Beryllium in Waters of Czech Forested Ecosystems and the Release of Beryllium from Granites

Tomáš NAVRÁTIL[1,2]

[1] Institute of Geology, Academy of Science, Rozvojová 135, Praha 6 - Suchdol, Czech Republic
[2] Department of Geochemistry, Mineralogy and Natural Resources, Faculty of Science, Charles University, Albertov 6, Praha 2, Czech Republic

ABSTRACT: The behavior of beryllium (Be) in forest ecosystem waters was monitored during July-98 to June-99 at three sites in the Czech Republic (catchments Lesní Brook, Lysina, and Plešné lake).
Beryllium speciation was modeled using Mineql+ version 3.01b software. Concentrations and speciation of Be are complex functions of abundance, pH and the concentrations of F, Al, DOC.
The stream draining Lesní Brook has a wide pH range (4.6-6.9), high F concentration (average 0.7 mg/l) and elevated concentrations of Al and Be (<5 μg/L). Speciation of the Be in the Lesní Brook water consists of two main complexes Be^{2+}, and BeF^+. $BeOH^+$, BeF_2 and $BeSO_4$ are minor. The sulphate complex never exceeds 1% of total Be concentration. $BeOH^+$ and BeF_2 can form over 80% of the total Be if pH > 5.7.
The Lysina brook has high DOC and Al concentrations, stable low pH values (3.9-4.2) and low F (~0.2 mg/l) and Be (~1 μg/l) concentrations. In the surface water of the Lysina catchment ionic Be^{2+} is over 95% of total Be. Approximately 5% is the fluorocomplex BeF^+. Speciation of the Be in groundwater of the Lysina catchment is quite different. The main species are BeF^+ and Be^{2+}, accounting for 90% of the Be. These changes are mainly caused by higher pH value (~5.3), higher F and Be, and lower Al concentrations. Be in the Plešné lake waters is mainly ionic Be^{2+}.
Beryllium concentrations in the granites are higher than crustal average. The highest Be concentration (16.8 ppm) occurs in the Říčanský granite.
The highest concentrations of Be were in the plagioclase (max. 43.1 ppm) and micas (max. 17.2 ppm). Lower Be concentration occurred in potassium feldspars (max. 6.3 ppm). Quartz contained the lowest Be concentrations (max. 1.7 ppm).

KEY WORDS: beryllium, granites, catchment, speciation, water, acidification.

Introduction

One of the very important changes caused by human activity is acidification of the environment. It is a phenomenon caused by burning of fossil fuels and connected emission of sulfur and nitrogen oxides and ash. Sulfur is present in all coals, and is especially abundant in coals of the North Bohemian Basin, Czech Republic. Because of past practice of burning this coal, no electrostatic fly ash separators, no desulfurisation, we are now surveying damage.

Precipitation is more acidic than it should be. Theoretical pH value for the precipitation in equilibrium with only atmospheric CO_2 is 5.7. Current pH values in Central Europe are as low as 4.5. The chemistry of the precipitation has changed dramatically. Precipitation affects the soil and soil water chemistry and these affect groundwater and surface waters.

At some sites acidification is not a serious problem. On sites where the bedrock or soils have abundant base cations, neutralization of acidic precipitation occurs. On sites with "acidic" bedrock (i.e., granitoids) the neutralization may be incomplete. Concentration of some trace elements has increased. One of those elements is aluminum (Al) which is toxic to fauna and flora. The chemistry of Al in the water environment and its toxicity has been studied for over 25 years.

Another mobilized element, more toxic than Al is Be. Speciation and forms in which the Be migrates through environment are not well known.

Beryllium enters the environment mainly by release from the soil and bedrock. In the past its elevated concentrations in waters were supported by atmospheric deposition of coal ash.

Ash is now electrostatically separated, producing lower Be concentrations to the atmosphere.

Sulfate concentrations have decreased in past 10 years due to desulfurisation but ecosystem acidification may continue because of rising concentrations of the nitric oxides in the atmosphere.

This paper deals with mobility and speciation of Be in the aqueous environment and processes of Be release.

Abbreviations List

AAS	atomic absorption spectrometry
CGS	Czech Geological Survey
FSCU	Faculty of Science Charles University
d.m.	dry matter
DOC	dissolved organic carbon
HPLC	high pressure liquid chromatography
L	Lysina catchment
LA-ICP-MS	laser ablation - inductively coupled plasma - mass spectrometry
LE	Lenka spring (Lysina catchment)
LB	Lesní Brook catchment
MWCO	molecular weight cut off
n	number of samples
OES	optical emission spectrometry
PAH	polyaromatic hydrocarbons
PL	Plešné Lake
QAP	quartz, alkali feldspar, plagioclase
r	correlation coefficient

Beryllium Geochemistry

Beryllium Chemical Properties and Use

Beryllium is in group II.A of the periodic table. It has one stable isotope, ^{9}Be, and three radiogenic isotopes ^{7}Be, ^{8}Be and ^{10}Be. The half-lives of these isotopes are 53 days, $5*10^{-4}$ s and $1.5*10^6$ years.

Beryllium usually occurs with oxidation number 2+. It has the highest charge to ionic radius ratio (64.5 nm^{-1}) of all elements but is similar to Al (60.0 nm^{-1}). This is one of the reasons why Al and Be show very similar chemical behavior in different environments.

Beryllium more easily forms covalent bonds and soluble complexes than Mg, Ca, or Sr. Atomic Be is one of the lightest and the smallest of the metals. Its density is 1.85 g/cm^3 in metal form.

Be is a rare but very wide spread element. It is lithofile and classified as toxic. In water, Be is toxic to fauna, e.g. fish (Jagoe et al. 1993). Toxicity of Be also can affect the vegetation. High concentration of Be can retard the development of the tree root systems (Edmunds et al. 1992). For humans the highest risk of toxicity is from inhaling Be particles.

^{7}Be is used as a tracer for studies of processes in recent soils, lakes and sediments. Production of ^{7}Be in the atmosphere is dependent on latitude and altitude. ^{10}Be is good for dating of soils, ice and marine sediment. ^{10}Be is formed and accumulated in oxygen containing minerals exposed to cosmic rays (von Gunten and Beneš 1995).

Beryllium in Rocks

The average concentration of Be in the earth crust is 2 to 3.5 ppm (Griffitts and Skilleter 1991). Beryllium occurs mainly in silicates and its highest concentrations are connected with pegmatite mineralization. The most important Be mineral is beryl (Be$_3$Al$_2$(Si$_6$O$_{18}$). Beryllium can substitute for Al and Si in silicates.

Beryllium associates with elements of acidic magmas (Table 1). The concentration of Be in granitoids commonly exceeds

Rock/author	1	2	3	4	5	6
Ultrabasic	0.X	0,25	0.X	0,2	<1,0	-
Basaltic and gabbroic	0,4	1,00	1,0	0,4	<1,0	<0,7
Intermediate	1,8	1,60	1,0	1,8	-	1,5
Granitic	5,0	3,00	2,5	5,5	6,5	5,5
Alkalic	7,0	-	-	-	11,4	6,0

1 - Beus (1952), 2 - Sandell (1956), 3 - Turekian (1961), 4 - Vinogradov (1961), 5 - Shawe (1964), 6 - Wedepohl (1969).

Tab. 1. Concentrations of Be in plutonic rocks [ppm], (Wedepohl, 1967).

Rocks	Be [ppm]
USSR biotite granites	4,0
USSR two mica + muscovite granites	9,0
USSR granites average	5,0
USA granites	3,0
California granites	2,4
Texas granites	5,5
Canada granites	2,4
Africa granites	3,3

Tab. 2. Be concentration in various granites, (Sandell 1952), (Beus 1956).

10 ppm. In pegmatites the Be concentration can exceed 10,000 ppm. The average concentrations found in various granites are listed in Table 2.

The concentrations of Be in Ore mountains granites Czech Republic was between 7 and 16 ppm (Štemprok et al. 1996). The average Be concentration in granites of Ore mountains was 6.5 ppm for Horské and intermediate granites, 15 ppm for Ore mountain granites (the youngest granites of the formation) (Macháček 1966). Other data about Be concentrations in minerals are in Tab.3.

	Be [ppm]				
	total	quartz	biotite	muscovite	feldspars
Ore mountains granite	11-34	2-4	14-76	17-49	4-13
Intermediate granite	6	1-3	7	5	2-3
Horský granite	5-8	0-1	2-4		3-4

Tab. 3. Be concentration in minerals of the Karlovy Vary pluton granites (Macháček 1966).

Rocks of the Central Bohemian pluton contain between 1 and 12 ppm. Maximum Be concentrations (12 ppm) occurs in the Říčanský granite. Higher Be concentration (8 to 12 ppm) are associated with rocks rich in K. Correlation occurs between Be - Li (r^2=0.81), Be - Rb (r^2=0.69) and Be - Sn (r^2=0.65) (Vejnar, 1974). According to Minařík (1975) the Be concentrations in the minerals of the Říčany granite are as follows: plagioclase > biotite > orthoclase > quartz.

Němec (1978) describes the Říčany granite as typical Sn-bearing granite containing considerable amounts of volatile components and elevated concentrations of B, Be, F, Nb, Sn and W. Concentrations of Be for the rock types of Říčany massif are in Tab.4.

Rock type	Be [ppm]	
	Average	Range
Říčany granite	13 (33)	<4-24
Aplites of Říčany granite	43 (10)	10-90
Jevany granite	7 (5)	4-12

Tab. 4. Average concentration of Be in Říčany massif rock types (number of analysis), (Němec 1978).

Weathering and Sorption

The feldspars in granites weather rapidly. The extent of weathering of the granites is indicated by the Na$_2$O/K$_2$O ratio. Decrease in the Na$_2$O concentration means preferential weathering of plagioclase. According to Beus (1960) 60 to 85% Be is bound in feldspars. Then, during the weathering of the granites the beryllium is released mainly from feldspars. In micas there are normally higher concentrations of Be but micas in granites are less abundant than feldspars. The amount of Be released from micas is thus less important.

The precursors of coal and coal clays (organic-rich sediments) are very good sorbers for metals, including Be. Lignite of the Josef stratum in Sokolov basin, Czech Republic, contains up to 62 ppm Be (Macháček 1966). Coals from the Sokolov basin contain 85ppm average (Bouška and Pešek 1997). Clay minerals formed during granite weathering sorb Be and may contain up to 1200 ppm Be (Kubizňáková 1987).

Beryllium in Soils and Soil Waters

Be concentrations in soils range between 0.01 and 30 ppm (Bowen 1979). Soils in Czech Republic are contaminated with Be from atmospheric deposition. Němeček (1995) concluded that regional contamination of the soils by As, Be, Cd and PAHs was the greatest in regions with the highest level of emissions (e.g. regions Most, Teplice, and Ústí nad Labem). Be in uncontaminated soils in forest ecosystems reflects its abundance in the bedrock. Some portion of Be originated in emissions from the past times when the atmospheric deposition of Be was higher (Skřivan et al. 2000).

In soils of Lesní brook catchment, the concentrations of total Be ranged between 4 and 6 ppm. In soils on limestone sediments around the Koněpruské caves total Be was 4 to 5.5 ppm (Zajíc 1998).

At the Lysina catchment Be concentration in soilwater increased downward (Tab.5) (Krám et al. 1998).

	pH	Be [µg/l]
Surface water	3,9	1,51
Horizon O	3,4	0,21
Horizon E	3,2	0,41
Horizon C	4,4	1,10
Groundwater	5,2	3,30

Tab. 5. Be concentrations in waters of the Lysina catchment (Krám et al. 1998).

Beryllium in Water

Be concentrations in bulk precipitation are typically <0.01 µg/l (Skřivan et.al 2000). Throughfall and stemflow may have 4 times higher Be concentrations. This is caused by capture of Be from the atmosphere and leaching of Be from foliage.

In middle Wales, concentrations of Be in bulk precipitation were around 0.06 µg Be/l. Throughfall and stemflow were 2 or 3 times higher in Be. High Be concentrations up to 0.36 µg Be/l were detected in the mist (Neal et al. 1992).

Concentration of Be in bulk precipitation in the Czech Republic near the Lesní brook catchment was usually less than <0.02 µg/l. Throughfall had up to 1.0 µg Be/l (Skřivan 1993). Average concentration of Be in bulk precipitation at the Lysina catchment was 0.04 µg/l. Throughfall had 0.06 µg/l (Krám et al. 1998).

Surface waters commonly have higher concentrations of Be than precipitation. A map of the Be concentrations in Czech Republic water bodies was published by Veselý and Majer (1998). Concentration of the Be depends on abundance and distribution in the bedrock as well as pH (Tab.6).

	Uconsolidated sediments	Consolidated sediments	Eruptives and suberuptives	Plutonic	Metamorphic rocks
Be	0,02	<0,02	0,02	0,08	0,03

Tab. 6. Average Be concentration in surface waters on different bedrock (µg/l) (Veselý, 1998).

The average concentration of Be in waters of the Czech Republic is 0.02 µg/l (Veselý and Majer 1998). On areas where the bedrock has high acid neutralizing capacity Be is less mobile. The average concentration of Be in water bodies on gran-

itoid bedrock is 0.16 µg Be /l. That is 8 times more than average concentration for all the water bodies (Veselý and Majer 1998).

