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**Biogeochemistry of the II.A group elements in a forested
catchment**

DISSERTATION

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List of Abbreviations

ASCR	- Academy of Sciences, Czech Republic
AAS	- atomic absorption spectrometry
BC	- base cations
BS	- base saturation
C _(ox)	- oxidable carbon
CEC	- cation exchange capacity
CR	- the Czech Republic
DF	- depletion factor
DI	- deposition intensity of water [mm]
DOC	- dissolved organic carbon
EF	- enrichment factor
HBEF	- Hubbard Brook Experimental Forest
ICP MS	- inductively coupled plasma mass spectrometer
K _{sp}	- solubility product
LP	- Lesní Potok
Lys	- Lysina catchment
N _(t)	- total nitrogen
NA	- not available
Plb	- Pluhův bor catchment
THB	- throughfall beech
THS	- throughfall spruce
SAA	- strong acid anions
V/m	- volume/mass ratio

1 Introduction

1.1 Mass cycling processes

Mass cycling is the term used to describe the movement of certain materials into, within, and out of an ecosystem. This dynamic takes place because there are sufficient supplies of energy in the ecosystem as well as because the energy is being further delivered into the ecosystem. Cycling of mass is important for maintenance of the ecosystem balance. Earth's life is inextricably linked to climate through a variety of interacting cycles and feedback loops. The environmental transport and transformations of substances, where living organisms are involved, are denoted as biogeochemical cycles. These global cycles include the circulation of certain elements, or nutrients, which directly affect the earth's life and climate.

In recent years there has been a growing awareness of the extent to which human activities, such as deforestation and fossil fuel burning, have directly or indirectly modified the biogeochemical and physical processes involved in determining the earth's climate. These changes in atmospheric processes can disturb a variety of the ecosystem functions. In addition to helping to maintain relative climate stability and a self-cleansing, oxidizing environment, these beneficial functions include protection from most of the sun's harmful ultraviolet rays, mediation of runoff and evapotranspiration (which affects the quantity and quality of fresh water supplies and helps control floods and droughts), and regulation of nutrient cycling.

1.2 Purpose of dissertation

Acid deposition and air pollution are the most disturbing impacts on forest ecosystems in the Northern Hemisphere. These phenomena are causing significant impacts in the natural cycle of elements, which may lead to their accumulation in one compartment of the environmental system but also to depletion in another compartment. These accumulations and deficits may then negatively affect the health and productivity of forest ecosystems.

The major objective of this dissertation is to compare field behavior and distribution of II.A group elements under this anthropogenic impact.

The elements of the II.A group include important nutrients (Ca, Mg), essential elements (Sr) and also toxic elements (Be, Ba). The chemical properties and abundance of calcium and magnesium have caused them to become not only important nutritional elements, but also important acid buffering substances. Recent studies of calcium and strontium reveal the importance of Sr in evaluating the calcium origin. Consequently, pathways of the essential elements of the II.A group will also be analyzed with respect to the ratios Mg:Ca and

(Sr:Ca)*1000. The behavior of Be and Ba was evaluated as important because of their toxic character. This study, however, treats all five of these elements in context and as a group.

The biogeochemical cycling of the II.A group of elements is influenced by such phenomena as acid deposition buffering, base saturation, tree nutrition, and acidification of streamwater, soil and soil solution. The study of anthropogenic effects on II.A group elements was performed by means of a small catchment study at a strongly impacted part of Europe, in the central Czech Republic.

2 Literature review

2.1 Acid Deposition

Acidic deposition is the transfer of strong acids and acid-forming substances from the atmosphere to the surface of the Earth. R.A. Smith first identified acid deposition in the 19th century in England (Smith 1872). The ecological effects of acid deposition emerged in the late 1960s and early 1970s in Sweden and around Scandinavia (Oden 1968). The first report of acid deposition in the North America was made at Hubbard Brook Experimental Forest (HBEF) in the early 1960s (Likens et al. 1972). However the acidification of soils in Orlické Mountains was studied regularly in the Czech Republic since 1953 (Pelišek 1984). More scientific investigations on acidification of the environment in the Czech Republic were made in 1970s (e.g. Pačes and Pištora 1979). Over the last quarter of the past century scientists have identified acidification as a critical environmental stress that affects forested landscapes and aquatic ecosystems in North America, Europe, and Asia (Driscoll et al. 2001). Effects of acid deposition on terrestrial ecosystems include those on soils, vegetation, crops, animals and human health (Mihaljevič 1999). Due to major negative effects of acidic deposition, North American and European legislative actions aimed at the recovery of damaged natural resources have resulted in recent decreases in both emissions and deposition of acidic S compounds.

Scientists in the 1960s demonstrated the relationship between sulfur emissions in continental Europe and the acidification of Scandinavian lakes. This raised the need for international authority action, which was fulfilled by the Convention on Long-range Transboundary Air Pollution (LRTAP) signed in 1979. The convention established a framework for cooperation on reducing the impact of air pollution and defined a process of negotiating particular measures to control emissions of air pollutants by means of legally binding protocols. The EMEP programme (Co-operative Programme for Monitoring and Evaluation of the Long-

Range Transmission of Air pollutants in Europe) was initiated in 1977 as a special programme under the United Nations Economic Commission for Europe (UNECE). Its aim is to regularly provide governments and subsidiary bodies under the LRTAP Convention with qualified scientific information to support the development and further evaluation of the international protocols on emission reductions negotiated within the Convention.

