0,00105	1,96884	5,32641	
	3.IX.96	8	29	28,52	n.d.	0,02	0,020	31,6	176,4	23,0	0,00087	1,37575	7,67644	
	3.X.96	9	30	32,34	4,82	0,02	0,022	81,1	420,4	45,3	0,00049	1,79095	9,28571	
	4.XI.96	10	32	27,91	4,65	0,02	0,017	43,1	218,1	51,5	0,00033	0,83661	4,23729	
	2.XII.96	11	28	20,69	4,39	0,02	0,015	27,3	35,7	11,1	0,00133	2,46600	3,22048	
	9.I.97	12	38	11,59	4,18	0,02	0,006	38,6	21,9	20,1	0,00030	1,91924	1,09042	
	sum				<b>92,53</b>									
mean				<b>38,37</b>	<b>4,53</b>		<b>0,027</b>	<b>77,1</b>	<b>178,2</b>	<b>59,6</b>				
1997	4.II.97	1	26	1,91	n.d.	0,21	0,015		16,7	15,4	0,00100		1,07975	
	5.III.97	2	29	26,42	4,34	0,03	0,027		49,4	83,8	0,00033		0,58937	
	2.IV.97	3	28	26,23	4,34	0,02	0,019		42,5	50,6	0,00037		0,83981	
	5.V.97	4	33	29,89	4,43	0,02	0,018		43,8	108,7	0,00017		0,40256	
	4.VI.97	5	30	17,06	4,79	0,02	0,011		168,2	39,2	0,00029		4,28636	
	4.VII.97	6	30	81,64	3,61	0,02	0,054		209,3	141,5	0,00038		1,47879	
	31.VII.97	7	27	72,76	4,36	0,02	0,054		318,8	97,0	0,00056		3,28621	
	3.IX.97	8	34	49,30	4,99	0,02	0,029		200,1	88,5	0,00033		2,26264	
	2.X.97	9	29	14,43	4,85	0,02	0,010		127,6	59,7	0,00017		2,13604	
	3.XI.97	10	32	18,72	5,06	0,02	0,012		213,3	58,5	0,00020		3,64769	
	1.XII.97	11	28	22,11	6,06	0,25	0,197		692,7	23,7	0,00833		29,24725	
	9.I.98	12	39	34,79	4,53	0,02	0,018		114,3	13,4	0,00133		8,54414	
sum				<b>395,26</b>										
mean				<b>32,94</b>	<b>4,15</b>		<b>0,039</b>		<b>183,1</b>	<b>65,0</b>	<b>0,00091</b>	<b>1,82604</b>	<b>4,49075</b>	
											<b>MF<sub>TR</sub></b>	<b>6,00000</b>	<b>1,30000</b>	<b>9,40000</b>

1): precipitation height (mm)

Tab. 13a. Concentration of Be ( $\mu\text{g}\cdot\text{L}^{-1}$ ), and flux of Be, Al, Mn, Fe ( $\mu\text{g}\cdot\text{m}^{-2}\cdot\text{day}^{-1}$ ) in beech throughfall at LP6, GCTC samplers.

year	date	month	n (days)	P (mm) <sup>1</sup>	pH	cBe	f/Be	fAl	f/Mn	f/Fe	fBe/fFe	fAl/fFe	fMn/fFe
1996	6.II.96	1	28	6,20	4,15	0,13	0,0290	n.d.	30,90	22,35	0,00129		1,38448
	1.III.96	2	24	20,53	4,00	0,15	0,1280	n.d.	86,10	29,55	0,00434		2,91462
	2.IV.96	3	32	29,17	3,92	0,10	0,0910	n.d.	90,20	89,18	0,00102		1,01165
	3.V.96	4	31	29,33	4,08	0,07	0,0660	n.d.	109,00	123,29	0,00054		0,88451
	30.V.96	5	27	73,70	5,24	0,02	0,0550	209,9	417,70	113,20	0,00048	1,85387	3,68966
	2.VII.96	6	33	78,27	4,56	0,02	0,0470	n.d.	399,10	83,04	0,00057		4,80577
	5.VIII.96	7	34	91,03	4,98	0,02	0,0540	n.d.	345,30	40,16	0,00133		8,59800
	3.IX.96	8	29	27,96	5,87	0,02	0,0190	n.d.	197,40	22,90	0,00084		8,62021
	3.X.96	9	30	33,81	5,18	0,06	0,0680	n.d.	574,80	37,19	0,00182		15,45455
	4.XI.96	10	32	27,23	6,21	0,14	0,1190	n.d.	553,00	40,84	0,00292		13,54167
	2.XII.96	11	28	21,60	5,64	0,02	0,0150	n.d.	331,80	11,57	0,00133		28,66667
	9.I.97	12	38	39,02	4,46	0,02	0,0210	n.d.	113,00	15,40	0,00133		7,33333
sum				477,84									
mean				39,82	4,54		0,0593		270,69	52,39			
1997	4.II.97	1	26	3,84	4,05	0,26	0,0380	n.d.	35,50	13,44	0,00286		2,63736
	5.III.97	2	29	29,01	4,35	0,03	0,0300	n.d.	110,00	15,00	0,00200		7,33333
	2.IV.97	3	28	48,52	4,32	0,02	0,0350	n.d.	69,30	25,99	0,00133		2,66667
	5.V.97	4	33	36,71	4,38	0,02	0,0220	n.d.	74,50	16,69	0,00133		4,46667
	4.VI.97	5	30	18,33	6,34	0,02	0,0120	n.d.	201,70	20,17	0,00061		10,00000
	4.VII.97	6	30	72,65	4,59	0,02	0,0480	n.d.	290,60	36,32	0,00133		8,00000
	31.VII.97	7	27	71,20	4,53	0,05	0,1320	n.d.	421,90	39,55	0,00333		10,66667
	3.IX.97	8	34	52,97	5,80	0,02	0,0310	n.d.	134,00	51,41	0,00061		2,60606
	2.X.97	9	29	13,67	5,77	0,02	0,0090	n.d.	89,60	14,14	0,00067		6,33333
	3.XI.97	10	32	19,83	6,26	0,07	0,0430	n.d.	247,90	26,03	0,00167		9,52381
	1.XII.97	11	28	22,63	5,60	0,56	0,4530	n.d.	1551,90	65,47	0,00691		23,70370
	9.I.98	12	39	27,71	4,81	0,12	0,0850	n.d.	213,10	10,66	0,00800		20,00000
sum				417,07									
mean				34,76	4,62		0,0783		286,66	27,91	0,00183	1,21280	6,92594
									MF <sub>TH</sub>		12,20000	0,90000	14,40000