Surface waters of the middle Wales had 0.01 to 0.25 µg Be/l (Neal et al. 1992). An Argentinean water body with pH 3 to 4 had 1.4 to 1.8 µg Be/l (Fernandez – Turiel et al 1995).

The Be concentration in Lesní brook depends on pH. Be bound in soils on the Fe, Mn hydroxides, or organic matter is mobilized by lowered pH (Skřivan et al. 1993).

Be [µg/l]				pH		
n	min.	max.	median	st. dev.	min	max.	median
20	3	10,5	5,785	1,796	4,63	5,83	5,01

Tab. 7. Be mean concentrations, and ranges in Lesní brook (Skřivan 1993).

Acid precipitation (pH 4.3) decreases the pH of the surface water and releases the Be. The main source of the Be is the bedrock and its weathering products. The pH is limiting for the Be concentrations in the surface waters (Skřivan et al. 1994).

Be at the Lysina catchment averaged 1.5 µg/l in the surface water and 3.3 µg/l in shallow groundwater during the hydrologic year 1991-1992. There was no relationship between Be concentration and discharge, pH or Al concentration. Al is highly correlated with pH ($r^2=0.83$; n=244). Be concentration correlates with F ($r^2=0.35$; n=145) and also with SO_4^{2-} ($r^2=0.61$; n=146). From 1991 until 1998 Be, SO_4 and F have decreased. With higher discharge the concentrations of Al, DOC and H^+ increase (Krám et al. 1998).

Groundwaters can under certain conditions contain up to X0 µg Be/l. Higher values are associated with higher F concentrations (Macháček et al. 1966).

In the Sokolov basin (Czech Republic) the groundwater and spa springs contained 0.6 to 70 µg Be/l (Macháček et al. 1966). Ondrušová (1997) detected concentrations of Be between 0.1 and 0.4 µg/l in Bohemian Forest lakes in 1996 (Tab.8).

	Be [µg/l]
Černé jezero	0,24
Čertovo jezero	0,13
Jezero Laka	0,07
Plešné jezero	0,39
Prášilské jezero	0,11
Žďárské jezero	0,40

Tab. 8. Concentrations of Be in Bohemian Forest lakes, (Ondrušová, 1997).

Beryllium Speciation in Waters

Be is mobilized into water during acidification. In acidified surface water, Be may be 10 times higher than Cd, Pb, Cu (Veselý 1994).

One of the first speciation studies for Be in Czech Republic is the work of Macháček et al. (1966). They concluded that most Be in area of Karlovy Vary Spa occurs as fluorocomplexes. The main complexes were BeF^+, BeF_2, BeF_3^-, BeF_4^{2-}. Be concentration was 75 µg Be/l (8.3 µmol/l). The average fluorine concentration was 6 mg/l (320 µmol/l). Speciation of beryllium under specified conditions was: BeF^+ 0.16%, BeF_2 53.4%, BeF_3^- 1.4%,

Site	Plant	Roots mineral horizon	Roots organic horizon	Bark	Bole	Foliage	Cones	Litter
Lesní brook catchment	Spruce			78,3	13,7	16,6		309,8
Koněprusy caves	Spruce			10,7	3,1			
Lysina catchment	Spruce	126,8	55,4	16,0	1,2		6,2	
Lesní brook catchment	Beech			68,2	20,5			193,9
Koněprusy caves	Beech			18,7	3,2			

*all data about Koněprusy caves and Lesni brook catchment (Samek 1998)
*all data about Lysina catchment (Kaste and Krám, 1999 unpublished)

Tab. 9.   Concentrations of Be in plants [μg/l].

BeF_4^{2-} 1.4%. When pH was 6, less than 10% of the total Be was present as Be^{2+}. However Al was not included in the calculation.

During low pH, Be occurs as Be^{2+} or as an organic complexes. Formation of the BeF^+ complex increases with increasing (neutral) pH. In water and especially in acidified water the BeF^+ is less stabile than Al complexes AlF^{+2} and AlF_2^+ (Veselý et al. 1989).

Low Be concentrations in precipitation (Skřivan et al. 1994; Skřivan et al. 1993; Krám et al. 1998) show that Be is mobilized from soils or bedrock. Low pH and higher F⁻ enhance mobilization. Concentrations of Be and F correlate when F⁻ > 0.1mg/l (5 µmol/l) and in the pH range 4.2 to 6.0. At pH 4.2 the average Be concentrations are lower because the waters have lower free F⁻ because of Al and F complexes (Veselý 1994).

The Be and Al hydroxide complexes decrease and Be and Al fluoride increase during acidification. At the Beryllium Stream catchment in Maine, Rissberger (1993) determined that Al was dominated by: $Al(OH)_4^-$, $Al(OH)_3$ aq, AlF_2^+. As pH declined the portion of AlF_2^+ increased. The ratio of Be/Al was near 0.01. It decreases slightly during acidification. Be and Al are highly correlated.

In waters with low F concentration (<0.05mg/l) pH controls the Be concentrations. At Bear Brook catchments (Maine, USA) the artificially acidified brook contained 100% more Be than unacidified brook. The concentration of Be was highest during high discharges. Kaste (1999) concluded that:

high discharge ⇒ low pH ⇒ high Be concentration

At the reference Bear Brook catchment with pH 5.36 to 6 and artificially acidified catchment with pH 4.8 to 6 the portion of the ion Be^{2+} for pH < 5.5 was around 75% and for pH < 5 up to 90%. For pH ~ 6 $BeOH^+$ reached 35%. Other species $BeSO_4$, BeF^+ and $BeCl^+$ were <<1%.

BeF^+ was the dominant species at the Halfmile catchment (USA, Maine). In the range of pH 6.5 to 7 $BeOH^+$ was second in importance but for pH depression below 6.5 the portion of BeF_2 increased. $BeSO_4$ and $BeCl^+$ were minor <<1% (Kaste 1999).

The dominant species of the Be in the surface water of the Lysina catchment was Be^{2+} (93%) and BeF^+ (4.5%). $BeSO_4$ (2.0%), $BeOH^+$ (0.4%) and $BeCl$ (0.1%) were minor. Strong complexation of Al by F is the reason for low of BeF^+. (Krám et al. 1998).

Macháček (1966) suggested that in acid environments Be can migrate as fluoride and chloride complexes. Borovec (1993) determined that in surface waters with neutral pH, Be migrates as dissolved $Be(OH)_2$ or as $BeOH^+$.

Beryllium in the Biosphere
Toxicity of the Be salts (chloride, sulfate, fluoride, nitrate) depends on their solubility. Beryllium lowers the vitality of the organisms decreases because of the cellular protoplasma denaturisation. Different Be complexes cause different effects even though their toxicity which is catalyzed by presence of the Be^{2+} ion (Bencko et al. 1984).

Plants on the natural soils commonly contain only trace concentrations Be (Griffitts and Skilleter 1991).

In needles of the 2 years old spruces at Slovakia (Banská Bystrica region) Mankovská (1995) found Be concentrations between 0.0001 and 0.464 mg/kg, while the critical value is considered to be 0.1 mg/kg. Beryllium in vegetation data are shown in Tab.9.

Materials and Methods
Study Sites
The Lesní Brook (LB) Catchment
Lesni Brook is in the middle of Bohemia approximately 30 km east of Prague near the town Kostelec nad Černými lesy, region Kolín (Fig. 1). Area of the catchment is 0.76 km². The lowest point is 400 m.a.s.l and the highest is 495 m.a.s.l. Average annual precipitation is 635 mm (Zajíc 1998). The valley of the brook is
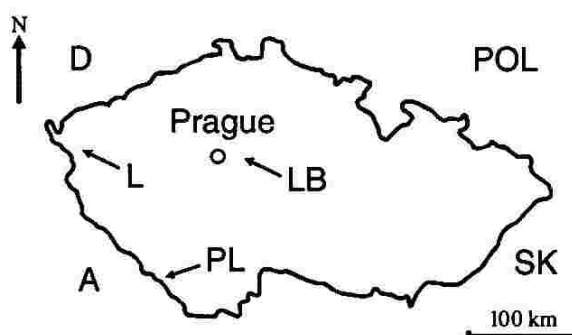

Fig. 1.   Location of the sites in Czech Republic.

filled with up to 10 m of fluvial sediment. Near the weir is a well equipped with inert material.

Bedrock is the Říčany light gray granite, the most northern part of the Central Bohemian massif. It is a biotite granite with trace amounts of muscovite. Grain size varies between 0.1 and 4 mm. The phenocrysts are mainly orthoclase. Table 10 contains the modal composition by Palivcová (1965).

Lenses of the fine-grained aplitic granite occurs in the area between Louňovice, Vyžlovka and Jevany. This younger granite is called jevanský. It is finer-grained, lower in mafic minerals, and its plagioclase is more sodic than in Říčany granite. Typical soils are cambisoils with horizons A, Bv, Go, and Gr (Zajíc 1998). The catchment is forested predominately by beech

Minerals	%
Quartz	28,0
Orthoclase	28,0
Plagioclase	35,0
Biotite	6,0
Others	<0,5

Tab. 10. Modal composition of the *Říčany granite*.

(*Fagus sylvatica*) (40%) and Norway spruce (*Picea abies*) (31%) (Macek 1998).

The Lysina Catchment (L)

Catchment Lysina is in western Bohemia approximately 10 km from Mariánské Lázně, region Karlovy Vary (Fig. 1). The closest village is Kladská. Area of the catchment is 0.273 km². Elevation ranges from 829 to 949 m.a.s.l. Average annual precipitation is approximately 950 mm. The bedrock is topaz-lithonitic granite (so called Krušné Hory granite), type Jelení (Fiala 1966). Krušné Hory granite is a part of the Karlovy Vary pluton. The Karlovy Vary pluton consists of numerous granite types: horský granite, Krušné Hory granite, and transmission granite. Krušné Hory granite is younger than horský granite and may be the bearer of the metal mineralization. All granites are SiO_2-oversaturated.

Quartz in the Jelení type granite occurs as porphyritic round grains. Plagioclase is commonly more sodic and sometimes albitised. Mica occurs as zinwaldite which was formed from biotite. Krušné Hory is very rich in volatile components (B, Cl, F, H_2O) and is called an autometamorphosed granite. The rock is white. Topaz in granites are less rich in fluorine. Accessory minerals are mainly cassiterite, apatite, zircon, fluorite, biotite and muscovite.

Minerals	%
Quartz	25
Orthoclase	40
Albite	17
Zinwaldite	11
Topaz	5
Accessories	3

Tab. 11. Modal composition of the Krušnohorský granite.

Modal composition is listed in Table 11 (Novák 1999; unpublished).

Soils are dominantly podsolic brown soils. Soil horizons are: O, E, B, C. (Krám et al. 1998). Gravitation zero-tension lysimeters are at depths 5, 10, 15 and 20 cm. Lysimeters 5 and 10 (L5, L10) are placed beneath the organic horizon (they collect water from the O horizon), lysimeters 15 and 20 (L15, L20) are between horizon E (elluvial) and horizon B (illuvial) (they collect water from the E horizon) (personal communication, P. Krám 1999). A spring (Lenka) in the catchment was sampled for groundwater samples. The catchment is forested nearly 100% by Norway spruce (*Picea abies*).

Plešné Lake (PL)

Plešné Lake is approximately 15 km south of the town Volary in the south of Czech Republic (Fig. 1). It lies at an elevation of 1090 m.a.s.l. on the slope of the Plechý mountain (1378 m.a.s.l.). Above the lake is a 220 m high cirque wall. The lake area is 0.666 km². Average depth is 8.24 m and the maximum is 18.3 m. Plešné lake is dimictic.

Bedrock is composed of two mica granite (eisgarn type). Eisgarn granite is the youngest member of the Moldanubian pluton. Moldanubian pluton is in the southeast of the Czech Republic and partially in Austria. Fresh rock is gray and medium-grained. Sparse biotite occurs in up to 6 mm porphyroblasts. Plagioclase is sericitised.
Modal composition of the Eisgarn granite is in Table 12.

Minerals	%
Quartz	28
Plagioclase	35
Orthoclase	30
Biotite	~3
Muscovite	~5

Tab. 12. Modal composition of the Eisgarn granite.

The dominant soils are podsolic brown soils. Soil cover is very discontinuous and includes horizons A, E, Bh and Bs. Tree cover is nearly all Norway spruce (*Picea Abies*).

Methods of sampling

Water samples were collected from August 1998 until February 1999, once a week or biweekly at the Lesni brook catchment and monthly at the Lysina catchment. Lake water, groundwater and soil water samples were collected irregularly. All samples were unfiltered.

Sample containers for cations determination were leached at least 24 hours with 10% HNO_3 and filled with deionized water. Another 500 ml sample was collected for ion exchange column treatment in the laboratory. Samples for DOC determination were collected in 0.33 l PE bottles.

Soil water samples were collected from the lysimeters storage bottles and treated the same as surface water samples. All samples for cations analysis were stabilized with 1 cm³ HNO_3 (distilled under the boiling temperature) per 100 ml of sample.

Water and air temperature were measured at the time of sample collection. Discharge was measured with aid of calibrated container and watch at the V-notch weir. The measurement result was checked by the equation for a Thomson spillway ($Q = 0.0146 * h_0^{2.5}$, where Q [l/s] is discharge, h_0 [cm] is height of the water in the notch).