Acid deposition can occur as wet deposition (i.e. rain, snow, sleet, hail, vapor, fog) or as dry deposition (i.e. particles). Acid deposition can originate from transboundary air pollution and can affect large geographic areas. Oxides of sulfur and nitrogen, which are primarily products of the fuel combustion, are the dominant contributors to acid deposition. The process of acidification alters the interactions of many elements (e.g. sulfur, nitrogen, hydrogen, calcium, magnesium and aluminum).

The major changes in the S emission budgets of Czech Republic culminated in 1999, when all the coal power plants were largely desulphurized (Hruška et al. 2002). However, while the controls on emissions of S were maximized, the emissions of the second major acidifier N remain significant.

2.2 The elements of the II.A group

The II.A group is characterized by strong metallic properties, because of their electronic configuration (ns^2 , where n is period) and very high third-stage ionization energies. Elements of the II.A group are divalent with a tendency towards covalence in the lighter elements (Be and Mg) (Greenwood & Earnshaw 1984).

Table 1 Selected parameters of the II.A group elements (Lide et al. 1994)

Element	Atomic number	Atomic mass	Electronic configuration	Electronegativity (Pauling)	Ionic radius (pm)	Hydrated radius (pm)
Be	4	9.012	[He]2s ²	1.57	57	?
Mg	12	24.305	[Ne]3s ²	1.31	72	296
Ca	20	40.078	[Ar]3s ²	1.00	100	272
Sr	38	87.620	[Kr]4s ²	0.95	126	274
Ba	56	137.327	[Xe]5s ²	0.89	142	248

Table 2 Abundances of the II.A group elements in the Earth's spheres (Roessler & Lange 1972), last two columns (Zýka 1971; Beneš 1994), all data in meq.kg⁻¹ or meq.L⁻¹

Element	Continental Crust	Abundance in granitic rocks high in Ca	Abundance in granitic rocks low in Ca	Seawater	Abundance in plants (d.m.)	Abundance in soils on granites
Be	0.53	0.40	1.20	2.2E-08	NA	NA
Mg	1810	1794	132	107	58	595
Ca	1921	2320	788	20	225	435
Sr	7.6	18.3	6.9	0.2	0.5	4.2
Ba	8.5	9.5	12.1	8.7E-05	0.4	11.5

2.2.1 Beryllium

Beryllium is a low abundance lithophile trace element in geologic systems. In terms of geochemical behavior Be shows little similarity to other alkaline earth elements. However in terms of ionic radius Be^{2+} (0.45Å) is closest to Al^{3+} and appears to substitute for Al in crystal lattices. The most economically significant mineral of Be is beryl ($\text{Be}_3\text{Al}_2[\text{Si}_6\text{O}_{18}]$), which is found commonly in pegmatites and less commonly in metamorphic associations. Beryllium has two naturally occurring radioisotopes, ^7Be with half-life of 53.2 days and ^{10}Be with half-life of 1,520,000 years, and one stable isotope ^9Be . Both of the radiogenic isotopes are used in geochemistry as tracers.

In the Czech Republic, as well as in other industrialized countries, beryllium in precipitation has been reflecting above all the impact of the element released into the atmosphere during the process of coal combustion in power plants (Bezačinský 1980; Kubizňáková 1987; Moore 1991). The majority of coal burned in Czech power plants comes from the Tertiary lignite basins in the NW part of the Czech Republic. The mean Be concentration in these coal types was 0.67 meq.kg^{-1} with a range of $0.0 - 14.0 \text{ meq.kg}^{-1}$ (Bouška & Pešek 1999). Solid atmospheric particles containing anthropogenic ^9Be , as well as its radioisotopes ^7Be and ^{10}Be , are transported to the Earth's surface mostly through the wash-out effect of the liquid or solid precipitation (Vogler et al. 1996; Tanaka et al. 1997).

Krám et al. (1998) reported an annual deposition flux of $9.9 \text{ } \mu\text{eq.Be.m}^{-2}$ in years 1991-92 to the Lysina forested catchment (W Bohemia, 12 km south of the Sokolov Coal Basin). Results of Skřivan et al. (2000a) based on the monitoring of bulk precipitation at Lesní potok forested catchment since 1994 show that the annual Be flux in bulk precipitation steadily declined from $8.8 \text{ } \mu\text{eq.m}^{-2}$ in 1995 to $3.1 \text{ } \mu\text{eq.m}^{-2}$ in 1998. In 1997, 50% of values were below the detection limit of the analytical determination (0.04 ppb, ETA AAS), whereas in 1998 it was 94%. The data from 1998 – 99 based on analyses of preconcentrated samples of bulk precipitation show that the annual Be- flux is less than $2.2 \text{ } \mu\text{eq.m}^{-2}$.