<sup>1</sup>/l: precipitation height (mm)

Tab. 13b. Concentration of Be ( $\mu\text{g.L}^{-1}$ ), and flux of Be, Al, Mn, Fe ( $\mu\text{g.m}^{-2}.\text{day}^{-1}$ ) in beech throughfall at LP6, VOSS samplers.

Values of the MF<sub>TH</sub> were calculated according to the following equation:

$MF_{TH} = fMe_{TH} * fREF_p : fREF_{TH} * fMe_p$ , where fMe<sub>p</sub>, fREF<sub>p</sub> are the fluxes of the examined- and reference elements, respectively, in precipitation, and fMe<sub>TH</sub>, fREF<sub>TH</sub> are their fluxes in throughfall.

Iron was applied as a reference element owing to the abundance of available data, in spite of its certain role in the metabolism of the forest vegetation. Mean annual values of fFe are presented in Tab. 9 to 15, together with the mean values of the ratios of fBe, fAl, and fMn with the fFe. Besides beryllium, aluminium was tested (as an examined element) to verify its similar behaviour with iron in throughfall, and manganese was chosen as an example of a typical strongly metabolised element. Estimated value  $fBe_p/fFe_p = 0.00015$  derived from the actual values of cBe (see the Table 11) was employed for the evaluation of Be- MF<sub>TH</sub> presented in the Tables 12 to 15. Rounded values for  $fAl_p/fFe_p$  and  $fMn_p/fFe_p$  (1.40, 0.48, respectively) were derived from the mean ratios presented in the Tables 9 and 10. Calculated values of the Al- MF<sub>TH</sub>'s (within the range 0.9 to 2.0) show good agreement with the assumption that the characteristics of Al and Fe with respect to their concentration in throughfall are similar. Increased values of Mn- MF<sub>TH</sub>, in spite of its high concentration in the compared bulk precipitation, reflect the importance of Mn in the biochemical assimilation processes of the forest vegetation. Its broad range in the beech throughfall (Tables 12 to 15) reflects differences in the intensity

of interaction between the tree crowns of coniferous- and deciduous trees, and the characteristics of the two types of throughfall collectors. Calculated values of the Be- MF<sub>TH</sub> resemble those of Mn- MF<sub>TH</sub> (Fig. 10). They could, therefore, indicate certain metabolic uptake of Be, probably together with Mg. Reliable interpretation of the Be fluxes in throughfall is problematic however, owing to the uncertainty of values of the Be fluxes. Nevertheless, more precise analytical data

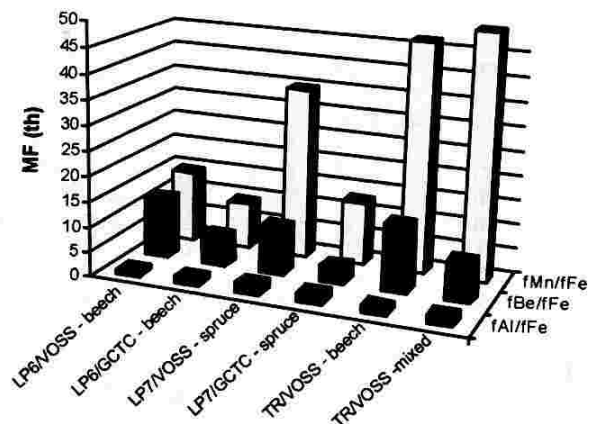


Fig. 10. Mobilisation throughfall factors (MF<sub>TH</sub>) of Al, Be, and Mn in beech- and spruce throughfall at Truba and Lesni potok.

year	date	month	n (days)	P (mm) <sup>1</sup>	pH	cBe	f/Be	f/Al	f/Mn	f/Fe	fBe/fFe	fAl/fFe	fMn/fFe
1996	2.XII.96	11	28	22,15	4,04	0,02	0,016	46,5	253,2	26,9	0,000588	1,73029	9,41176
	9.I.97	12	38	12,29	3,80	0,05	0,016	91,4	200,5	26,2	0,000617	3,49136	7,65432
sum				<b>34,44</b>									
mean				<b>17,22</b>	<b>3,94</b>		<b>0,016</b>	<b>69,0</b>	<b>226,8</b>	<b>26,5</b>			
1997	4.II.97	1	26	4,90	3,19	0,36	0,068	n.d.	509,0	50,9	0,001333		10,00000
	5.III.97	2	29	22,98	3,73	0,06	0,048	n.d.	396,2	87,2	0,000545		4,54545
	2.IV.97	3	28	33,17	3,81	0,02	0,024	n.d.	296,1	88,8	0,000267		3,33333
	5.V.97	4	33	25,85	3,85	0,05	0,039	n.d.	266,3	133,1	0,000294		2,00000
	4.VI.97	5	30	26,23	3,81	0,02	0,017	n.d.	288,5	104,9	0,000167		2,75000
	4.VII.97	6	30	112,55	4,09	0,02	0,075	n.d.	562,8	202,6	0,000370		2,77778
	31.VII.97	7	27	102,70	4,14	0,02	0,076	n.d.	289,1	129,3	0,000588		2,23529
	3.IX.97	8	34	74,04	4,24	0,02	0,044	n.d.	261,3	163,3	0,000267		1,60000
	2.X.97	9	29	16,95	4,31	0,02	0,012	n.d.	70,1	42,1	0,000278		1,66667
	3.XI.97	10	32	22,66	4,24	0,02	0,014	n.d.	177,1	58,1	0,000244		3,04878
	1.XII.97	11	28	29,94	3,92	0,02	0,021	n.d.	588,0	69,5	0,000308		8,46154
	9.I.98	12	39	31,30	5,80	0,02	0,016	n.d.	321,1	12,0	0,001333		26,66667
sum				<b>503,26</b>									
mean				<b>41,94</b>			<b>0,038</b>		<b>335,5</b>	<b>95,2</b>	<b>0,000514</b>	<b>2,61083</b>	<b>6,15369</b>
									<b>MF<sub>TH</sub></b>		<b>3,400000</b>	<b>1,90000</b>	<b>12,80000</b>