Element	Detection limit
SiO_2	0,30 mg/l
Al^{n+}(FAAS)	0,20 mg/l
Al^{n+}(GFAAS)	10,00 µg/l
Na^+	0,01 mg/l
K^+	0,01 mg/l
Mg^{2+}	0,01 mg/l
Ca^{2+}	0,01 mg/l
Mn^{2+}	5,00 µg/l
Fe^{2+}	10,00 mg/l
Be^{2+}	0,02 µg/l
Cd^{2+}	0,04 µg/l
Cl^-	0,20 mg/l
F^-	0,02 mg/l
SO_4^{2-}	0,50 mg/l
NO_3^-	0,30 mg/l

Tab. 13. Detection limits for determined elements.

Cation and Anion Determination

Cations were determined in the Czech Geological Survey (CGS) laboratories. Concentrations of Na^+, K^+, Mg^{2+}, Ca^{2+}, Mn^{2+}, Fe^{2+}, Al^{3+} and SiO_2 were measured by flame AAS (FAAS). Determination of Cd^{2+}, Be^{2+} and Al^{3+} (< 0.2mg/l) was performed with graphite furnace AAS (GFAAS). Cl^-, NO_3^- and SO_4^{2-} were determined in the CGS laboratories by high pressure liquid chromatography (HPLC). Columns were Tessek HEMA-S1000 Q-L 10 mm, the mobile phase was 0.5 mM sulfosalicylic acid buffered to pH=5.4 with borax. Total F was determined with a fluoride ion selective electrode (F-ISE) after addition of the TISAB buffer, which frees the F bound in complexes. Detection limits for each determination are listed in Table 13.

Conductivity, pH and DOC Determination

Determination of pH and conductivity was performed on the day of sampling with a combined electrode (Radiometer GK2401C) and portable pH-meter (Radiometer PHM). Conductivity was determined with a Radiometer CDM 80 and platinum electrode Radiometer CDC104.

DOC was determined after filtration of the sample through glass fiber filter MN-5 0.4 µm (Macherey Nagel Germany®). Analysis was performed on the LiquiTOC Analyser (Foss Flesh Heraeus®).

Element Speciation

Element speciation was modeled with the software Mineql+ version 3.01b (Schecher and McAvoy 1992). Data inputs were: water temperature, pH, anion and cation concentrations. Input cation concentration was the Me(dif) concentration as explained later in the text.

Positively charged elements were removed with catex DOWEX 50W (Strongly Acidic Cation Exchange Resin). After pH measurement the sample was poured through the column with a pH value that corresponded with the sample pH. Pouring speed was 100 ml per 10 min. After passing through the column the sample pH was remeasured. If the pH value changed by less than 0.5 unit the extraction was considered valid.

The sample that passed through column was analyzed the same way as the "total" sample. The difference between the two samples equals the positively charged ion concentration Me(dif). Concentration Me(0) of the sample that passed through the column is composed of negatively charged and neutral species and Me(p) particle-bound element, and organic species Me(org). If the pH>5.5 , the portion of neutral complexes increases during the exchange and must be corrected. The molar concentration of these species was calculated from the value Me(tot). This correction causes little over estimation of those species but it is necessary.

Me (e.g., Be, Al, Fe)
Me(tot.) - acid soluble concentration Me
Me^0 - concentration of Me in neutral species, e.g., BeF_2^0
Me(0)   - concentration of Me passed through column, Me^0+Me(p)+Me(org)
Me(p)   - concentration of Me bound to particles
Me(org) - concentration of Me bound to organic substances
Me(dia) - concentration of Me passed through 8000 MWCO membrane
Me(spe) - concentration forming the speciation without Me(org) and Me(p)
Me(dif) - concentration of positively charged Me species captured by catex
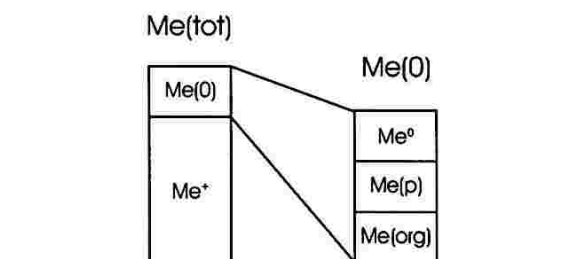
Fig. 2. Element speciation description.

$$Me(tot.) = Me(0) + Me(dif)$$
$$Me(0) = Me^0 + Me(p) + Me(org)$$

Dialysis

Sample was transported from the site in 1 L PE bottles at constant temperature. Dialysis was performed in the laboratory refrigerator with temperature similar to field temperature using the Spectra/Por® CE (Cellulose Ester) membranes with 5 ml volume and 8000 MWCO. Dialysis membranes were leached with 10% HNO_3 at least 24 hours before use. Dialysis was performed for at least 96 hours.

Rock Parameter Determination

Positions of the granites in QAP diagram were determined by means of the software Newpet. Some petrochemical calculations were performed by software Norman (Janoušek 1996). The petrochemical calculations are listed in table 18. Determination of the mineralogy was performed on rock thin sections with a scanning electron microscope Cam Scan S4 (Cambridge) with energy dispersive spectrometer Link ISIS 300 (Oxford Instruments) at the FSCU. Concentrations of Be in rock-forming minerals were measured using laser ablation in connection with a mass spectrometer LA-ICP-MS (VG PlasmaQuad 3) at FSCU. For standardization was used standard NIST-612. The Be concentration for NIST-612 39 ppm ($\pm$ 5.6) was published in Jackson et al. (1992).

Whole rock concentrations of Be were determined after total dissolution of the sample by AAS in the CGS laboratories. For the Eisgarn type the concentration was determined by OES method and had an orientation character (personal communication J. Vesely).

Because of problems during separation of minerals and possible contamination by other minerals (i.e., biotite enclosed in quartz), the Be concentration in each mineral was determined by the LA-ICP-MS method.

Results

Beryllium Distribution in Surface Waters

Lesní Brook

Beryllium concentrations in surface waters during the period (July 98-June 99) were < 5 µg/l. Fluorine concentrations were as high as 0.9 mg/l averaging F concentration were 0.7 mg/l. Concentrations of Al were < 1 mg/l. DOC concentrations averaged 8.27 mg/l. The concentrations of SO_4 averaged 66.1 mg/l.

Be behaved very similarly to Al (Fig. 3). During high discharge (Fig. 3) and decrease of the pH (Fig. 3) concentrations of Al and Be were elevated. Three hydrologic events were chemically and hydrologically characterized. Two events (Septem-
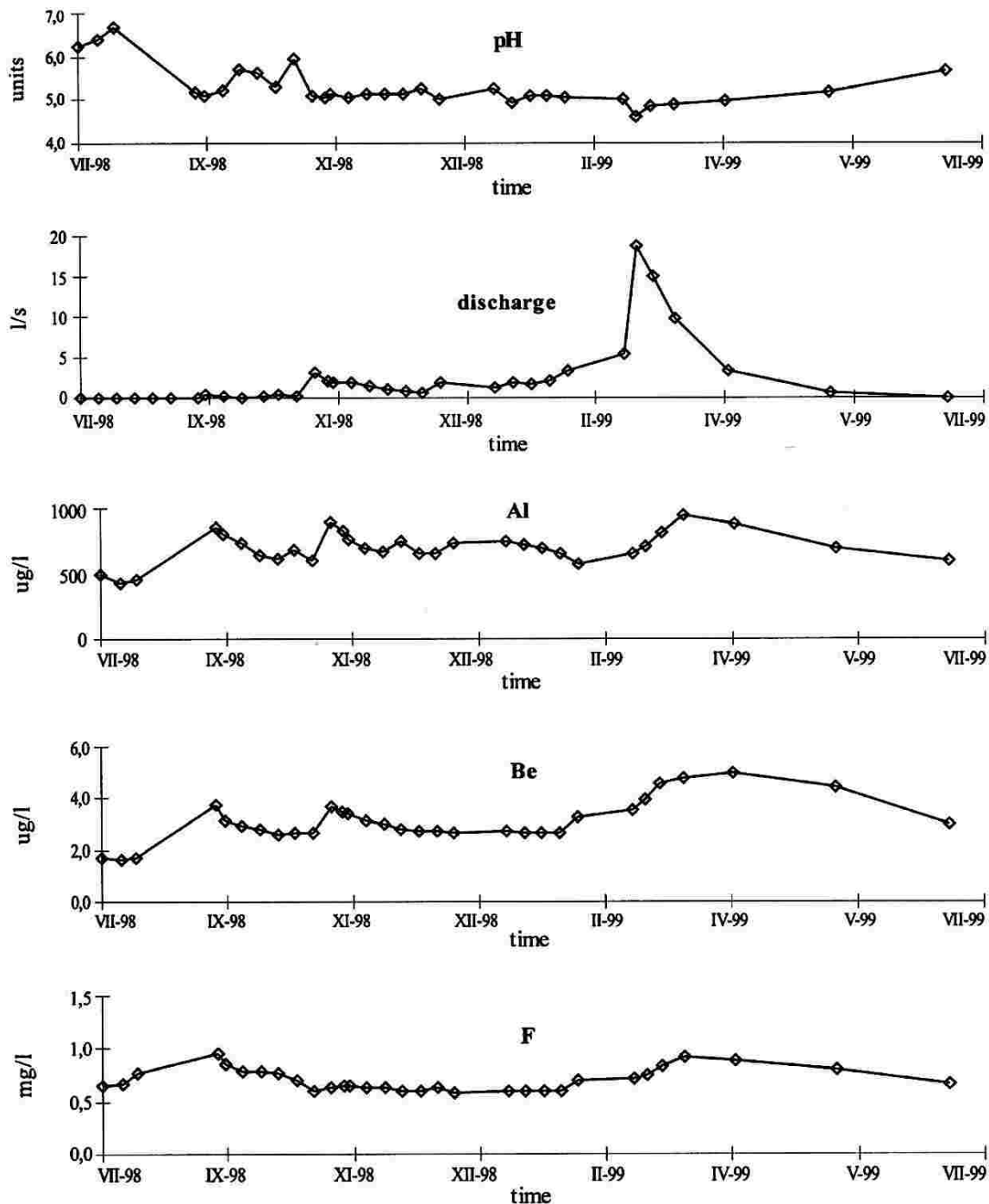
;. 3. Seasonal variations of the pH, discharge, Be, Al and F concentration at the Lesni brook.

14th, 1998; October 29th, 98) were caused by high rainfall. e third event was the spring snowmelt. The beginning of the ing snowmelt occurred at the end of February 99 (Fig. 3). ring the snowmelt the Be and Al concentration increased with very minor pH rise and discharge decrease. This phenomenon is caused by penetration of water as soils defrost. The first waters of the spring melt flow quickly on the frozen soil cover. Consequently the lowest pH value does not coincide with the

highest Be concentration. The concentration of Al at the end of snowmelt is slightly lower as the Be concentrations continue to increase slightly (Fig. 3).

The lowest concentrations of total Be occurred during nearly neutral pH (August 98). Uncharged Be species were the highest (Appendix, Fig. 21).

The changes in concentrations of all parameters for studied samples are listed in Appendix, Fig. 21 and Fig. 22.

Lysina brook

The surface water of the Lysina catchment is characteristically low in pH (3.9 to 4.2). Concentrations of Al averaged 1 mg/l but commonly exceeded 1 mg/l but the F concentration is lower than at Lesni Brook. The average F concentration was 0.2 mg/l. DOC concentration averaged 19 mg/l, but during the high discharge events reached up to 30 mg/l. At the Lysina catchment concentrations of Be averaged about 1 µg/l.
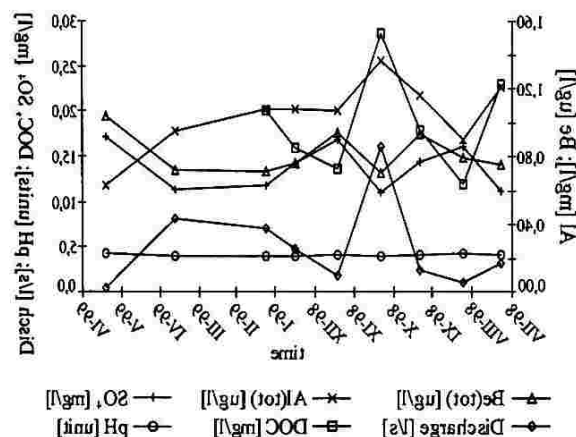

Fig. 4. Seasonal variations of Lysina brook chemistry.

On (October 29th, 1998) discharge increased to 16 l/s during a high precipitation event (Fig. 4). Water table rose and majority of shallow water flowed horizontally through the layers with no penetration of the deeper soil profile. The main cation (Ca, K, Mg, Na) concentrations and Be decreased. Al and DOC rose to maximal values. Concentrations of F and SO$_4$ decreased. The highest Be concentration and the lowest Al concentration occurred during low discharge. Variations of all the other studied factors are shown in Appendix, Fig. 19 and Fig. 20.

Lysina Soil waters

Soil waters from lysimeters were sampled only on July 9th, 1999. Concentrations of the Be in soil waters from the top soil horizons were a maximum of 0.11 µg/l. The first two lysimeters (5 and 10 cm) represent O horizon and the other two the E horizon. Concentrations of the Be increased with depth, reflecting the the pH decrease and F concentration increase (Fig. 5). Heterogeneity in soils and each horizon is very high.