Neal et al. (1992) reported the volume-weighted mean concentration of Be in throughfall in mid-Wales to be 60% higher than that in rainfall. The concentration of Be in throughfall and stemflow was 1.5 and 3 times higher than in rain, respectively. Krám et al. (1998) reported a higher concentration of Be in Norway spruce (*Picea abies* L.) throughfall than in bulk precipitation ($0.013 \text{ } \mu\text{eq.L}^{-1}$ vs. $0.009 \text{ } \mu\text{eq.L}^{-1}$) in the Lysina watershed. Fluxes of Be in beech (*Fagus sylvatica* L.) and Norway spruce throughfall in the Lesní Potok watershed ranged from < 2.2 to $4.4 \text{ } \mu\text{eq.m}^{-2}.\text{yr}^{-1}$ for 1997 to 1999. Skřivan et al. (2000) documented for 1999

that the flux of Be to the forest floor was dominated by litterfall (averaging $39 \mu\text{eq.m}^{-2}.\text{yr}^{-1}$ and $30 \mu\text{eq.m}^{-2}.\text{yr}^{-1}$, for beech and spruce, respectively), whereas bulk precipitation and throughfall were about 0.88 to $1.77 \mu\text{eq.m}^{-2}.\text{yr}^{-1}$.

The concentration of Be ranges over three orders of magnitude in natural fresh water systems, from a few ng.L^{-1} to a few $\mu\text{g.L}^{-1}$ (Veselý et al. 2002). Concentrations of Be typically decrease in the order: soil solution > groundwater > low order stream water > rivers > estuaries > ocean. Determination of Be in dissolved and suspended material from rivers with a wide range of chemical composition indicates that its geochemistry is primarily controlled by (1) its abundance in the rocks and soil of the watershed (Measures and Edmond 1983), (2) the extent of its adsorption onto particle surfaces (Veselý et al. 1989), and (3) water chemistry. Veselý et al. (1998) monitored Be in six acidified lakes and their tributaries during 1984 – 1995. The strong decrease of Be was concurrent with a sharp decline in acidic deposition after 1986 and increased pH in the surface water. The mean concentrations of Be in Czech surface waters with mean pH 5 is $0.11 \mu\text{eq.L}^{-1}$ (Veselý 1994).

Skřivan et al. (1994) reported 0.04 to $5.3 \mu\text{eq.L}^{-1}$ in the Lesni Potok (LP) stream, draining a granite catchment with high aqueous F concentrations (mean $25.8 \mu\text{eq.L}^{-1}$) and with highly variable pH (4.6 to 5.9). Many other authors have reported an inverse relationship between Be in water and pH (Measures and Edmond 1983; Veselý et al. 1989; Kaste 1999; Navrátil 2000, Navrátil et al. 2002). Also a regional freshwater survey (13,000 water samples) in the Czech Republic showed a clear inverse relationship between the concentration of Be and pH (Veselý and Majer 1996). Kaste (1999) found that Be concentrations increased approximately 100% in the stream water of the artificially acidified watershed in Bear Brook, Maine, USA.

Veselý et al. (1989) found that the relationship between Be concentration and pH is not straightforward; there was substantial scatter at lower pH, indicating that other factors influence dissolved Be. The main form of Be in the LP surface water is the BeF^+ complex, which always formed >50% (Navrátil 2000; Navrátil et al. 2002). Under low pH conditions the portion of free Be^{2+} ion becomes important. But at high pH (such as during low flow), BeOH^+ and BeF_2 dominate over Be^{2+} and BeF^+ . The most important factors determining the Be speciation in Lesni potok surface water are Al^{3+} , F^- , Be^{2+} concentrations and pH (Navrátil 2000; Navrátil et al. 2002).

Krám et al. (1998) reported an average concentration of Be 0.044 , 0.089 and $0.24 \mu\text{eq.L}^{-1}$ in soil solution from O, E and C soil horizons at the granite catchment Lysina.

Total soil Be ranges from 0.02 to 8.87meq.kg^{-1} , with the world average near 1.33meq.kg^{-1} (Drury et al. 1978). Total and acid soluble concentrations (2M HNO_3) of Be were investigated

in agriculture soils (A_p horizon) of the north Czech Republic region with high atmospheric pollution (Podlešáková et al. 1994). The average total Be concentration ranged from 0.47 to 1.15 meq.kg⁻¹. Acid soluble Be ranged from 0.12 to 0.22 meq.kg⁻¹ (22 to 27 % of total Be).

Exchangeable Be was weakly negatively correlated with soil depth, whereas total Be increased with depth (Veselý et al. 2002). Exchangeable Be and Al were unrelated. Exchangeable Be in the forest floor increased nearly by 300% on a transect of 17 m from well-drained upland soils to poorly drained riparian soil. Exchangeable Al followed a similar trend, but Ca was the opposite, decreasing towards the riparian zone. The increased Al and Be concentrations occurred where the soils have a higher pH because of mixing of emerging groundwater and degassing of CO₂ in the riparian zones. Soils over Be-rich granite (3.33 meq.Be.kg⁻¹) had 0.84 to 1.62 meq.Be.kg⁻¹, 3 to 17% of which was extractable (Skřivan et al. 2000). Profiles of concentrations of Be in two acid-sensitive soils of forested regions receiving different loadings of acid deposition suggested the depletion of Be in humic and upper mineral soils in more acidified areas (Veselý 1987; Gooddy et al. 1995; Veselý and Majer 1996).