<sup>1</sup>l: precipitation height (mm)

Tab. 14a. Concentration of Be ( $\mu\text{g}\cdot\text{L}^{-1}$ ), and flux of Be, Al, Mn, Fe ( $\mu\text{g}\cdot\text{m}^{-2}\cdot\text{day}^{-1}$ ) in spruce throughfall at LP7, GCTC samplers.

obtained from the preconcentrated samples, are necessary for the evaluation of the metabolic cycling of Be.

#### Concentration of beryllium in the beech stemflow

Concentration of selected trace elements including Be, and pH of the beech stemflow were determined in 1994, in order to assess their impact on the lateral and vertical distribution of the elements in soil close to the stem of the particular tree (Skřivan et al. 1995). The elevated metal- and proton concentrations in the stemflow, and high water flux occurring near the stem, would strongly affect the vertical and lateral distribution of heavy metals in the forest soil.

Concentration of Be in the stemflow, and pH data are in Table 16. Higher concentration of protons in the stemflow in com-

parison with the bulk precipitation results from leaching of strong acids ( $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ) deposited and adsorbed on the tree surface and of the organic acids present in the bark or foliage. Samples of stemflow from the locality LP6, with the bedrock of the Be-rich Řičany granite, are (with one exception) higher in Be than their counterparts sampled at the same time on the Be-poor locality TR. The differences may be caused by differential uptake of Be by the forest vegetation, different chemical composition of local terrigenous dust, or different soil chemistry.

#### Concentration and flux of beryllium in the surface discharge of the Lesní potok catchment

Concentration of the dissolved- and acid soluble forms of Be in the surface stream of the Lesní potok catchment have been

year	date	month	n (days)	P (mm) <sup>1</sup>	pH	cBe	f/Be	f/Al	f/Mn	f/Fe	fBe/fFe	fAl/fFe	fMn/fFe
1996	2.XII.96	11	28	15,46	3,99	0,13	0,072	93,9	1237,1	21,0	0,00342	4,47368	58,94737
	9.I.97	12	38	22,76	4,02	0,07	0,042	56,3	569,0	32,3	0,00130	1,74074	17,59259
sum				<b>38,22</b>									
mean				<b>19,11</b>	<b>4,01</b>		<b>0,057</b>	<b>75,1</b>	<b>903,0</b>	<b>26,7</b>			
1997	4.II.97	1	26	9,42	3,39	0,31	0,112	18,8	815,5	76,1	0,00148	0,24762	10,71429
	5.III.97	2	29	14,23	3,56	0,26	0,128	240,5	912,9	49,1	0,00260	4,90000	18,60000
	2.IV.97	3	28	32,86	3,70	0,09	0,106	223,0	833,2	88,0	0,00120	2,53333	9,46667
	5.V.97	4	33	19,35	3,72	0,12	0,070	176,0	504,4	58,7	0,00120	3,00000	8,60000
	4.VI.97	5	30	14,58	4,12	0,08	0,039	179,8	476,3	32,6	0,00119	5,52239	14,62687
	4.VII.97	6	30	89,16	4,07	0,03	0,089	297,2	1248,3	193,2	0,00046	1,53846	6,46154
	31.VII.97	7	27	66,59	4,02	0,06	0,148	193,4	739,9	88,8	0,00167	2,17778	8,33333
	3.IX.97	8	34	56,02	4,43	0,02	0,033	131,8	576,7	105,5	0,00031	1,25000	5,46875
	2.X.97	9	29	11,33	4,70	0,02	0,008	34,4	129,0	20,3	0,00038	1,69231	6,34615
	3.XI.97	10	32	14,38	4,48	0,05	0,022	35,2	480,7	23,8	0,00094	1,47736	20,18868
	1.XII.97	11	28	22,50	3,84	0,17	0,137	217,0	1502,6	71,5	0,00191	3,03371	21,01124
	9.I.98	12	39	18,00	3,87	0,11	0,051	106,1	558,4	21,2	0,00239	5,00000	26,30435
sum				<b>368,43</b>									
mean				<b>30,70</b>	<b>3,95</b>		<b>0,079</b>	<b>154,4</b>	<b>731,5</b>	<b>69,1</b>	<b>0,00146</b>	<b>2,75624</b>	<b>16,61870</b>
									<b>MF<sub>TH</sub></b>		<b>9,70000</b>	<b>2,00000</b>	<b>34,60000</b>

<sup>1</sup>l: precipitation height (mm)

Tab. 14b. Concentration of Be ( $\mu\text{g}\cdot\text{L}^{-1}$ ), and flux of Be, Al, Mn, Fe ( $\mu\text{g}\cdot\text{m}^{-2}\cdot\text{day}^{-1}$ ) in spruce throughfall at LP7, VOSS samplers.