Soil water data are depicted on Fig. 5. It is remarkable that Be concentrations reflect the changes in F concentration better than the pH. The concentration of Be(0) was, for all the horizons, lower than 0.02 µg/l.
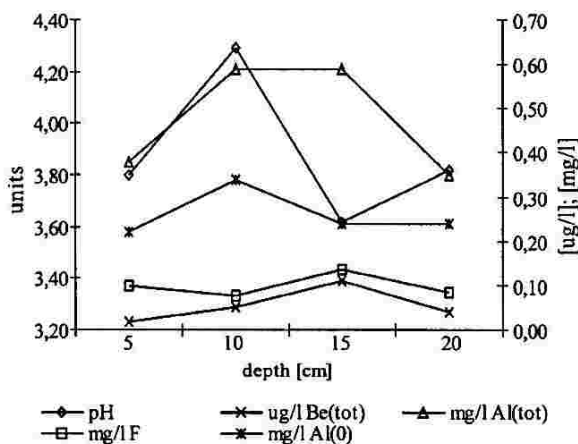

Fig. 5. Variations of pH, F, Be, Al with depth in catchment Lysina soil horizons (L).

Be Speciation - Surface Waters

Lesní brook

The important Be species, calculated by MINEQL, in the Lesni brook waters were: Be^{2+}, BeF$^+$, BeF$_2$^{0}, BeSO$_4$^{0} and BeOH$^+$. BeSO$_4$^{0} never exceeded 1% of the total concentration. Changes in concentration species are depicted on Fig. 6. Concentrations of Be^{2+} increase with decreasing pH and range from 0.15 to 0.01 µmol/l (Fig. 6).

BeF$^+$ was the major species of beryllium in the LB water. Its concentrations are usually not lower than 0.15 µmol/l (1.35 µg/l) and increased with decreasing pH. (Fig. 6). This complex always formed > 50% of total Be concentration.

BeOH$^+$ increases at higher pH values ranging from 0.002 and 0.025 µmol/l (max. 0.2 µg/l) (Fig. 6).

Complex BeF$_2$ is the only significant non-charged species of Be. Its proportional concentration increases with increasing pH. (Fig. 6).

Lysina brook

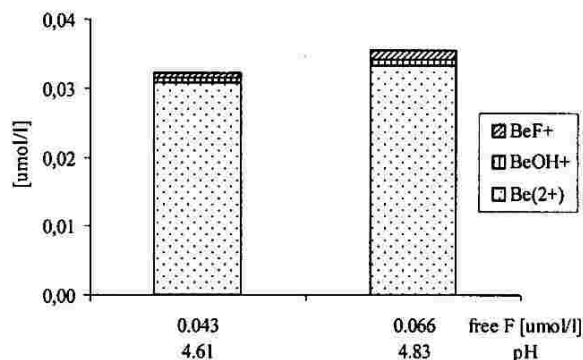Be speciation at the Lysina catchment varies little because of the small pH range (Fig. 6). Main forms of Be are Be^{2+} and
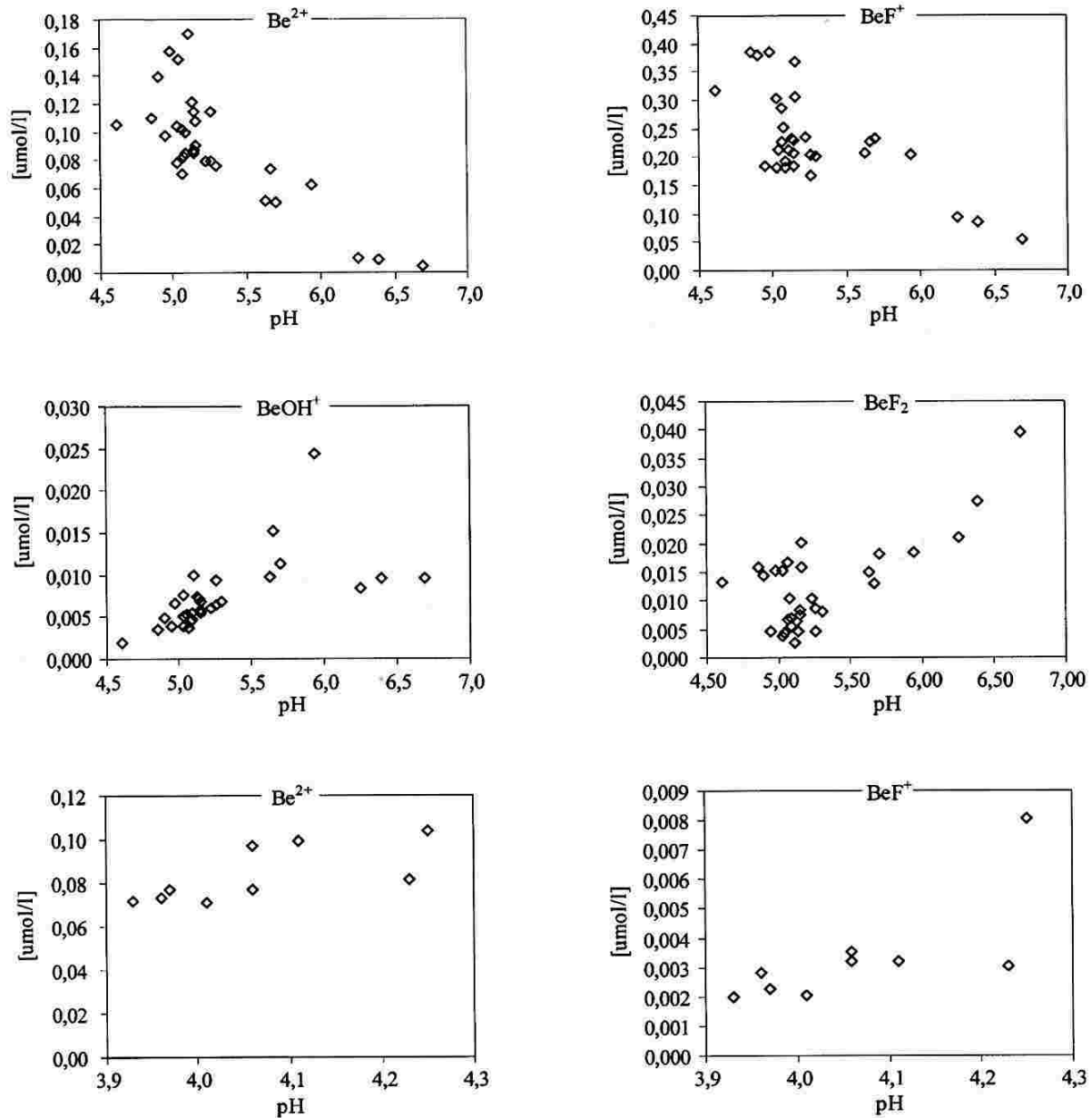

Fig. 7. Be Speciation in Plešné Lake (PL).

Fig. 6.   Main Be species concentrations versus pH.

BeF$^+$. BeF$_2^0$, BeSO$_4^0$ and BeOH$^+$ comprise less than 1% of the total Be. Be^{2+} comprises over 95% of the total Be concentration. Concentrations of BeF$_2$ and BeOH$^+$ increase at higher pH.

Plešné Lake

Plešné Lake water was sampled on May 28th, 1999 and June 19th, 1999. Total Be concentration was about 0.3 μg/l. Total Al concentration exceeded 0.6 mg/l on June 19th, 1999; the organic Al(0) was approximately 0.1 mg/l. Fluoride concentrations were as low as 0.1 mg/l.

More than 95% of the Be was Be^{2+} (Fig. 7). BeF$^+$ and BeOH$^+$ total and less than 5% of the total Be concentration. Concentration were slightly higher at higher pH and F$^-$ concentration.

Be Speciation - Groundwaters

Lesní Brook catchment

The first sample of water from well EH-8 was stagnant water. The second sample was taken after pumping. The Be concentration after pumping was lower than the detection limit (0.02 μg/l).
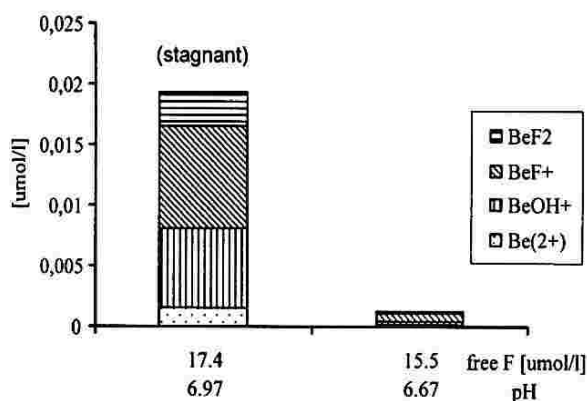
Fig. 8. Speciation of Be in the EH-8 well (LB).

Fig. 10. Be speciation in the soil water (L).

The pH of the shallow groundwater on the Lesní brook catchment was 6.4 to 6.9 and concentrations of Be and Al were very low (< 0.2 µg Be/l and < 54 µg/l Al). BeF$^+$ plus BeOH$^+$ were approximately 80% of the total Be concentration. BeF$^+$ was approximately 15% and 5% was Be^{2+} (Fig. 8).

Lysina Catchment
Speciation of the beryllium in the Lenka spring, Lysina catchment was very different from the surface waters. Be in the shallow groundwater (2.5 µg/l) was 3 times the concentration in surface waters. F$^-$ concentrations 0.6 mg/l are approximately 3 times higher than surface water. Concentration of Al was approximately half (0.6 mg/l) in comparison to stream water. The pH was about 5.5. Be occurred mainly as: Be^{2+}, BeF$^+$, BeF$_2$ and BeOH$^+$ (Fig. 9). Be^{2+} plus BeF$^+$ comprise 90% of the total Be.
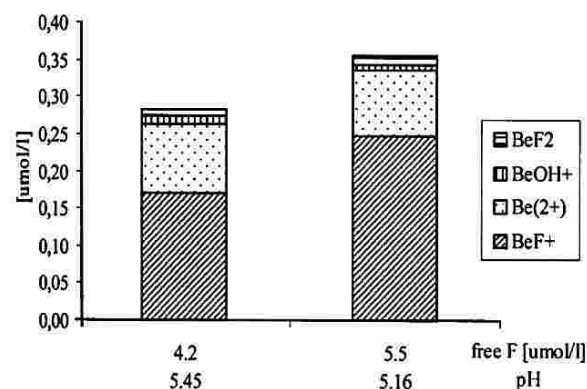

Fig. 9. Be speciation in groundwater (L).

Be Speciation - Soil Waters

Lysina Catchment
Soil waters on the Lysina catchment had pHs between 3.6 and 4.3. The speciation for Be in soil waters from depths 5, 10, 15 and 20 cm is shown on Fig. 10. Be^{2+} was the dominant species. Another species was BeF$^+$ but in low concentrations. The BeF$^+$ concentration increased with greater depth.
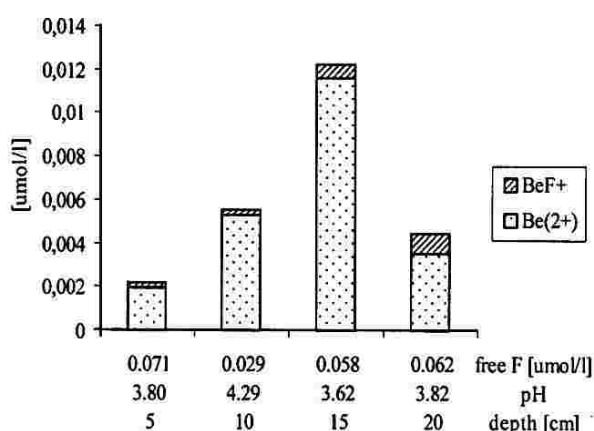
Relationships

Lesní Brook
The Fig. 11a,b demonstrate the similarity in behavior of Al and Be. Both elements respond to pH. Their concentration is increasing with decreasing pH. Aluminum was more strongly correlated with pH than Be. The concentrations of Al(0) and Be(0) also correlate with pH (Fig. 11c,d).

Relationships between Be(tot) and Al(tot), respectively Be(0) and Al(0) are shown on Fig. 11e,f. Correlation of the Be(tot) and Al(tot) was much higher in period before the beginning of snowmelt. The biggest differences in the behavior of Be and Al occurred thus in time of the spring snowmelt.

The relationship of Al(0) and Be(0) on DOC concentration is shown in Fig. 11g,h. The DOC concentrations were not determined for all the samples so the figures contain fewer points than others. Relationship of the Al tot. and Be tot. concentrations on the discharge is shown on Fig. 11i,j.

Lysina Brook

Concentrations of Be in the waters of Lysina brook are not well correlated with pH (Appendix, Table 17). The concentration of Be correlates the best with SO$_4$ concentration (Fig. 12a). Apart of that Al does not correlate with SO$_4$ that much (Fig. 12b). Be(tot) correlates with F weakly but Al(tot) with F show no relationship (Fig. 12c,d). Concentrations of Al(tot) are related to DOC concentration. Be is unrelated to DOC concentrations (Fig. 12e,f). Fig. 12h demonstrates the strong relationship of Al(0) and DOC. Aluminum forms strong complexes with DOC. Be(tot) and Be(dif) are strongly correlated (Fig. 12g). Because there is no organic, charged or particulate Be, the Be(tot) concentration is not changing.