The physiological role of Be in living organisms is still not well understood. Soil microorganisms grown in a magnesium-deficient medium grow better in the presence of beryllium, because of the partial substitution of beryllium for magnesium in metabolism. Similar growth-stimulating effects have been noted in algae and crop plants. This phenomenon seems to be pH-dependent, as it only occurs at high pH. At pH 7 or below, beryllium is toxic for aquatic and terrestrial plants, regardless of the magnesium levels in the growth medium. Roots accumulate most of the beryllium taken up, and very little is translocated to the upper parts of the plant (Anonymous 1962).

Stunting of roots and foliage was noted in soil cultures of beans, wheat, and ladino clover, but no chlorosis or mottling of the foliage occurred (Romney & Childress 1965). In soil culture, beryllium phytotoxicity is governed by the nature of soil, particularly its cation exchange capacity and the pH of the soil solution. Apart from the magnesium-substituting effect, the diminished phytotoxicity under alkaline conditions also results from the precipitation of beryllium as unavailable phosphate salt. The mechanism underlying the phytotoxicity of beryllium is probably based on the inhibition of specific enzymes, particularly plant phosphatases. Beryllium also inhibits uptake of several essential mineral ions. (Anonymous 1962)

2.2.2 Magnesium

Magnesium has three naturally occurring isotopes with mass numbers (and percentage abundances) 24 (78.99%), 25 (10.00%) and 26 (11.01%). Magnesium is a major element in most (especially mafic) rock systems and is a major constituent of many rock-forming minerals, where it is typically bound in 6 - fold coordination. The main Mg bearing minerals are olivine, orthopyroxene, clinopyroxene, serpentinite, talc, brucite, chlorite, pyrope, amphiboles, biotite, tourmaline, magnesite and spinel. Typical Mg contents of granites are between 160 - 480 meq.kg⁻¹.

Magnesium is concentrated in the Earth's mantle, while in the Earth's crust it is most abundant in the oceanic crust and the lower continental crust. During the weathering of rocks Mg readily dissolves in weathering solutions and enters the hydrosphere. Magnesium is removed from ocean water by carbonate precipitation, but even so Mg is a conservative element in the seawater.

Krám et al. (1997) reported a bulk precipitation flux of Mg of 4.4 meq.m⁻².yr⁻¹ at the granitic catchment Lysina in 1993. Ragsdale et al. (1992) reported rates of total Mg deposition ranging between 1.6 and 21.4 meq.m⁻².yr⁻¹ with wet and dry deposition being the predominant processes.

The main sources of Mg in the atmosphere are sea salts (at marine areas), mineral dusts (industrial and natural) and fly ashes (from point-source emissions). Armbruster et al. (2002) reported an overview of European sites (including Czech sites) with Mg throughfall fluxes ranging from 1.9 to 184 meq.m⁻².yr⁻¹. Authors have reported good correlation of Mg and Ca fluxes in deciduous throughfall at inland sites at least 200 km from the coast. High throughfall fluxes at some Czech sites were due to local alkaline dust emissions, however the Mg and Ca correlation was retained. Krám et al. (1997) reported greater Mg throughfall fluxes of 33.8 meq.m⁻².yr⁻¹ on a catchment with bedrock rich in Mg (serpentinite) compared to 20.4 meq.m⁻².yr⁻¹ on a catchment with bedrock low in Mg (granite). Enhanced fluxes of Mg in throughfall with respect to bulk precipitation are due to both dry deposition to the canopy and leaching from plant tissues (Armbruster et al. 2002). According to experiments with artificial trees (Stachurski et al. 2000) magnesium flux increased below beech trees but remained unchanged below spruce. Beech was more effective than spruce in modifying the ionic fluxes from atmosphere; this is related to greater adsorption of H⁺ and greater leaching of Mg²⁺ (Stachurski et al. 2000).

The output from catchments did not differ according to bedrock type, however Mg losses were higher from sites with deciduous than from those with coniferous vegetation

(Armbruster et al. 2002). Norton et al. (1999) reports selective depletion of Mg over Ca from a two-catchment study in Maine, USA. The concentration of Mg in surface water of an artificially acidified catchment increased sharply after the start of $(\text{NH}_4)_2\text{SO}_4$ addition. In periods with increased discharge the concentration of Ca and Mg sharply increased in the acidified watershed but after 5 years of acidifying the Ca and Mg concentrations remain unchanged during similar events. Authors attribute this behavior to the depletion of Mg and Ca in the surface soil horizons. The soil solutions in O and A(E) horizons of the catchments studied by Krám et al. (1997) contained 18.2 and 16.4 $\mu\text{eq.L}^{-1}$, respectively in the Mg poor site, and 1380 and 1400 $\mu\text{eq.L}^{-1}$ respectively in the Mg rich site. It is typical for forest ecosystems that the Mg storage in soil is by far the largest pool, constituting more than 90% of total Mg in the ecosystem (Feger 1997). Vegetation accounts for less than 5% of total pools.