year	date	month	n (days)	P (mm) <sup>1</sup>	pH	cBe	f/Be	f/Al	f/Mn	f/Fe	fBe/fFe	fAl/fFe	fMn/fFe
1994	3.V.94	4	34	35,66	n.d.	0,04	0,0420	n.d.	346,1	51,40	0,00082		6,73469
	2.VI.94	5	30	35,66	5,58	0,07	0,0830	n.d.	1902,0	90,30	0,00092		21,05263
	30.VI.94	6	28	21,95	4,30	0,09	0,0710	n.d.	572,2	33,70	0,00209		16,97674
	28.VII.94	7	28	54,86	5,65	0,07	0,1370	n.d.	1606,7	160,70	0,00085		10,00000
	31.VIII.94	8	34	34,75	5,73	0,05	0,0510	n.d.	817,6	89,90	0,00057		9,09091
	28.IX.94	9	28	30,63	4,77	0,60	0,6560	n.d.	4780,8	74,40	0,00882		64,26471
	1.XI.94	10	34	24,87	4,69	0,05	0,0370	n.d.	534,0	60,00	0,00061		8,90244
	1.XII.94	11	30	83,67	3,72	0,20	0,5580	n.d.	8004,2	164,50	0,00339		48,64407
	10.I.95	12	40	80,92	4,33	0,02	0,0400	n.d.	283,2	30,30	0,00133		9,33333
sum				<b>402,98</b>									
mean				<b>44,78</b>	<b>4,22</b>		<b>0,1860</b>		<b>2094</b>	<b>83,90</b>			
1995	31.I.95	1	21	49,38	3,87	0,08	0,1880	n.d.	611,3	178,70	0,00105		3,42105
	1.III.95	2	29	24,87	4,02	0,03	0,0260	n.d.	274,4	35,20	0,00073		7,80488
	3.IV.95	3	33	42,43	4,48	0,03	0,0390	n.d.	5721,4	92,60	0,00042		61,80556
	2.V.95	4	29	33,47	3,95	0,05	0,0580	n.d.	819,4	103,90	0,00056		7,88889
	2.VI.95	5	31	86,96	5,70	0,03	0,0840	n.d.	1991,7	115,00	0,00073		17,31707
	3.VII.95	6	31	42,61	4,43	0,05	0,0690	108,9	1360,8	67,40	0,00102	1,61633	20,20408
	7.VIII.95	7	35	38,59	5,93	0,08	0,0880	75,4	848,9	56,20	0,00157	1,34118	15,09804
	4.IX.95	8	28	91,44	4,80	0,06	0,1960	150,2	2318,7	127,40	0,00154	1,17949	18,20513
	3.X.95	9	29	77,63	4,82	0,02	0,0540	99,9	2141,6	40,20	0,00133	2,48667	53,33333
	2.XI.95	10	30	16,28	5,32	1,70	0,9220	390,6	634,8	97,70	0,00944	4,00000	6,50000
	7.XII.95	11	35	49,74	4,70	0,10	0,1420	n.d.	3439,4	109,40	0,00130		31,42857
	9.I.96	12	33	37,31	4,12	0,20	0,2260	n.d.	2577,6	237,40	0,00095		10,85714
sum				<b>590,70</b>									
mean				<b>49,23</b>	<b>4,42</b>		<b>0,1740</b>	<b>165,0</b>	<b>1895,0</b>	<b>105,10</b>			
1996	6.II.96	1	28	5,12	4,17	0,20	0,0370	n.d.	71,3	29,30	0,00125		2,43750
	1.III.96	2	24	24,32	3,16	0,20	0,2030	n.d.	2726,2	293,90	0,00069		9,27586
	2.IV.96	3	32	37,49	3,43	0,30	0,3510	n.d.	3116,4	269,50	0,00130		11,56522
	3.V.96	4	31	31,64	3,89	0,20	0,2040	n.d.	1326,8	163,30	0,00125		8,12500
	30.V.96	5	27	94,18	4,68	0,04	0,1400	254,6	2372,0	310,50	0,00045	0,82022	7,64045
	2.VII.96	6	33	75,44	5,46	0,04	0,0910	148,6	2057,4	86,90	0,00105	1,71053	23,68421
	5.VIII.96	7	34	94,37	5,25	0,02	0,0560	n.d.	1332,2	41,60	0,00133		32,00000
	3.IX.96	8	29	69,49	5,70	0,02	0,0480	n.d.	1126,3	35,90	0,00133		31,33333
	3.X.96	9	30	39,96	4,69	0,16	0,2130	n.d.	3636,3	66,60	0,00320		54,60000
	4.XI.96	10	32	40,97	5,87	1,00	1,2800	n.d.	7424,9	113,90	0,01124		65,16854
sum				<b>512,98</b>									
mean				<b>51,30</b>	<b>4,12</b>		<b>0,2623</b>	<b>201,6</b>	<b>2519,0</b>	<b>141,14</b>	<b>0,00204</b>	<b>1,87920</b>	<b>22,40946</b>
										<b>MF<sub>TH</sub></b>	<b>13,60000</b>	<b>1,30000</b>	<b>46,70000</b>

<sup>1</sup>/l: precipitation height (mm)

**Tab. 15.** Concentration of Be ( $\mu\text{g}\cdot\text{L}^{-1}$ ), and flux of Be, Al, Mn, Fe ( $\mu\text{g}\cdot\text{m}^{-2}\cdot\text{day}^{-1}$ ) in beech throughfall at Truba (TR), VOSS samplers.

studied since March 1989. Be concentration (ppb), water discharge ( $\text{L}\cdot\text{s}^{-1}$ ), output of Be from the catchment ( $\mu\text{g}\cdot\text{m}^{-2}\cdot\text{day}^{-1}$ ), and pH values measured in the field (T) or in a laboratory (L), up to the end of 1997, are in Table 17. Differences in the Be concentration of the two sample types (pvf, pvx), which represent the particulate beryllium leachable in the acid environment, were found in most samples negligible and within the analytical error (ETA AAS), as the content of suspended matter in the stream water is generally low (less than  $10\text{ mg}\cdot\text{L}^{-1}$ ). Mean daily Be output from the catchment ( $2.7\text{ }\mu\text{g}\cdot\text{m}^{-2}\cdot\text{day}^{-1}$ ), together with selected statistic characteristics, were calculated from the presented set of 57 samplings, when the water discharge was measured.