Surface Water Dialysis

Water dialysis was performed to evaluate of cation-exchange procedure for Be speciation. Dialysis was performed on four samples. Three were from Lesni brook catchment (March 3rd, March 9th and July 1st, 1999) and one was from the Lysina catchment (April 7th, 99). For two of three samples from the Lesni Brook Be(tot) exceeded Be(dia). This difference was greater at higher pH (Fig. 13).
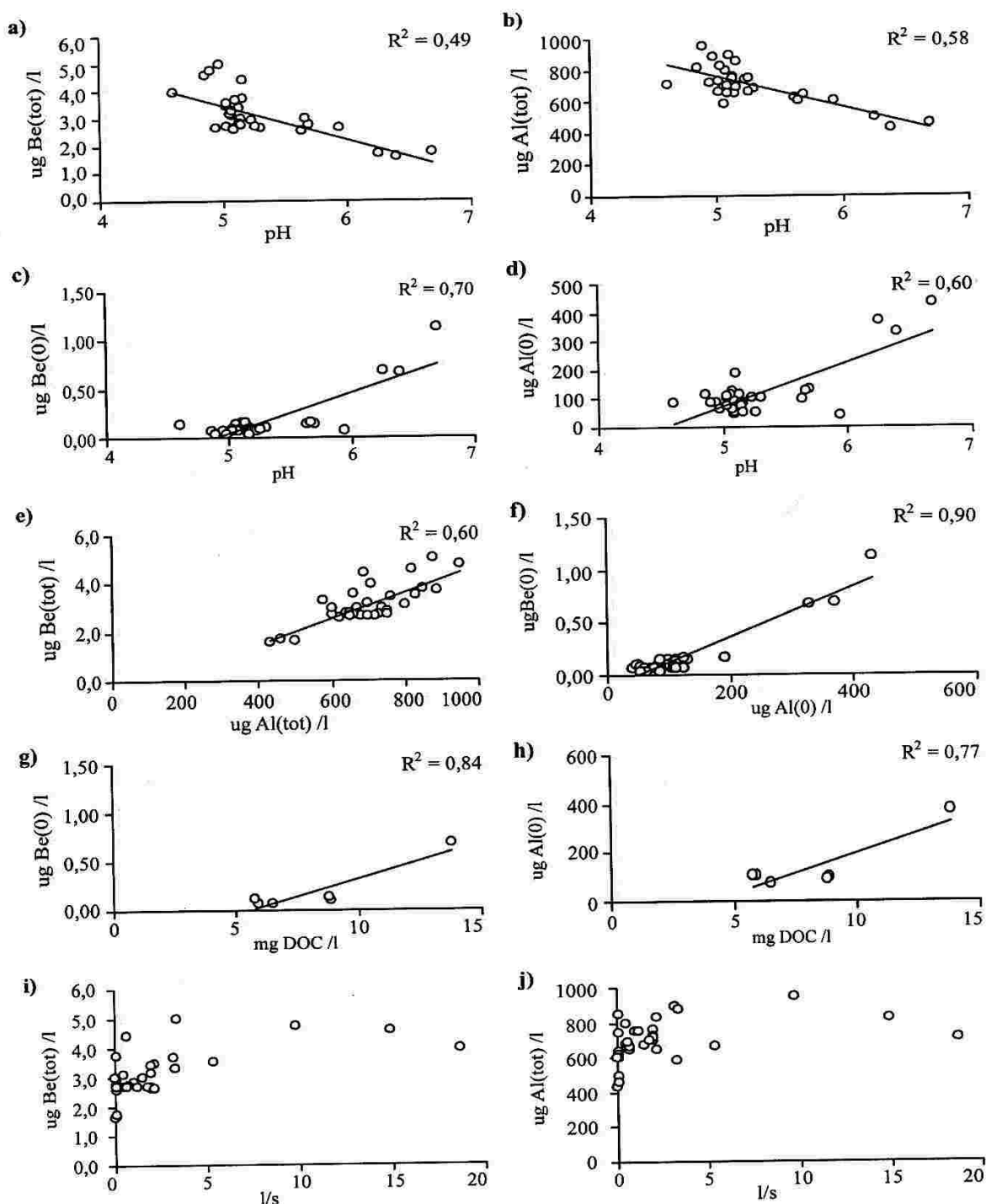
Fig. 11a-j. Relationships of the Be, Al fractions with pH, DOC, discharge (LB).

Beryllium in Bedrock and Minerals

The results of the analysis are in table 14. The highest K and the lowest Na concentration are in the Říčany type. Fluorine concentrations are the highest in the Jeleni granite, but there is approximately 5% topaz in the rock (Table 11). Apparently the fluoride in topaz is not very mobile. The Jeleni granite is typical with very low MgO and CaO concentrations.

The positions of each granite in the QAP diagram is shown on Fig. 14. The samples belong to the field 3b, monzogranites.
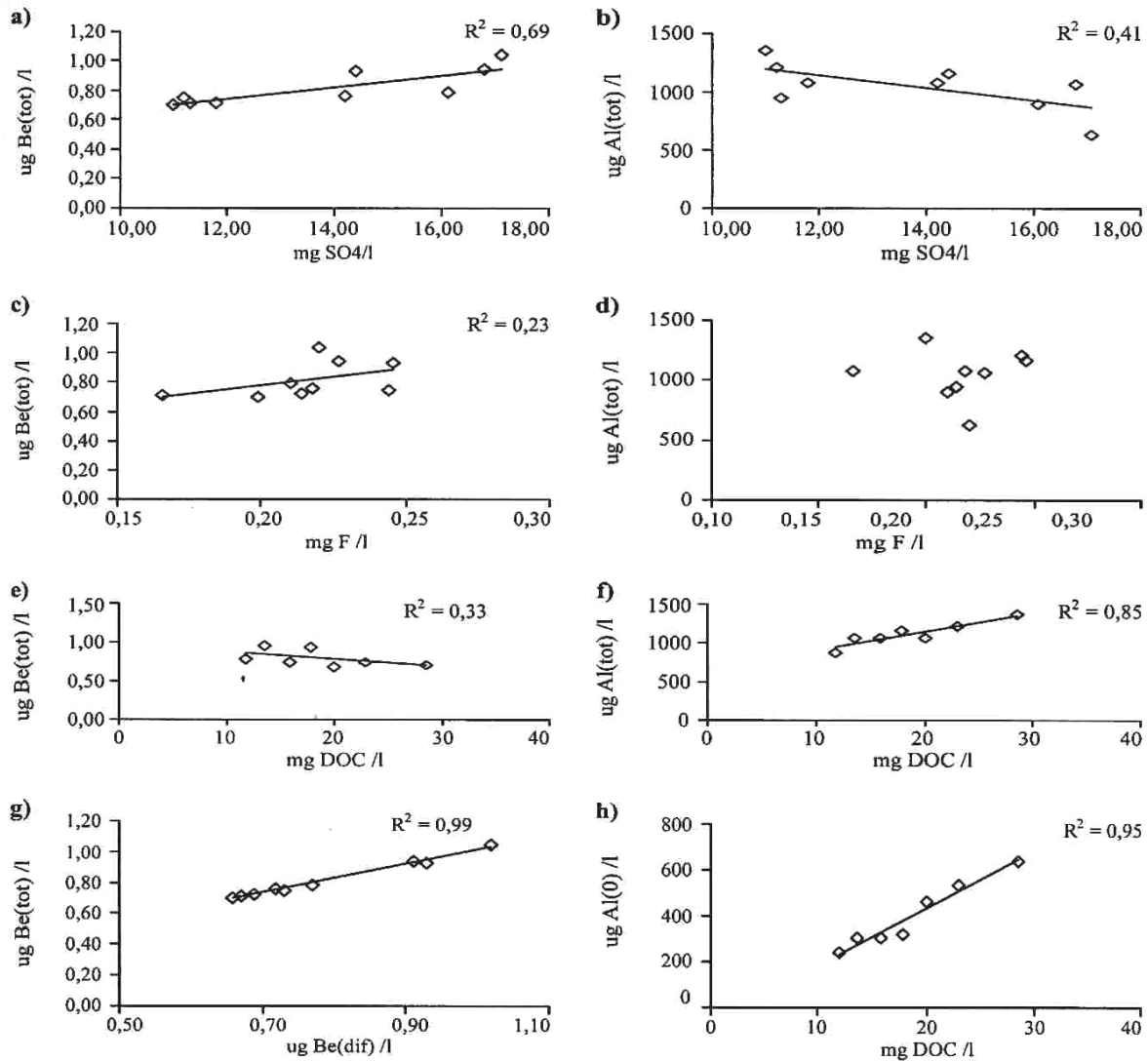
Fig. 12. Relationship of the Be, Al fractions with SO₄, F, DOC (L).

The highest total Be concentration contained the Říčany granite (16.8 ppm). The highest concentrations of Be in minerals occurred in the micas (up to 17.2 ppm). The major portion of the rock Be was in plagioclase. In oligoclase of the Říčany granite, concentrations of Be ranged between 5.3 and 43.1 ppm. In albite of the Jelení granite the concentrations ranged from 1.5 to 4.2 ppm. Higher concentrations (AAS) of the Be in feldspars mixture are caused by mica inclusions. Quartz had the lowest Be concentration. Be concentrations in orthoclase were low except the Jelení granite.

Discussion

It is clear that most Be in surface water and groundwater is not of atmospheric origin (Skřivan et al. 1994; Skřivan et al. 1993; Krám et al. 1998).

The highest concentrations of Be in catchment minerals occur in micas and plagioclase. Low concentrations occur in orthoclase and quartz. Most Be released during weathering is

from plagioclase. All results are in accordance with previous works (e.g., Minařík 1975; Němec 1978; Macháček 1966). The data acquired by LA-ICP-MS technique were more accurate.

Be behavior in the surface waters is different for each catchment. Different behavior was caused by different chemistry of

Fig. 13. Be concentration (μg/l) for dialyzed samples.

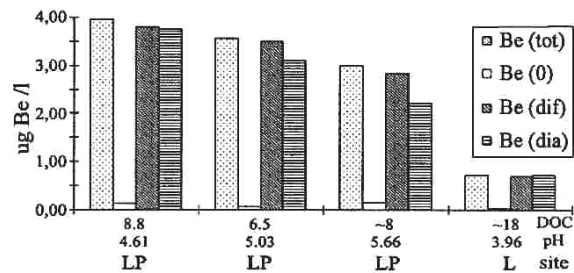| Pluton Granite type	Karlovarský Jelení	Central Bohemian Říčany	Moldanubian Eisgarn
SiO_2	72,64	71,00	73,12
TiO_2	0,07	0,23	0,19
Al_2O_3	14,92	14,74	14,37
Fe_2O_3	0,12	0,52	0,38
FeO	0,66	0,83	0,89
MnO	0,04	0,03	0,03
MgO	0,06	0,89	0,32
CaO	0,42	0,89	0,76
Na_2O	4,11	3,76	3,40
K_2O	4,29	5,53	4,70
H_2O^+	0,81	0,64	0,85
P_2O_5	0,39	0,15	0,26
CO_2	0,02	0,01	0,07
F^-	0,63	0,21	0,12
S	0,01	0,00	0,01
Sum	99,19	99,42	99,47

Tab. 14. Studied granites chemical analysis.

the waters as well as different Be distribution and amount in the bedrock. The main factors affecting the Be aqueous speciation are the discharge, pH, Al, F^-, SO_4^{2-} and Be concentrations.

At the Lesni Brook catchment there was clear dependence of the Al and Be concentrations on pH (Fig. 11a,b). This trend was not detected at the Lysina catchment. This produces differ-

Říčany granite

Rock-forming mineral		Be [ppm]	
Generally	Composition	LA-ICP-MS	AAS
Quartz	SiO_2	0,4	<0,8
Oligoclase	$Na_{(90-70\%)}Ca_{(10-30\%)}(Al,Si)AlSi_2O_8$	16,9	19,6
Orthoclase	$KAlSi_3O_8$	0,7	
Biotite	$K(Fe, Mg)_3AlSi_3O_{10}(F, OH)_2$	17,2	11,6
Whole Rock			16,8

Jelení granite

Rock-forming mineral		Be [ppm]	
Generally	Composition	LA-ICP-MS	AAS
Quartz	SiO_2	1,0	1,7
Albite	$NaAlSi_3O_8$	2,3	4,7
Orthoclase	$KAlSi_3O_8$	3,0	
Zinwaldite	$KLiFeAl(AlSi_3)O_{10}(OH, F)_2$	13,2	13,7
Whole Rock			9,1

Eisgarn granite

Rock-forming mineral		Be [ppm]	
Generally	Composition	LA-ICP-MS	AAS
Quartz	SiO_2	0,2	
Plagioclase		11,7	
Orthoclase	$KAlSi_3O_8$	1,0	
Mica	$K(Fe, Mg)_3AlSi_3O_{10}(F, OH)_2$	11,2	
Whole Rock			~8,0*

* determined by OES method (based on personal communication Veselý 1999)

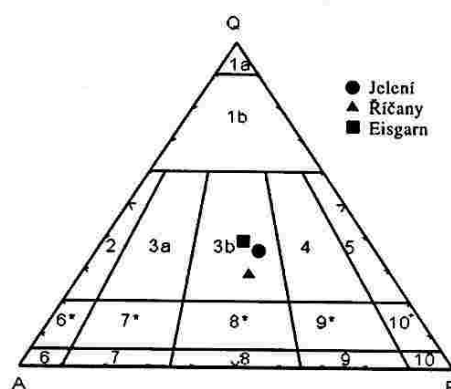**Tab. 15.** Concentrations of Be rock-forming minerals and granites, (averages).