Magnesium is a critical structural component of the chlorophyll molecule and is necessary for functioning of plant enzymes to produce carbohydrates and fats. Magnesium is also dissolved in the nucleoplasm of the cells. It is involved in fruit and nut formation and is essential for germination of seeds. Magnesium deficient plants appear chlorotic, show yellowing between veins of older leaves; leaves may drop. Magnesium is leached by watering and must be supplied when feeding. It can be applied as a foliar spray to correct deficiencies. However extreme amounts of Mg may cause defects of vegetation growth and forms of plants known as nanisms.

2.2.3 Calcium

Calcium has six naturally occurring isotopes with mass numbers (and percentage abundances) 40 (96.941%), 42 (0.647%), 43 (0.135%), 44 (2.086%), 46 (0.004%) and 48 (0.187%).

Calcium is the most common of the alkaline earth elements in the Earth's crust (Wedepohl 1995). Common Ca bearing minerals include clinopyroxene, plagioclase, heulandite, stilbite, laumontite, prehnite, tremolite, actinolite, hornblende, epidote, zoisite, grossularite, andradite, calcite, dolomite, gypsum, apatite and sphene. Calcium is a lithophile element and is divalent under natural conditions. During weathering Ca readily dissolves to weathering solutions and enters the hydrosphere. Calcium also plays an important role in global climate through partial buffering of carbon dioxide in the atmosphere. Feldspars constitute the most abundant minerals in both continental and oceanic crust. Rapid feldspar weathering in mountainous terrain enhances Ca transport to the ocean. This may also lead to CO_2 extraction from the atmosphere. The supply of CO_2 from decaying organic matter in soils also enhances feldspar

dissolution, at least if the pH of the water is at a sufficiently low level (below about 7) to make feldspar solubility pH dependent (Blum and Stillings 1995). The majority of Ca found in granitoid rocks resides predominantly in plagioclase feldspar. Garrels (1968) originally proposed that proportions of aqueous Ca and Na associated with the weathering of granitoid rocks approximate the ratio found in plagioclase. However recent studies demonstrate that excess Ca occurs in many surface and ground waters relative to this plagioclase stoichiometry (Stauffer 1990). Short-term Ca excesses in water can result from selective loss of exchangeable Ca in soils during catchment acidification (Hyman et al. 1988), loss from biologic storage due to deforestation and fires (Chorover et al. 1994)

Longer-term excesses in Ca relative to plagioclase stoichiometry have been attributed to accelerated weathering of other silicate phases such as hornblende (Clow et al. 1993), selective leaching of an anorthite component of plagioclase (Clayton 1986; Williams et al. 1993), or the presence of small amounts of calcite even in plutonic rocks.

The bulk precipitation flux of Ca was $15.2 \text{ meq.m}^{-2}.\text{yr}^{-1}$ for two catchments (Lysina and Pluhův Bor) at western part of the Czech Republic in 1993 (Krám et al. 1997). Likens et al. (1998) reported a 21% difference between Ca flux in bulk deposition ($4.38 \text{ meq.m}^{-2}.\text{yr}^{-1}$) and wet-only deposition ($3.46 \text{ meq.m}^{-2}.\text{yr}^{-1}$) during 11 years (1979 - 1989) at Hubbard Brook HBEF, attributing the difference to vertical sedimentation of particles.

Element fluxes in throughfall may reflect the base cation status of forest ecosystems. They are measured readily but it is difficult to separate throughfall flux into its individual components. Nutrients in throughfall may result from (a) incident precipitation passing through a canopy; (b) material deposited as particles, gases, or cloud droplets prior to precipitation passing through the canopy; and (c) exchange processes within the canopy (including foliage, woody parts, epiphytes and microorganisms) (Berger et al. 2001). Spruce throughfall flux at Lysina catchment with granitic bedrock was $68.8 \text{ meq.m}^{-2}.\text{yr}^{-1}$, compared to $36.6 \text{ meq.m}^{-2}.\text{yr}^{-1}$ at the Pluhův Bor catchment with low-Ca serpentinite bedrock (Krám et al. 1997).

The annual streamwater Ca concentrations reported from HBEF declined from $81.3 \text{ } \mu\text{eq.L}^{-1}$ in 1969-70 to $42.4 \text{ } \mu\text{eq.L}^{-1}$ in 1991-92 (Likens et al. 1998). The Ca output fluxes from the granitic and serpentinite catchment in western Czech Rep. were 69.8 and $19.8 \text{ meq.m}^{-2}.\text{yr}^{-1}$, respectively (Krám et al. 1997).