Be increases significantly as pH declines (Fig. 11); there is a weak increase of Be concentration as discharge increases (Fig. 12).

date	locality LP6		locality TR	
	Be conc.	pH	Be conc.	pH
3.V.94	<0,04	3,77	n.d.	n.d.
18.V.94	0,46	3,15	0,42	3,17
2.VI.94	0,08	4,04	0,06	3,88
8.VI.94	0,13	3,73	<0,04	3,93
30.VI.94	0,19	3,96	<0,04	4,00
28.VII.94	0,13	4,19	0,07	5,03
31.VIII.94	0,04	4,88	0,05	4,42
28.IX.94	0,06	4,35	<0,04	4,53
1.XI.94	0,14	4,15	0,06	4,01

n.d. = not determined

**Tab. 16.** Be concentration ( $\mu\text{g}\cdot\text{L}^{-1}$ ) and pH of the beech stemflow at LP6 and TR.

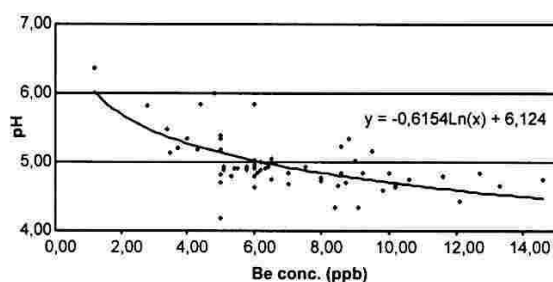


Fig. 11. Dependence of the Be- concentration in the Lesni potok stream on pH.

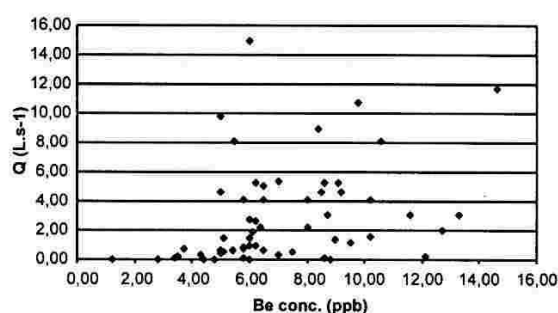


Fig. 12. Dependence of the Be- concentration in the Lesni potok stream on the discharge.

date	sample type	Be conc.	discharge L.s <sup>-1</sup>	Be flux	pH (field)	pH (lab)	date	sample type	Be conc.	discharge L.s <sup>-1</sup>	Be flux	pH (field)	pH (lab)
29.III.89	pvf	6,00	n.d.	n.c.	5,03	n.d.	1.III.95	pvx	6,40	2,25	1,630	n.d.	4,93
29.III.89	pvx	6,00	n.d.	n.c.	5,03	n.d.	3.IV.95	pvx	8,60	5,22	5,070	n.d.	4,83
31.V.89	pvf	6,00	n.d.	n.c.	4,95	n.d.	2.V.95	pvx	9,20	4,62	4,800	n.d.	4,85
13.IX.89	pvf	10,50	n.d.	n.c.	4,85	n.d.	2.VI.95	pvx	9,80	10,71	11,850	n.d.	4,59
13.IX.89	pvx	9,50	n.d.	n.c.	4,85	n.d.	3.VII.95	pvx	10,20	1,57	1,810	n.d.	4,66
26.IX.89	pvf	5,20	n.d.	n.c.	4,91	n.d.	7.VIII.95	pvx	8,80	0,05	0,050	n.d.	5,34
26.IX.89	pvx	7,50	n.d.	n.c.	4,91	n.d.	4.IX.95	pvx	10,20	4,06	4,680	n.d.	4,63
23.III.90	pvx	4,00	n.d.	n.c.	5,35	n.d.	3.X.95	pvx	11,60	3,08	4,040	n.d.	4,79
20.VI.90	pvx	3,50	0,19	0,08	5,13	n.d.	2.XI.95	pvx	12,70	2,03	2,910	n.d.	4,85
21.III.91	pvf	5,00	0,59	0,33	4,82	n.d.	7.XII.95	pvx	6,10	1,89	1,300	n.d.	4,83
11.IV.91	pvf	6,00	1,00	0,67	5,03	n.d.	9.I.96	pvx	6,50	5,09	3,740	n.d.	4,75
31.V.91	pvf	5,00	n.d.	n.c.	5,38	n.d.	6.II.96	pvx	5,30	1,00	0,600	n.d.	4,80
11.VII.91	pvf	5,00	0,43	0,24	5,18	n.d.	1.III.96	pvx	6,00	1,50	1,020	n.d.	4,90
9.VIII.91	pvf	6,00	14,95	10,13	4,63	n.d.	2.IV.96	pvx	6,50	4,06	2,980	n.d.	4,76
16.IX.91	pvf	5,00	n.d.	n.c.	5,35	n.d.	3.V.96	pvx	14,60	11,69	19,280	n.d.	4,76
9.X.91	pvf	5,00	n.d.	n.c.	5,83	n.d.	30.V.96	pvf	10,60	8,07	9,660	n.d.	4,75
9.X.91	pvx	7,00	n.d.	n.c.	5,83	n.d.	2.VII.96	pvf	8,50	4,62	4,440	n.d.	4,66
4.XII.91	pvx	9,50	1,15	1,23	5,15	n.d.	5.VIII.96	pvf	8,70	3,08	3,030	n.d.	4,70
5.III.92	pvf	7,00	5,37	4,25	4,84	5,00	3.IX.96	pvf	5,10	0,50	0,290	n.d.	4,94
15.IV.92	pvf	5,00	9,77	5,52	4,71	n.d.	3.X.96	pvf	7,50	0,56	0,470	n.d.	4,93
20.V.92	pvf	9,00	1,35	1,37	5,03	4,68	4.XI.96	pvf	6,50	0,59	0,440	n.d.	5,04
21.VII.92	pvf	6,00	0,04	0,03	5,85	n.d.	2.XII.96	pvf	5,80	0,86	0,560	n.d.	4,92
2.IV.93	pvf	8,00	2,25	2,03	4,73	n.d.	9.I.97	pvf	5,10	1,50	0,860	n.d.	4,88
1.VI.93	pvf	7,00	0,31	0,24	4,68	n.d.	4.II.97	pvf	6,20	1,00	0,700	n.d.	4,99
2.III.94	pvf	5,00	4,60	2,60	4,18	n.d.	5.III.97	pvf	6,20	5,22	3,660	n.d.	4,89
30.III.94	pvf	8,40	8,90	8,44	4,35	n.d.	2.IV.97	pvf	5,50	8,07	5,010	n.d.	4,92
3.V.94	pvf	9,10	5,22	5,36	4,33	4,33	5.V.97	pvf	5,80	4,06	2,660	n.d.	4,90
2.VI.94	pvf	13,30	3,08	4,63	4,66	n.d.	4.VI.97	pvf	5,80	0,70	0,460	n.d.	4,93
30.VI.94	pvf	12,10	0,18	0,24	4,43	n.d.	4.VII.97	pvf	6,20	2,64	1,850	n.d.	4,88
31.VIII.94	pvf	4,80	0,01	n.c.	6,01	n.d.	31.VII.97	pvf	8,00	4,06	3,670	n.d.	4,77
28.IX.94	pvf	1,20	0,00	n.c.	6,36	n.d.	3.IX.97	pvf	5,80	0,13	0,090	n.d.	4,89
1.XI.94	pvf	4,40	0,01	n.c.	5,85	n.d.	2.X.97	pvf	2,80	0,01	0,003	n.d.	5,82
1.XII.94	pvf	8,60	0,12	0,12	n.d.	5,23	3.XI.97	pvf	3,40	0,10	0,040	n.d.	5,47
10.I.95	pvx	5,40	0,63	0,38	n.d.	4,91	1.XII.97	pvf	3,70	0,74	0,310	n.d.	5,20
31.I.95	pvx	6,00	2,70	1,83	n.d.	4,80	9.I.98	pvf	4,30	0,34	0,160	n.d.	5,18
mean Be output from the catchment (μg.m <sup>-2</sup> .day <sup>-1</sup> )							2,70						
median							1,37						
n							57,00						
st. dev.							3,54						
min.							0,00						
max.							19,28						
lower quartile							0,31						
upper quartile							4,04						