Fig. 14. Positions of studied granites in QAP figure.

ent Be behavior. Al and Be behave very similarly (Appendix Table 16). This behavior is less during the spring snowmelt.

During the high discharge events the concentrations of A and Be in Lesni brook increased as the pH decreased (Fig. 3) Precipitation decreases stream pH and mobilizes metals boun(to soil organic substances and Fe, Mn and Al hydroxide: (Skřivan et al. 1993).

The response to high discharge at Lysina was quite differ ent. Soil was saturated by the precipitation and some of the com ponent concentrations were diluted. Concentrations of F^-, SO_4^{2-} and Be decreased and concentration of Al, DOC increased t(maximal values (Fig. 4). Almost 50% of the Al(tot) concentra tion in stream water occurred as Al(0). The increase of the Al(0 fraction is caused by concurrent increase of the Al and DOC concentrations, thus forming more organic complexes.

Be speciation at Lysina and Lesni Brook are different too At Lesni Brook with pH ~ 5 more than 80% of the Be(tot) is Be^{2+} and BeF^+. At higher pH Be^{2+} is replaced by BeF_2^0 anc $BeOH^+$. BeF^+, was the dominant Be complex, is produced by relatively high free F^- concentration. As F^- is depleted by pref erential Al complexation, the Be-F complexes become less abun dant and domination of the ion Be^{2+} takes place. This occurs a the Lysina catchment where the low F^- concentration causes the Be^{2+} domination. The ion Be^{2+} forms 95% of the Be(tot) con centration. BeF^+ comprises less than 5%. This speciation was also described by Krám et al. (1998).
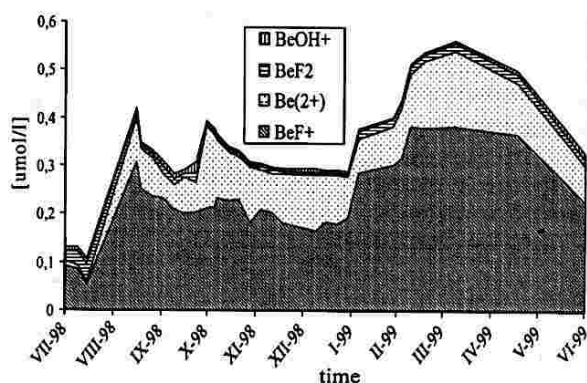

Fig. 15. Seasonal variations of the Be species in the Lesni Brook water.

Dependence of the Be(0) and Al(0) fraction on increasing pH in case of Lesni Brook (Fig. 11c,d) may be caused either by growth of the un-charged complex formation (e.g., BeF_2) or increase of the organic complex formation and finally increase in Be adsorbed onto particulate Al or Fe. Correlations between Be(0), Al(0) and Fe(0) are strong at Lesni Brook catchment (Appendix, Table 16). Correlation coefficient between Be(0) and Al(0) was 0.95; for Be(0) and Fe(0) was 0.97.

Dialysis results for Lesni Brook samples show that with increasing pH there was less Be passing through membrane. Concentrations Be(dia) are not similar to Be(dif) concentrations. This means that during the solution passage through catex, Be may desorb from the solid particles or decomposition of weak organocomplexes or colloidal Al or Fe forms may occur. Released Be ions are than captured by catex. For the dialyzed sample from the Lysina catchment almost, all Be passed through the membrane. During passage of the sample through the catex column, minimal concentrations passed through. This fraction is probably composed by Be complexes with organic matter smaller than 8000 MWCO.

In the water from the Lenka spring the Be speciation was more diverse compared to surface water. The spring has higher F-and Be concentrations than Lysina brook. DOC values usually do not exceed 1 or 2 mg/l and Al concentrations were lower too. The Al was lower mainly because of slightly higher pH (5,3). Speciation was dominated by BeF^+ and Be^{2+}, comprising over 90% of the Be(tot) concentration. Groundwater of the Lesni Brook (well EH-8) has a circum-neutral pH and F surplus (over 98% as free F-). The free F- surplus was caused by low Al concentration. Speciation in stagnant water was similar to speciation in Lesní brook during very low discharge.

Be speciation of the Lenka spring (Lysina catchment) and in Lesni Brook water were different (Fig. 16 and Fig. 17). Concentrations of Be and F were nearly the same, but the Al and SO_4^{2-} concentration were quite different. In groundwater (LE) there was dramatically lower SO_4^{2-} concentration.

Be^{2+} and BeF^+, formed in all four cases more than 90%. Molar concentrations of the BeF^+ are slightly higher for the Lenka spring because of higher free F concentration. Higher free F concentration was caused by low Al concentrations (Fig. 16). Surface water contained higher fractions of Al(0) and Be(0). That is caused by higher DOC concentration and formation of organic complexes. Also there was more particulate matter be-

cause of turbulent flow. There is also a possibility of precipitated but suspended Al due to CO_2 degassing at Lesni Brook. However no data on CO_2 are available on either catchment.

In Plešné Lake the main specie of Be was the Be^{2+}. This is caused by low F- concentration or high Al concentrations. Al(0) was relatively high, probably because of organic complexes, not particulate Al.

Speciation of the Be in soil waters of the Lysina catchment was related to pH and concentrations of available ligands. Be concentrations were low. Al bound all available F. Thus the main specie was Be^{2+}.

Be^{2+} is the dominant form of Be in the Lysina surface water and soilwater. Groundwater has more Be and speciation of Be is more diverse (Fig. 18). This is caused by higher pH and free F-.

Plants growing on the soils with higher Be content contain more Be (Table 9). This Be may be from the soil water with very mobile Be^{2+}. The soil water is captured by the plant root systems.

Some Be in the bark and foliage originated from the atmosphere. Near the Koněpruské caves were found higher concentrations of Be in soils correspond to the bedrock composition. But in the alkaline soils, the Be is very immobile and not available for the plants.

Fig. 17. Percent comparison of Be speciation in LB and LE.

Fig. 16. Molar comparison of Be speciation in LB and LE.

Fig. 18. Speciation changes with depth at Lysina catchment.

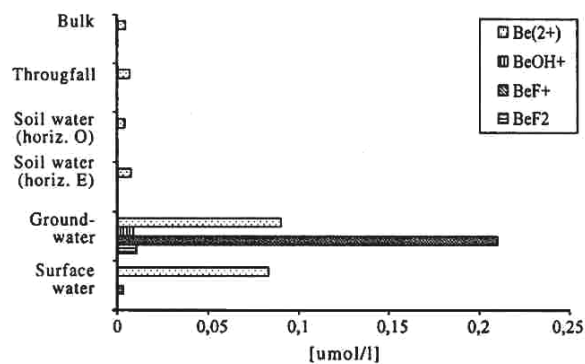| Granite type	Jeleni	Říčany	Eisgarn
Orthoclase	24,3	29,7	26,0
Albite	34,8	31,8	28,8
Anorthite	0,0	3,4	1,6
Quartz	32,5	26,5	34,6
Apatite	0,9	0,4	0,6
Magnetite	0,2	0,8	0,6
Ilmenite	0,1	0,2	0,2
Biotite	1,8	4,7	3,0
Amphibole	0,0	0,0	0,0
Calcite	0,0	0,0	0,2
Corundum	3,7	1,3	3,1
Rest	0,7	0,4	0,7
Sum	98,5	99,2	99,3
qz	63,5	55,4	64,7
F	24,4	34,2	23,9
fm	12,1	10,4	11,5
F_fm	12,3	23,8	12,4
Sum	100,0	100,0	100,0
Q	33,1	27,6	35,4
C	3,6	2,2	3,5
Or	25,1	30,2	26,5
Ab	35,6	32,2	29,2
An	0,0	1,2	0,7
Mt	0,2	0,8	0,6
Il	0,1	0,0	0,0
Tn	0,0	0,6	0,5
Ap	0,8	0,4	0,6
Fr	0,0	0,4	0,2
Bi	1,5	4,4	2,8
MgBi	0,2	3,0	1,1
FeBi	1,3	1,5	1,7
Sum	100,0	100,0	100,0
W.I.	9,9	7,8	9,6

Tab. 18. Some petrochemical calculations for the studied granites, data in %.

Conclusions

1. Be in water originates mainly from the weathering of rock and soil, not from the atmosphere. Its mobility is regulated by concentrations of H^+ (Lesni Brook) or by concentrations of F^- and SO_4^{-4} anions (L,LB). During high flow, Be concentrations are elevated.
2. At the Lesni Brook catchment the main forms of the Be in the surface water were Be^{2+} and BeF^+. Under low dischargeand high pH, $BeOH^+$ and BeF_2 species increased.
3. The Be(0) concentration increases with increasing pH and DOC.
4. At Lysina catchment the main Be specie is Be^{2+} because of low F concentration. In the F-rich groundwater from the Lenka spring the BeF^+ and Be^{2+} species dominate.
5. Speciation of the Be in Plešné Lake and soil waters of the Lysina catchment was dominated by Be^{2+}, because of low pH and low F^- concentrations.
6. The concentration of Be in studied granites are higher than crustal average. The highest Be concentration were found in plagioclases (up to 43 ppm) and micas (up to 33 ppm).

Acknowledgements

References

BENCKO, V., CIKRT, M. and LENER, J., 1984. Toxické kovy v pracovním a životním prostředí člověka, *Avicenum*, 264 pp, (in Czech).

BENEŠ, S., 1994. Obsahy a bilance prvků ve sférách životního prostředí, II. Part, MŽP ČR, Praha,154 pp., (in Czech).

BEUS, A.A., 1960. Geochimija berillija i genetičeskije tipy berillievich mestorožděnij. Moskva, (in Russian).

BEUS, A.A., 1956. Geochemistry of berylium. *Geochemistry (USSR)*, 1: 511-531.

BOROVEC, Z., 1993. Partitioning of silver, beryllium and molybdenum among chemical fractions in the sediments from the Labe river in Central Bohemia - Czech Rep. *GeoJournal*, 1993: 359-364.

BOUŠKA, V. and PEŠEK, J., 1997. Distribution of Sulfur and Arsenic in Coal of the Sokolov Basin, *Research Report, Charles University, Prague* (in Czech).

BOWEN, H.J.M., 1979. Environmental Chemistry of the Elements. *Acad. Press, London*.

EDMUNDS, W.M., KINNIBURGH, D.G. and MOSS, P.D., 1992. Trace metals in interesticial waters from sandstones: acidic inputs to shallow groundwaters. *Environ. Pollut.*, 77: 129-141.

FERNANDEZ-TURIEL, J.L., 1995. Environment monitoring using surface waters, river sed. and vegetation in Argentina, *Environment Int.*, 21: 6.

FIALA, F., 1961. Závěrečná zpráva o výzkumném úkolu: Základní geologický výzkum Císařského lesa za léta 1955-1960. MS Ústř. Úst. Geol.Praha (in Czech).

GRIFFITTS, W.R. and SKILLETER, D.N., 1991. Beryllium, Chapt II4. In: E. MERIAN (Editor), Metals and their compounds in the environment, *VCH, Weinheim*.

von GUNTEN, M.R., BENEŠ, P., 1995. Speciation of radionuclides in the environment. *Radiochimica Acta*, 69: 1-29.

JAGOE, C., HAINES, T.A. and MATEY, V., 1993. Beryllium ion effects on fish in acid waters analogous to aluminum toxicity: *Aq. Toxic.*, 24: 241-256.

JACKSON, S.E., LONGERICH, H.P., DUNNING, G. R. and FRYER, B.J., 1992. The application of laser ablation microprobe-inductively coupled plasma-mass spectrometry (LAM-ICP-MS) to in situ trace element determinations in minerals. *Canadian Mineralogist*, 30: 1049-1064.

JANOUŠEK, V., 1996. NORMAN: Program pro petrochemické

a normativní přepočty analýz hlavních prvků na IBM PC. *Zpr. geol. výzk. za rok* 1995, 95: 99–100 (in Czech).

KASTE, J., 1999. Dynamics of Cosmogenic ⁷Be and Bedrock-Derived ⁹Be in Forested Ecosystems in Maine, U.S.A. Unpub. M.Sc. Thesis, Department of Geological Sciences University of Maine, Orono.

KRÁM, P., HRUŠKA, J. and DRISCOLL, C.T., 1998. Beryllium chemistry in the Lysina catchment, Czech Republic. *Water, Air, and Soil Pollution*, 105.

KUBIZŇÁKOVÁ, J., 1987. Behavior of Beryllium in the Sokolov District. In: B.MOLDAN and T.PAČES (Editors), *GEOMON Extended Abstracts*, ČGÚ.

MACEK, L., 1998. Revize taxačních údajů a přírodních poměrů na modelovém povodí Lesní potok ve SPR Voděradské Bučiny. Thesis of the Czech Agricultural Univ. Prague, Faculty of Forestry (in Czech).

MACHÁČEK, V., ŠULCEK, Z. and VÁCL, J., 1966. Geochemie berylia v sokolovské pánvi. 3 *Sborník geol. věd*, TG, 7: (in Czech).

MANKOVSKA, B., 1997. Concentrations of nutritional and TE in spruce and beech foliage as environmental indicator Slovakia. *Lesnictví*, 43(3): 117-124.

MINAŘÍK, L., 1975. Distribuce prvků v hlavních horninotvorných minerálech plutonitů. *Čas. Pro min. a geol.*, 20 (2): 185-199, (in Czech).