Calcium is relatively easily released as a soluble cation from the majority of both primary and secondary minerals, the rate largely depending on solution pH. When liberated it moves into the soil solution, where it may be adsorbed onto the cation exchange complex, taken up by plants or microbial organisms, or leached through the soil profile. Due to its divalent charge,

relative abundance and modest extent of hydration, Ca is adsorbed strongly to clays and humates compared to other metallic cations (Likens et al. 1998). Calcium is usually the most abundant of the alkali and alkaline earth elements on the soil exchange complex and is important in the regulation of soil pH (Bowen 1979). Soil acidification accompanied by leaching of Ca from the soil exchange complex is a gradual natural process. The soil solutions in O and A(E) horizons of the catchments studied by Krám et al. (1997) contained 78 and 56 $\mu\text{eq.L}^{-1}$ (granite) and 176 and 48 $\mu\text{eq.L}^{-1}$ (serpentinite), respectively. The concentrations of exchangeable Ca at Lysina with granitic bedrock were highest in the organic horizon (50 - 90 meq.kg^{-1}) and they decreased with depth while the lowest were in the C horizon (1.56 meq.kg^{-1}). Acidification of watersheds in North America and Europe has led to depletion of base cations in soils to the extent that Ca has become a potential limiting element in forest productivity in severely impacted areas (Shortle and Smith 1988; Bailey et al. 1996; Lawrence et al. 1997). Rates of Ca replenishment and acid neutralization by weathering of granitoid rocks are therefore important factors in developing regulatory constraints on atmospheric emissions (Drever 1988).

Amounts of Ca in plants fluctuate between 250 and 2500 meq.kg^{-1} dry weight according to species, organ and stage of development. Calcium is the fifth most abundant element in trees and is an essential component for wood formation and the maintenance of cell walls. Calcium activates enzymes, is a structural component of cell walls, influences water movement in cells and is necessary for cell growth and division. Some plants must have calcium to take up nitrogen and other minerals. Calcium, once deposited in plant tissue, is immobile (non-translocatable) so there must be a constant supply for growth. Deficiency causes stunting of new growth in stems, flowers and roots. Symptoms range from distorted new growth to black spots on leaves and fruit. Yellow leaf margins may also appear. In contrast to potassium, calcium is not leached readily from living foliage due to its relative immobilization in pectates and on membranes. In forest ecosystems Ca typically cycles between plants and soil through uptake-litterfall-mineralization processes (Likens et al. 1998). Because Ca is a macronutrient for higher plants, spatial and temporal variations in its supply are important to the growth and vigor within a forest ecosystem. Sufficient amounts of Ca also contribute to binding of nutrients in soils (especially phosphoric acid). Calcium in soils may also neutralize some organic acids in the form of calcium oxalates. Calcium accumulates in old plant parts (Asta 1992; Marschner 1986; Mostafa and Ulrich 1976). The content of Ca in the biomass increases with time. Calcium also contributes on the movement of sacharides in plant tissues.

2.2.4 Strontium

Strontium has four naturally occurring stable isotopes with mass numbers (and percentage abundances) 84 (0.56%), 86 (9.86%), 87 (7.00%) and 88 (82.58%). These proportions vary because ^{87}Sr is the radiogenic daughter of ^{87}Rb (half-life 4.88×10^8 years). Consequently the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios are used in geochronology and as an isotopic tracer. In addition strontium has 24 short-lived radioactive isotopes. Strontium 90 (half-life 29.1 years) is a product of nuclear fallout and poses a significant health hazard. Because of the similar chemical behavior of Sr and Ca the radioactive isotope ^{90}Sr may accumulate in the bones of humans and animals.

Strontium forms the minerals celestite (SrSO_4) and strontianite (SrCO_3). The chemical properties of strontium closely follow calcium. Strontium can substitute for Ca^{2+} and K^+ in feldspars. The ionic radius of Sr^{2+} is between those of Ca^{2+} and Ba^{2+} and is somewhat smaller than the Pb^{2+} radius. The distribution of Sr in rock-forming and accessory minerals is controlled by its diadochy with calcium and potassium (Wedepohl 1969). The major host minerals of Sr are feldspars. Plagioclase and K-feldspars are almost equally important (Wedepohl 1969). The Mg-Fe minerals usually contain less than one tenth of the strontium of coexisting feldspars (Wedepohl 1969). Strontium is held more tightly on clay minerals as it is more weakly hydrated than Ca (Wedepohl 1969). All studies indicate that Sr is a rather mobile element during rock weathering, especially from feldspars, but it is less mobile than Ca (Wedepohl 1969). The mean Sr concentration in coal types from Tertiary lignite basins in the NW part of Czech Republic was 2.0 meq.kg^{-1} with a central range of $0.9 - 3.1 \text{ meq.kg}^{-1}$ (Bouška & Pešek 1999).

The chemical behavior of Ca and Sr is similar, so Sr is often used as a surrogate for Ca because Sr isotopes provide a valuable tracer of sources and pathways (Aberg 1995). Strontium isotopes have proven to be a useful tracer of weathering sources because minerals often have distinct $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (Miller et al. 1993; Blum et al. 1993; Bain and Beacon 1994; Blum and Erel 1995; Bullen et al. 1997; Clow et al. 1997). However there are still few data that relate the behavior of Sr during weathering to mineral dissolution kinetics (Brantley et al. 1998; White et al. 1999). Dissolution experiments by White et al. (1999) suggested that the initial stages of granite weathering are dominated by calcite dissolution.