n.d. = not determined  
n.c. = not calculated

Tab. 17. Be concentration (μg.L<sup>-1</sup>) of dissolved- (pvf) and dissolved + acid soluble forms (pvx), flux of Be (μg.m<sup>-2</sup>.day<sup>-1</sup>) in the surface discharge at LP6.

parameter	pH/field	pH/lab	F <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	Al <sup>3+</sup>	L/A*	parameter	pH/field	pH/lab	F <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	Al <sup>3+</sup>	L/A*		
sample type	pv	pvf	pv	pv	pvf		sample type	pv	pvf	pv	pv	pvf			
year	date						year	date							
1988	15.I.88	n.d.	5,09	0,37	80,70	n.d.	1,0	1995	10.I.95	n.d.	4,91	0,88	91,10	n.d.	5,0
	18.II.88	n.d.	6,95	0,40	79,25	n.d.	1,0		31.I.95	n.d.	4,80	0,79	81,30	n.d.	5,0
1989	29.III.89	5,03	n.d.	n.d.	n.d.	0,60	1,0		1.III.95	n.d.	4,93	0,73	77,40	n.d.	5,0
	31.V.89	4,95	n.d.	n.d.	n.d.	0,50	1,0		3.IV.95	n.d.	4,83	0,72	70,70	n.d.	5,0
	26.VII.89	4,87	n.d.	n.d.	n.d.	0,25	1,0		2.V.95	n.d.	4,85	0,67	81,30	n.d.	5,0
	13.IX.89	4,85	n.d.	n.d.	n.d.	0,45	1,0		2.VI.95	n.d.	4,59	0,96	111,00	n.d.	5,0
	26.IX.89	4,91	n.d.	n.d.	n.d.	0,35	1,0		3.VII.95	n.d.	4,66	1,03	108,00	2,07	5,4
	14.XI.89	5,16	n.d.	0,15	72,05	n.d.	1,0		7.VIII.95	n.d.	5,34	0,88	99,40	2,27	5,4
									4.IX.95	n.d.	4,63	n.d.	n.d.	1,15	5,4
1990	29.I.90	5,06	5,50	0,52	55,14	0,75	2,0		3.X.95	n.d.	4,79	n.d.	n.d.	2,55	5,4
	23.III.90	5,35	5,00	0,55	60,90	0,60	2,0		2.XI.95	n.d.	4,85	0,78	97,00	1,40	5,4
	20.VI.90	5,13	5,29	0,50	54,73	0,40	2,0		7.XII.95	n.d.	4,83	0,46	64,30	1,07	5,4
1991	21.III.91	4,82	6,10	0,58	92,49	0,60	2,0	1996	9.I.96	n.d.	4,75	0,93	94,00	0,73	5,4
	11.IV.91	5,03	5,18	0,55	89,90	0,70	2,0		6.II.96	n.d.	4,80	0,79	98,30	2,71	5,4
	31.V.91	5,38	5,20	0,45	85,01	0,50	2,0		5.III.96	n.d.	4,90	0,89	101,00	0,97	5,4
	7.XI.91	5,19	5,05	0,52	82,52	0,55	2,0		2.IV.96	n.d.	4,76	0,35	58,70	1,03	5,4
	8.IX.91	4,63	4,70	0,55	73,10	0,80	2,0		3.V.96	n.d.	4,76	0,87	96,60	1,05	5,4
	16/09/91	5,35	5,10	0,53	84,05	0,50	2,0		30.V.96	n.d.	4,78	1,04	105,00	2,86	5,4
	10.IX.91	5,83	5,80	0,59	76,91	0,60	2,0		2.VII.96	n.d.	4,66	0,97	99,15	0,75	5,4
	12.IV.91	5,15	6,45	0,44	70,15	n.d.	2,0		5.VIII.96	n.d.	4,70	1,01	95,25	0,85	5,4
1992	3.V.92	n.d.	5,00	0,60	90,19	n.d.	2,0		3.IX.96	n.d.	4,94	0,86	91,70	0,72	5,4
	15.IV.92	4,71	4,55	0,56	98,32	1,30	2,0		3.X.96	n.d.	4,94	0,86	83,90	1,75	5,4
1993	4.II.93	4,73	4,70	0,47	55,20	n.d.	2,0		4.XI.96	n.d.	5,04	0,83	79,80	2,85	5,4
	4.II.93	4,73	4,70	0,76	79,90	n.d.	5,0		2.XII.96	n.d.	4,92	0,67	82,10	0,92	5,4
	30.IV.93	n.d.	5,20	0,80	83,10	n.d.	5,0	1997	9.I.97	n.d.	4,88	0,77	82,20	0,88	5,4
	6.I.93	4,68	6,50	0,44	75,36	n.d.	2,0		4.II.97	n.d.	4,99	0,77	83,80	0,77	5,4
	6.I.93	4,68	6,50	0,77	83,70	n.d.	5,0		5.III.97	n.d.	4,89	0,79	81,90	0,95	5,4
	7.I.93	n.d.	5,18	0,76	78,40	n.d.	5,0		2.IV.97	n.d.	4,92	0,82	75,90	0,60	5,4
	27.VII.93	n.d.	5,25	0,71	75,00	n.d.	5,0		5.V.97	n.d.	4,90	0,71	89,40	0,67	5,4