NEAL, C., JEFFREY, H.A., CONWAY, T., RYLAND, G.P., SMITH, C.J., NEAL, M. and NORTON, S.A., 1992. Beryllium concentrations in rainfall, stemflow, throughfall, mist and stream waters for an upland acidified area of mid-Wales. *J. Hydrol.*, 136: 33-49.

NĚMEC D., 1978. Genesis of aplite in the Říčany massif, central Bohemia. *Neues Jahrbuch für Mineralogie, Abhandlungen*, 132: 322-339.

NĚMEČEK, J., 1995. Contamination of soils in industrial. affected regions of Czech Republic. *Arch. Ochr. Srodoniska*, (1): 23-8.

ONDRUŠOVÁ, M., 1997. Celková atmosférická depozice v povodí Černého a Čertova jezera, Speciace hliníku v šumavských jezerech. Thesis, Faculty of Science Charles University Prague, Ústav geochemie mineralogie a nerostných zdrojů, (in Czech).

PALIVCOVÁ, M., 1965. The Central Bohemian Pluton – a petrographic review and an attempt at new genetical interpretation. *Krystalinikum*, 99-131.

RISSBERGER, F.A., 1993. Beryllium transport as a result of episodic acidification of a small catchment in Hancock, Maine: Unpub. M.Sc. Thesis, Department of Geological Sciences University of Maine, Orono.

SAMEK J., 1998. Intensifikace exogenního cyklu esenciálních prvků a jejich neesenciálních homologů metabolickou činností buku lesního (Fagus sylvatica L.) na vybraných typech horninového prostředí. Thesis of the

Czech Agricultural Univ. Prague, Faculty of Forestry, (in Czech).

SANDELL, E.B. 1952. The beryllium content of igneous rock. *Geochim. Cosmochim. Acta*, 2: 211-216.

SHAWE, D.R. and BERNOLD, S., 1964. Distribution of beryllium in igneous rocks. U.S., Geol. Survey Profess Papers 550-B, B 100-104.

SCHECHER, W.D., MCAVOY, D.C., 1992. A Software Environment for Chemical Equilibrium Modeling – *Comput. Environ. and Urban Systems*, 16: 65-76.

SKŘIVAN, P., ARTNER, P. and KOTKOVÁ, P., 1993. Secondary anthropogenic contamination of surface streams through lithogenic beryllium, mobilized by acid atmospheric deposition. *Acta Universitatis Carolinae geologica*, 37.

SKŘIVAN, P., NAVRÁTIL, T. and BURIAN, M., 2000. 10 years of monitoring the atmospheric inputs at the Černokostelecko region, Central Bohemia. *Scientia Agriculturae Bohemica* (in press).

SKŘIVAN, P., MINAŘÍK, L., BURIAN, M. and VACH, M., 1994. Cycling of Beryllium in the Environment under Anthropogenic Impact. *Scientia Agriculturae Bohemica*, 25.

ŠTEMPROK, M., ZOUBEK, V., PIVEC, E., and LANG, M., 1996. Karlovy Vary pluton: an example of comagmatic sequence of Sn-bearing granite body. *Freiberger Forschhft. Bergakademie Freiberg*, 7-26.

TAYLOR, S.R., 1964. Abundance of chemical elements in the continental crust: A new table. *Geochim. Cosmochim Acta*, 28: 1273-1285.

TURKEIAN, K.K. and WEDEPOHL, K.H., 1961. Distribution of the elements in some major rocks units of the earth's crust. *Bull. Geol. Soc. Am.*, 72: 175-192

VEJNAR, Z., 1974. Trace elements of the Central Bohemian Pluton. *Věstník ČGÚ*, 49: 1974.

VESELÝ, J. 1994. Effects of Acidification on Trace Metal Transport in Fresh Waters. In: C.E.W. STEINBERG and WRIGHT R.F (Editors), Acidification of Freshwaters Ecosystems. John Wiley & Sons.

VESELÝ, J. and MAJER, V., 1998. Hydrogeochemical mapping of Czech freshwaters. *Věstník Českého geologického ústavu*, 73: 3.

VESELÝ, J., BENEŠ, P. and ŠEVČÍK, K., 1989. Occurrence and speciation of beryllium in acidified freshwaters. *Water Res.*, 23: 711-717.

VINOGRADOV, A.V., 1961. Average contents of chemical elements in the principal types of igneous rocks of the earth's crust. *Geochemistry USSR* (English Transl.), 6: 763-771.

WEDEPOHL, K.H., 1967. Handbook of Geochemistry, II-1. Springer Verlag.

ZAJÍC, P., 1998. Vývoj a sezónní změny v obsahu Mn, Pb, Be, Sr a Zn v půdních profilech zalesněných území na dvou rozdílných typech horninového podloží. Thesis of the Czech Agricultural Univ. Prague, Faculty of Forestry (in Czech).

Appendix

Fig. 19. Seasonal variations of pH, discharge, Al, Be, Na, K, Ca, Mg at Lysina Brook.
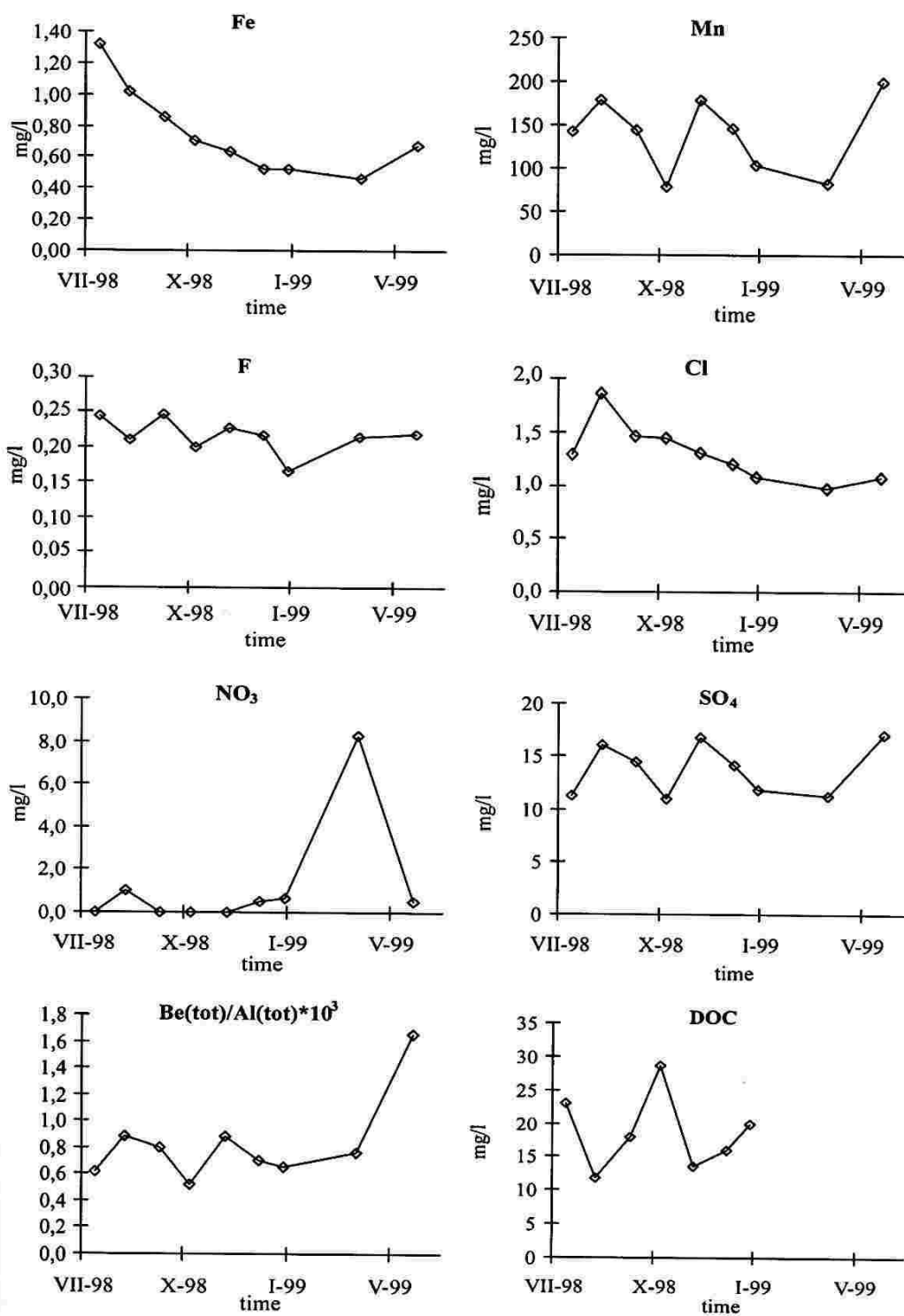
Fig. 20. Seasonal variations of Fe, Mn, F, Cl, NO3, SO4, Be/Al, DOC at Lysina Brook (DOC data from Hruška and Krám), *unpublished data*.