In most forest ecosystems, strontium (Sr) and Ca incorporated in trees originate from two primary sources: atmospheric inputs and primary soil minerals. Under favorable conditions the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of atmospheric deposition and weathering differ enough to enable measurement of the contribution of each Sr source to plant, soil exchange pool, and streamwater (Wickman 1996).

The annual deposition fluxes of Sr at six rural sites in Norway were in the range 5.5 – 59.3 $\mu\text{eq.m}^{-2}.\text{yr}^{-1}$ and Sr was evaluated as an element atmospherically transported from marine environments (Berg et al. 1994). Concentrations of Ca (0 – 0.46 meq.L^{-1}) and Sr (0 – 0.54 $\mu\text{eq.L}^{-1}$) were detected in bulk precipitation and throughfall at one site each in France and Switzerland (Poszwa et al. 2000). Atteia (1994) found little variation of Sr concentrations in bulk precipitation over an area of 3000 km^2 in Switzerland and he reported an average Sr concentration 0.06 $\mu\text{eq.L}^{-1}$ (median 0.02 $\mu\text{eq.L}^{-1}$) from six sites.

The output fluxes of Sr from a clear-cut catchment (374 $\mu\text{eq.m}^{-2}.\text{y}^{-1}$) increased by 200% compared to a reference catchment (120 $\mu\text{eq.m}^{-2}.\text{y}^{-1}$) at Hubbard Brook Experimental Forest (Scott et al. 2001). The initial changes of Sr concentration in the streamwater were attributed to release of readily exchangeable Sr from soils due to increased concentrations of H^+ in soil solution.

The soil solution at one site in France (granite) and one in Switzerland (limestone, sandstone) exhibited Sr concentrations of 0.02 – 1.30 $\mu\text{eq.L}^{-1}$ (Poszwa et al. 2000).

The worldwide average concentration of Sr in soils is 5.4 – 6.8 meq.kg^{-1} (Anonymous 1962). The exchangeable concentrations of Ca and Sr were always highest in humus layers of the soil profiles on sites underlain by sandstone, granite and limestone (Poszwa et al. 2000).

The behavior of the Sr was studied with respect to the threat emerging from the radioactive isotope ^{90}Sr , which may be introduced to the environment from nuclear explosions. The downward penetration of ^{90}Sr in soil is slow, although it is more rapid than for ^{137}Cs or ^{249}Pu . Even after several years ^{90}Sr remains in the upper few centimeters in undisturbed soil. The rate of movement varies with soil type; a low content of clay and humus, a high content of electrolytes and the rapid movement of water increase penetration (Anonymous 1962). The mechanism of movement is thought to involve both leaching and diffusion. Plants acquire ^{90}Sr by direct deposition onto foliage and by root uptake of ^{90}Sr from the soil. Uptake from soil is usually the primary mode of ^{90}Sr entry into plants. The quantity of absorbable calcium in soil is an important factor in determining the extent of ^{90}Sr absorption by plants. Uptake of Sr is greatest from soils of low calcium content. Uptake is thus reduced by the addition of lime, but usually not by a factor exceeding 3 (Anonymous 1962).

2.2.5 Barium

Barium has seven stable naturally occurring isotopes with mass numbers (and percentage abundances) 138 (71.70%), 137 (11.23%), 136 (7.854%), 135 (6.592%), 134 (2.417%), 130 (0.106%) and 132 (0.101%). Of the divalent cations, Ba^{2+} has the largest ionic radius except for Ra^{2+} . Barium ranks 14th among the elements in the order of abundance in Earth's crust. In terms of overall geochemical behavior barium most closely follows Sr and Ca.

Metallic barium does not occur in nature, due to its reactivity. The most important naturally occurring minerals are barite ($BaSO_4$) and witherite ($BaCO_3$). However barium usually does not form minerals of its own in igneous rocks. It is usually distributed as a trace constituent among the silicate minerals, especially potassium feldspars and micas, where it substitutes for potassium (Wedepohl 1969). Barium may substitute for large ions such as Pb^{2+} and Sr^{2+} . It may also substitute for Ca, usually in plagioclases, pyroxenes and amphiboles. Barium may enter plagioclase structures depending on An-Ab series, temperature and pressure, and competing elements. Apatite and calcite are the most important rock forming non-silicates containing barium.

Alkali rocks are usually highly enriched in barium. Granitic rocks with low Ca content (granites, quartzmonzonites) show extremely variable Ba values. Experimental weathering of K feldspar in distilled water (Puchelt 1967) showed that Ba is preferentially released from the silicate structure into solution. The factors affecting Ba behavior during weathering are: type of clay minerals that form during decomposition; climate; amount and type of organic material present; and sulfur or sulfate content. Barium adsorption onto clays decreases with ionic strength of the exchange solution (Puchelt 1967). Bentonite adsorbs Ba more strongly than NH_4^+ , Mg^{2+} and Ca^{2+} (Komlev et al. 1965). Manganese hydroxides ($\gamma MnO(OH)$) can absorb up to 20% Ba (by weight) of its manganese content (Puchelt 1967), and electrolytes did not influence the amount of adsorbed Ba. The mean Ba concentration in coal types from Tertiary lignite basins in the NW part of the Czech Republic was 1.5 meq.kg^{-1} with a central range of $0.4 - 2.8 \text{ meq.kg}^{-1}$ (Bouška & Pešek 1999).