	9.I.93	5,63	5,11	0,75	81,80	n.d.	5,0		4.VI.97	n.d.	4,93	0,45	57,60	1,32	5,4
	10.I.93	n.d.	5,39	0,66	81,20	n.d.	5,0		4.VII.97	n.d.	4,88	0,69	70,90	0,92	5,4
	11.II.93	n.d.	5,21	0,72	72,00	n.d.	5,0		31.VII.97	n.d.	4,77	0,74	69,30	0,61	5,4
	30.XI.93	n.d.	5,23	0,68	n.d.	n.d.	5,0		3.IX.97	n.d.	4,89	n.d.	68,30	0,75	5,4
1994	4.I.94	n.d.	4,76	0,83	n.d.	n.d.	5,0		2.X.97	n.d.	5,82	n.d.	60,00	1,02	5,4
	2.II.94	4,70	4,60	0,80	79,70	n.d.	5,0		3.XI.97	n.d.	5,47	0,56	75,80	0,64	5,4
	2.III.94	n.d.	4,90	0,69	72,10	n.d.	5,0		1.XII.97	n.d.	5,2	n.d.	n.d.	0,59	4,0
	30.III.94	4,35	4,80	0,73	83,30	n.d.	5,0		9.I.98	n.d.	5,18	n.d.	n.d.	0,61	4,0
	3.V.94	4,33	4,90	0,86	96,78	n.d.	5,0								
	02-VI.94	4,66	4,95	0,88	94,12	n.d.	5,0								
	30.VI.94	4,43	4,98	0,75	92,60	n.d.	5,0								
	28.VII.94	5,32	5,88	0,71	90,40	n.d.	5,0								
	31-VIII.94	6,01	6,10	0,77	102,00	n.d.	5,0								
	28.IX.94	6,36	6,88	0,71	60,60	n.d.	5,0								
	1.XI.94	5,85	7,16	0,77	84,70	n.d.	5,0								
	1.XII.94	n.d.	5,20	0,88	96,60	n.d.	5,0								

L/A\* (laboratory, author): 1 - Stavební geologie, Dr. Konopáčová  
2 - Geoindustria, Dr. Blahovec  
4 - Geological Inst. AS, Dr. Burian  
5 - Geological Survey, Dr. Sixta

pv = not filtered, not stabilised  
pvf = membrane filtered, stabilised

**Tab. 18.** Parameters significant for the Be forms in surface water of the LP catchment (mg.L<sup>-1</sup>).

Annual stream water output of beryllium from the catchment (985 µg.m<sup>-2</sup>.yr<sup>-1</sup>), calculated from the above presented mean daily output, is significantly higher than the corresponding value presented by Krám et al. (1998) for the Lysina catchment (586 µg.m<sup>-2</sup>.yr<sup>-1</sup>). This is in agreement with our value of the mean annual discharge-weighted Be concentration in the Lesní potok stream water (8,42 µg.L<sup>-1</sup>), and the arithmetic mean Be concentration (7,22 µg.L<sup>-1</sup>), calculated for the last 3 years from the Tab. 17. The corresponding values for the Lysina catchment (1,45 and 1,51 µgBe.L<sup>-1</sup>, respectively) are also considerably lower.

Concentration of the sum of dissolved forms of Be in surface water is dependent on the bulk chemical composition of the corresponding water (Veselý et al. 1989). On the other hand,

resulting concentration of dissolved Be is also controlled by the rate of its dissolution/desorption from the soil profile and riparian- or aquatic vegetation. Krám et al. (1998) found no strong relationship between the Be concentration in stream water of the Lysina catchment with either discharge, or with pH. They attribute this fact to the chemical character of Be (different from the compared Al) which is not a strongly hydrolysing metal, and that the Lysina water is strongly undersaturated with respect to the solubility of Be(OH)<sub>2</sub>.