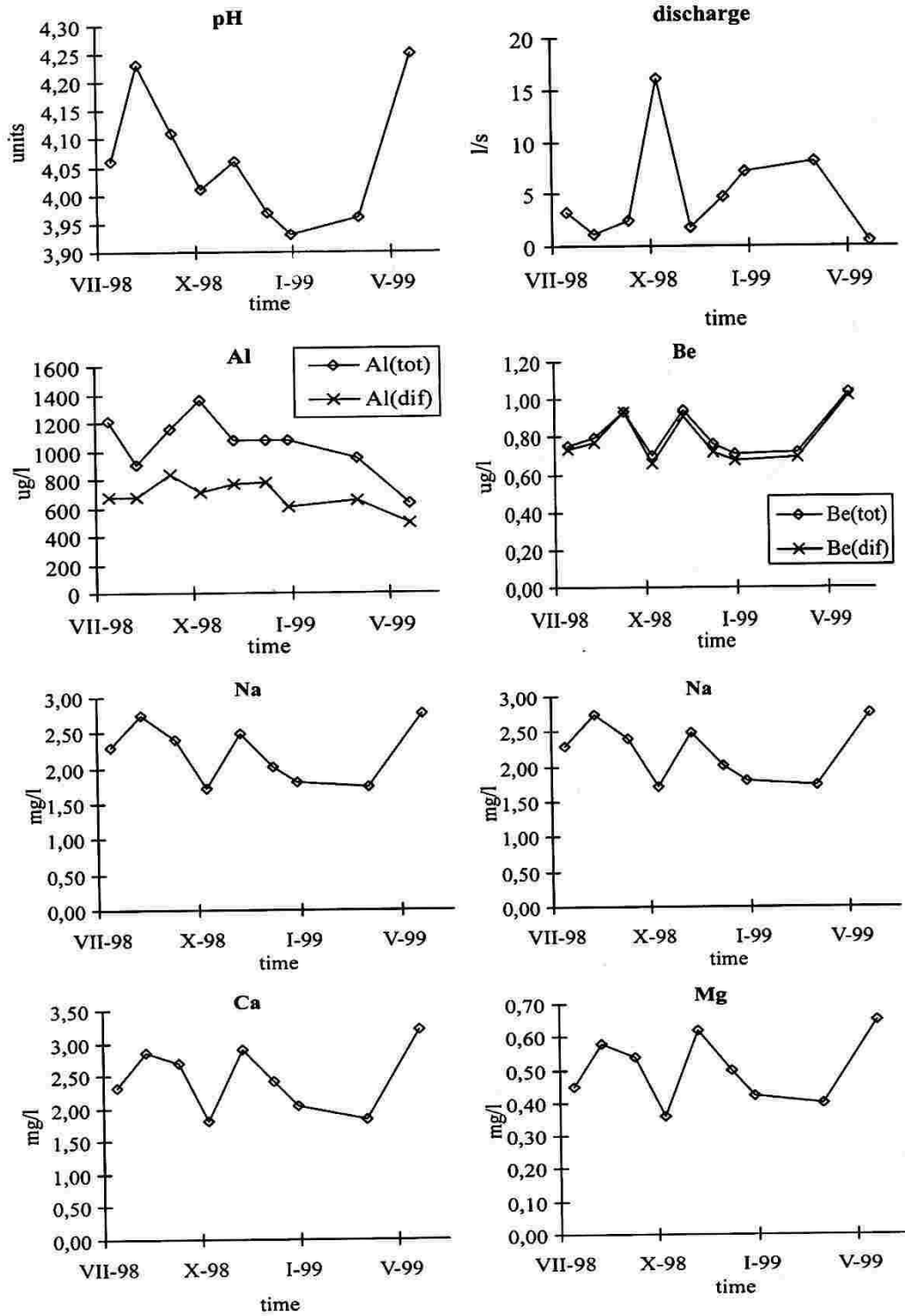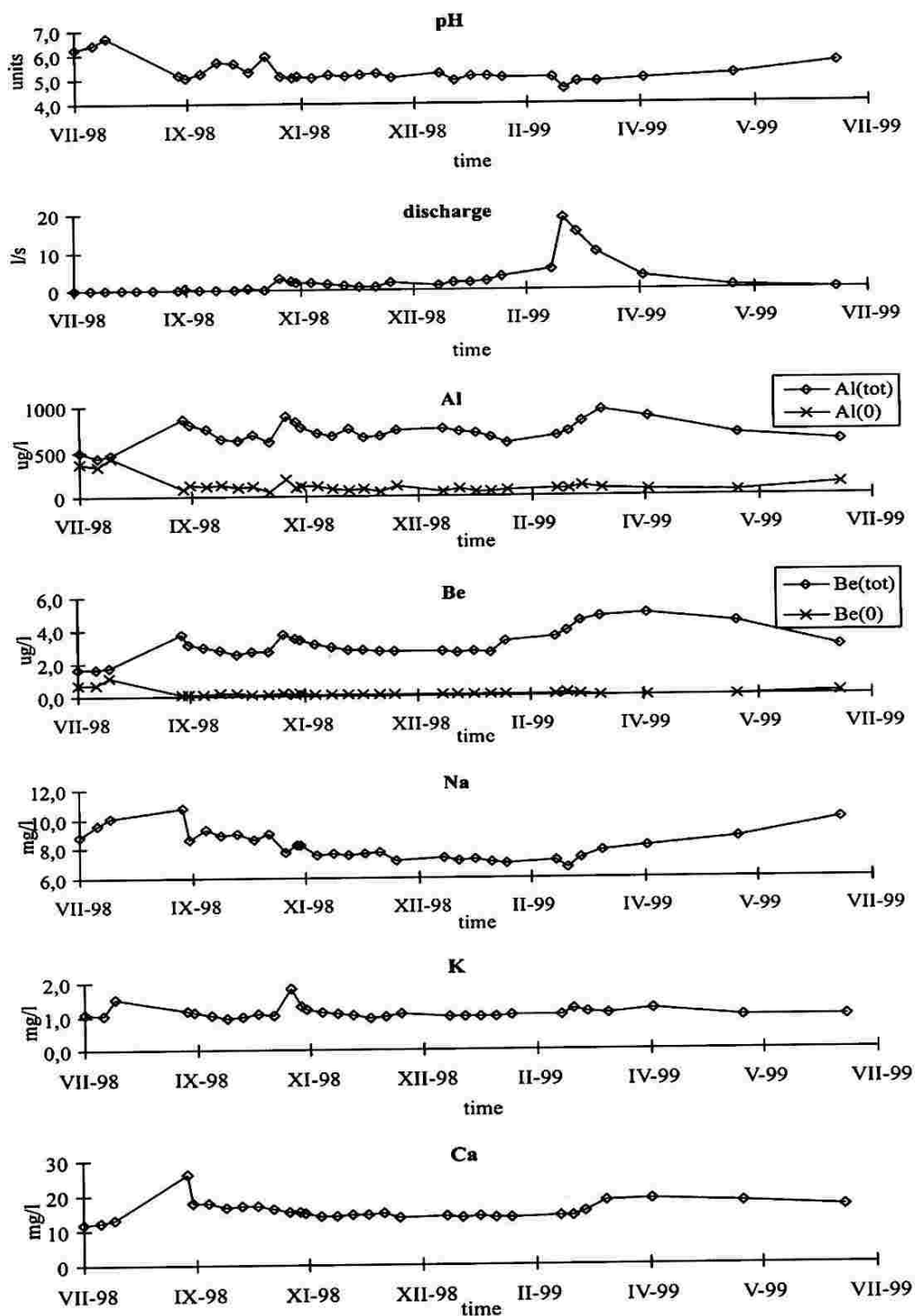Fig. 21. Seasonal variations of pH, discharge, Al, Be, Na, K, Ca at Lesni Brook.
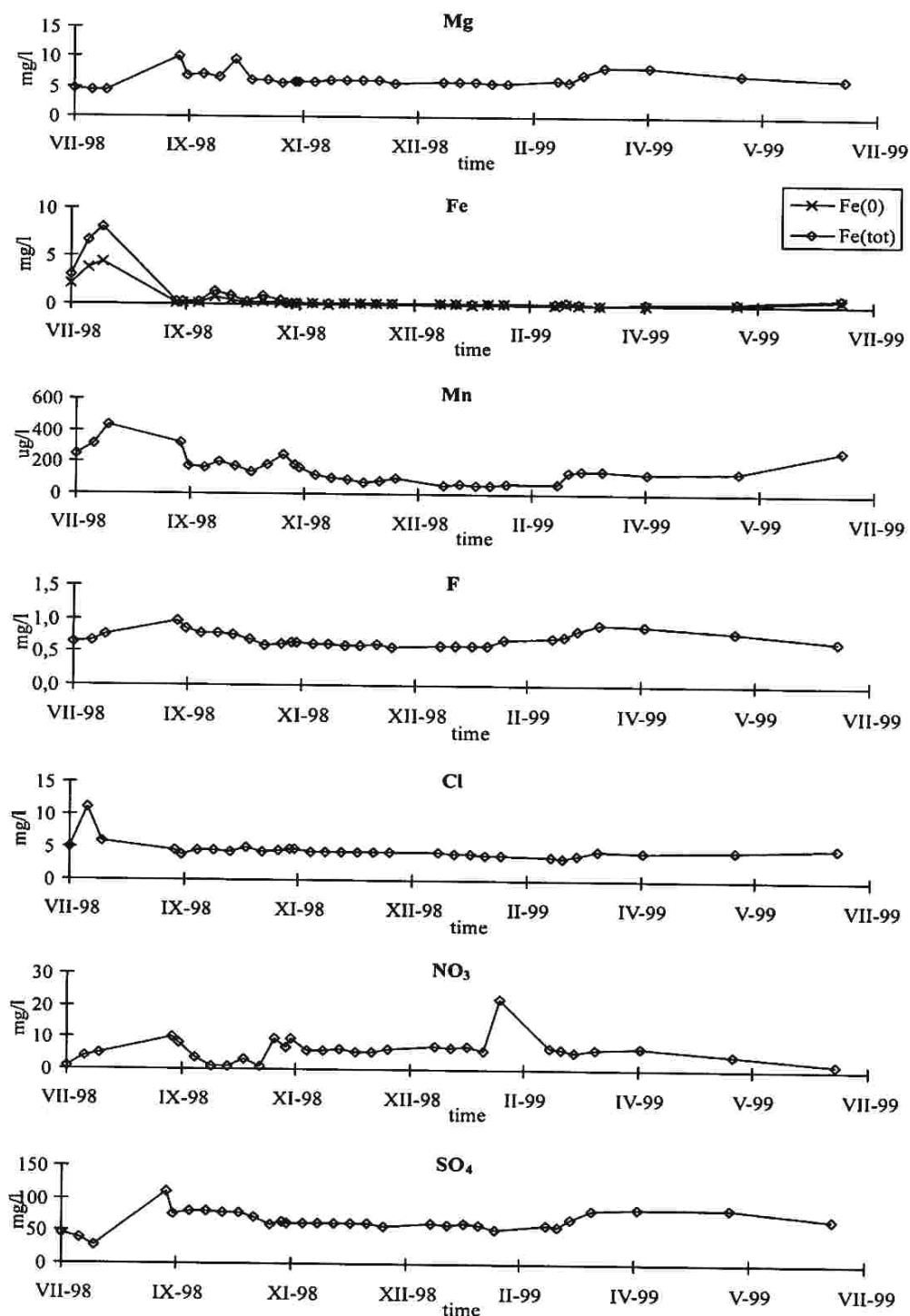
Fig. 22. Seasonal variations of Mg, Fe, Mn, F, Cl, SO₄, NO₃ at Lesni Brook.
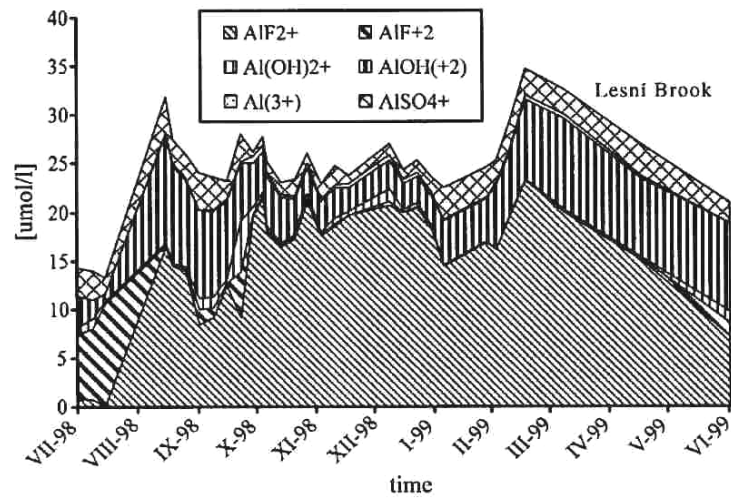
Fig. 23a. Seasonal variations of the Al speciation at Lesní Brook.
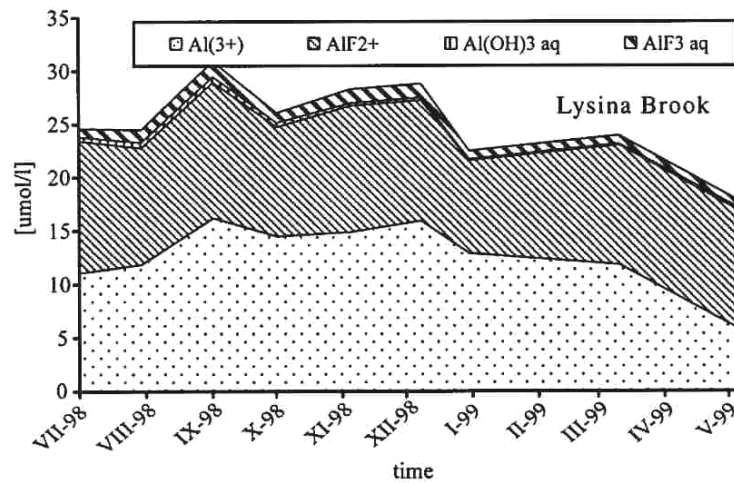
Fig. 23b. Seasonal variations of the Al speciation at Lysina Brook.

	pH	Be/Al	Bedif/Aldif	Color	Disch.	Kon.	Be tot.	Be (0)	Be dif	Al tot.	Al (0)	Al dif	Cd tot.	Na tot.	K tot.	Mg tot.	Fe tot.	Fe(0)	Fe dif	Ca tot.	Mn tot.	F	Cl	NO_3
Be/Al	0,67																							
Bedif/Aldif																								
Color	0,82	0,52	0,83																					
Disch.	-0,51	0,45																						
Kon.					0,58																			
Be tot.	-0,70	0,78		-0,56		0,66																		
Be (0)	0,83		0,88	0,94		-0,46	-0,58																	
Be dif	-0,79	0,75		-0,70	0,53	0,67	0,98	-0,73																
Al tot.	-0,76		-0,51	-0,59		0,59	0,78	-0,64	0,80															
Al (0)	0,78		0,78	0,90			-0,52	0,95	-0,67	-0,53														
Al dif	-0,87		-0,72	-0,83		0,59	0,76	-0,88	0,85	0,91	-0,84													
Cd tot.																								
Na tot.	0,66			0,50	-0,50			0,46			0,46													
K tot.											0,45													
Mg tot.	0,87		0,87			0,87	0,56	-0,48	0,59	0,54	-0,46	0,58												
Fe tot.	0,88		0,86	0,97			-0,57	0,95	-0,71	-0,67	0,89	-0,87		0,52		-0,42								
Fe(0)	0,84		0,86	0,97			-0,59	0,97	-0,73	-0,68	0,92	-0,89		0,52		-0,44	1,00							
Fe dif				0,96		-0,38	-0,54	0,92	-0,68	-0,64	0,84	-0,83		0,52			0,99	0,97						
Ca tot.						0,92	0,51		0,51	0,54		0,50		0,53		0,86								
Mn tot.	0,70		0,68	0,74		0,78	0,58	0,73	0,50		0,76	-0,55		0,83	0,51	0,70	0,74	0,74	0,73					
F	0,47												0,47							0,74				
Cl																								
NO_3																								
SO_4	-0,52		-0,52	-0,56		0,90	0,58	-0,64	0,65	0,61	-0,58	0,69				0,88	-0,58	-0,59	-0,56	0,91		0,61		

Tab. 16. Correlation table for measured values of Lesni brook (n=32, p<0,01).

	pH	Be/Al	Bedif/Aldif	Color	Disch.	Con.	Be tot.	Be (0)	Be dif	Al tot.	Al (0)	Al dif	Cd tot.	Na tot.	K tot.	Mg tot.	Fe tot.	Fe(0)	Fe dif	Ca tot.	Mn tot.	F	Cl	NO₃
Be/Al	0,97																							
Bedif/Aldif																								
Color																								
DOC	-0,94				0,84																			
Disch.																								
Kon.																								
Be tot.	0,83																							
Be (0)							1,00																	
Be dif	0,81																							
Al tot.	-0,89		-0,81		0,92																			
Al (0)					0,97																			
Al dif																								
Cd tot.											0,87													
Na tot.	0,91					-0,85				0,79														
K tot.					-0,82																			
Mg tot.					-0,91	-0,85	0,88			0,88			-0,80											
Fe tot.															0,92	0,88								
Fe(0)																								
Fe dif																		0,83						
Ca tot.	0,82				-0,88	-0,86	0,88			0,88					0,95		0,99	0,83						
Mn tot.					-0,89	-0,88				0,79					0,95		0,96			0,98				
F																								
Cl																								
NO₃																								
SO₄					-0,91		0,83			0,81			-0,81		0,85	0,88	0,97				0,94	0,91		

Tab. 17. Correlation table for measured values of Lysina brook (n=9, p<0,01).