For further computation and interpretation of results, concentration of significant dissolved chemical components affecting the equilibrium of Be between the liquid and solid phases is presented in the Table 18.

The observed annual surface water discharge from the catchment (expressed as discharge height D) fluctuated in the last four discussed hydrological years between 97 and 146 mm (Table 19). The water flux at Lesní potok amounts to 16 to 25% (average 18%) of precipitation, slightly less than expected. This

hydrolog. year	precipitation (P) mm	discharge (D) mm	mean discharge L/s	D/P %
1992	665,7	n.d.	n.d.	n.d.
1993	638,7	n.d.	n.d.	n.d.
1994	637,3	104,3	2,53	16,37
1995	771,0	127,4	3,09	16,52
1996	592,8	146,3	3,55	24,68
1997	609,2	97,3	2,36	15,97

Tab. 19. Lesní potok catchment, annual precipitation and surface discharge, 1992 -97.

#### springs

date of sampling	locality	Be conc.	pH	lab
23.III.90	LL3B	6,0	5,55	a
23.III.90	LP1	3,0	5,06	a
23.III.90	S2	4,0	4,76	a
23.III.90	S3	6,0	4,70	a
23.III.90	S4	7,0	4,51	a
23.III.90	S8	6,0	n.d.	a
21.III.91	LP1	5,0	4,87	a

#### streams

date of sampling	locality	Be conc.	pH	lab
31.V.89	BP10	5,4	5,59	b
26.IX.89	BP10	4,5	5,79	b
14.XI.89	BP10	2,0	5,71	a
23.III.90	BP10	4,0	5,14	a
3.V.90	2CV8	4,0	6,70	a
3.V.90	CV10	11,0	4,51	a
3.V.90	ZVL1	8,0	5,24	a
9.X.91	L7	2,0	5,81	a
9.X.91	LOP8	<1	6,86	a
15.IV.92	L7	4,0	5,45	a
15.IV.92	LOP8	2,0	6,26	a

#### reservoirs

date of sampling	locality	Be conc.	pH	lab
23.III.09	BPLJ	2,0	5,93	a
5.VII.89	VZh	<0.5	9,44	a
16.VIII.89	VZh	<0.5	8,85	a
13.IX.89	VZh	<0.5	9,15	a
9.X.91	VZh	<0.5	8,10	a
15.IV.92	VZh	<0.5	9,45	a

a/ AAS laboratory Geoindustria, Černošice

b/ analytical laboratory of the Inst. of Geology and Geotechnics, CSAS, Prague

Tab. 20. Be concentration ( $\mu\text{g}\cdot\text{L}^{-1}$ ) and pH of selected springs, streams and reservoirs underlain by Říčaný granite.

may be caused by subsurface drainage or by the lack of recording of some high discharge events. Thus fluxes of beryllium (and other elements) in the catchment must include the amount and chemical composition of the subsurface discharge.

#### Concentration of beryllium in several additional sources, streams and reservoirs of surface water in the territory of the Říčaný granite massif.

The concentration of Be in several springs, streams and lakes (mainly in the pond Vyžlovský, representing the recipient of the Lesní potok surface stream) (Fig. 1), together with their pH, is summarised in Table 20. All samples were filtered with the 0.45  $\mu\text{m}$  membrane filters and stabilised with diluted nitric acid prior to their AAS analyses. Values presented in the table confirm the primary significance of pH for the concentration of dissolved Be. This is most pronounced in the Be concentration of the pond Vyžlovský whose high pH values thus represent acid-basic barrier for the beryllium distribution between the solid and liquid phases of the surface water (Skřivan et al. 1996).

#### Conclusions

Recent exogenous cycling of beryllium is affected through several factors:

- low Be- input from atmospheric sources,
- its presence mostly in particulate matter of the atmospheric deposition, where it is soluble under acidic conditions,
- increased atmospheric input of protons from strong inorganic acids of anthropogenic origin, which enhances the mobility of Be in soil and in surface water,
- presumably low metabolic uptake of Be by forest trees.

Increased concentration of Be in the bedrock and its weathering products is additional specific factor of the studied area. Both types of granites forming the bedrock of the Lesní potok catchment are enriched in Be, but it is still not clear, in which minerals this element is present. Be- concentration in biotite is 8,3  $\text{mg}\cdot\text{kg}^{-1}$  in plagioclase is 14,8  $\text{mg}\cdot\text{kg}^{-1}$ . Progress in the investigation of the Be distribution in the particular minerals may be achieved through microanalyses (by laser- or ion microprobe). We presume at present that major part of the Be-content is bound in both feldspars (mainly in plagioclase) due to their dominant amount in the granite.

Experimental acidic leaching of the individual rock-forming minerals performed at room temperature and atmospheric pressure has shown high mobility of Be in biotite, whereas Be bound in feldspars is released more slowly.

In soil profiles, exchangeable and total Be increase downward. The Be output through the surface discharge greatly exceeds atmospheric input. Be is released from soil and weathering rock. The Be concentration in surface stream draining the Lesní potok catchment varies inversely with pH.

The Be concentration in most samples of the bulk precipitation is below the detection limit, and extensive preconcentration of samples is necessary to get correct analytical concentration of Be. Estimated annual Be- flux in bulk precipitation, based on new data from the preconcentrated samples, is below 20  $\mu\text{g}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$ . Export is approximately 990  $\mu\text{g}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$ . The concentration and flux of Be in throughfall are moderately- to considerably higher (especially at the locality Truba), which is attributed to the possibility of impact of local emission sources. Comparison of the results obtained by means of two different types of throughfall collectors has shown the importance of their construction and principles of their operation.



Concentration of Be in the tissues of the forest vegetation, including leaves seem to confirm its certain metabolic uptake. Concentration of Be in the beech stemflow may be proportional to Be concentration in the bedrock.

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