The annual deposition fluxes of Ba at six rural sites in Norway were in range $1.43 - 17.4 \text{ } \mu\text{eq.m}^{-2}.\text{yr}^{-1}$ and Ba was evaluated as both an element atmospherically transported from anthropogenic or crustal sources (Berg et al. 1994). Atteia (1994) found significant differences in Ba concentrations across an area of 3000 km^2 in Switzerland and he reported an average Ba concentration of $0.10 \text{ } \mu\text{eq.L}^{-1}$ (median $0.04 \text{ } \mu\text{g.L}^{-1}$) from six sites.

The streamwater flux of Ba from a clear-cut catchment ($390 \text{ } \mu\text{eq.m}^{-2}.\text{y}^{-1}$) increased by 450% compared to a reference catchment ($88 \text{ } \mu\text{eq.m}^{-2}.\text{y}^{-1}$) at Hubbard Brook Experimental Forest

(Scott et al. 2001). The increased Ba concentration in streamwater was attributed to release of readily exchangeable Ba from soils due to increased concentrations of H^+ in soil solution.

Most soils contain 1.46 to 43.7 meq.kg⁻¹ of Ba (Wedepohl 1969), of which traces can normally be extracted by 1N NH₄ acetate. Barium has a strong tendency to exchange for H^+ in peat (Bel'Kevich et al. 1966).

Barium concentrations in natural waters are controlled by the low solubility of BaSO₄ and by adsorption of Ba from solution by clays, hydroxides and organic matter. The median Ba concentration in North American rivers is 0.66 µeq.L⁻¹ (Durum and Haffty 1963). The highest Ba concentrations are found in waters draining areas underlain by sedimentary rocks (sandstone, slate). Lower Ba concentrations in surface water are typical for areas with granite and the lowest occur in quartzite bedrock. In regions with high sulfate concentrations, Ba concentration is low due to the low BaSO₄ solubility product (10^{-10} ; Krauskopf 1979). At pH values < 9 the Ba²⁺ ion is generally the dominant species, with BaSO₄ becoming significant in environments with high sulphate content. Barium forms relatively weak complexes with Cl⁻, NO₃⁻ and OH⁻ and forms complexes with organic matter to a limited extent. In many aqueous environments the Ba concentration is controlled primarily by ion exchange and sorption reactions (Palmer 1999). The solubility of witherite controls Ba concentration only in very alkaline systems, while at pH values >10 BaCO₃ becomes the dominant species. Increased pressure and temperature increase the barite solubility. Barium carbonate solubility depends largely on the CO₂ partial pressure. The solubility product of witherite is $10^{-8.64}$ under 25° C and 1 atm. CO₂ pressure (Garrels et al. 1962).

There is no physiological evidence that barium is an essential element (Palmer 1999). Soluble barium salts are known to be poisonous. Barium is present in recent and fossil plants, animals and fuels. Several investigators found barium accumulation in plants and animals, but there is no evidence that this element is physiologically necessary. Barium is moderately toxic for plants and slightly toxic for mammals. Fir and spruce have 7.2 to 90.3 meq.kg⁻¹ of Ba in ash with the highest concentrations in twigs (Lotspeich and Markward 1963). Ba is moderately phytotoxic in deionized water and non-toxic in river water. The low Ba phytotoxicity in river water is due to the presence of particulate material (Wang 1986). Filtered river water with 0.73 meq.L⁻¹ Ba inhibited the growth of duckweed by 10% compared to unfiltered water, which caused almost no effect.

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3 Methods

3.1 Site description

The region of central Europe including the Czech Republic has been strongly affected by extensive industrial activities. One of the most impacted areas is known as the Black Triangle. It includes the part of northwestern Czech Republic with large deposits of the soft coal (lignite). The lignite is high in sulfur content as well as significant amounts of various trace elements (Bouška & Pešek 1999). This lignite is the main source of fuel for most Czech coal-fired power plants. Due to the poor environmental policies of the former communist regime, coal burning became the most significant impact on the environment of Central Europe.

The Lesní potok catchment (LP) monitoring was started in 1993 as a part of the BIOGEOMON monitoring network, which monitors the inputs and output fluxes at 14 catchments throughout the Czech Republic (Skřivan et al. 1995; Minařík et al. 1997; Skřivan et al. 1997; Fottová et al. 1998; Navrátil et al. 2002). It is located in the central part of the Czech Republic approximately 30 km ESE from Prague (Figure 1). The LP catchment is approximately 50 km directly downwind from the Black Triangle. The catchment is located within the Voděradské bučiny (Voděradské beech stands) National Nature Reserve. The Reserve covers an area of 6.82 km² (682 ha).

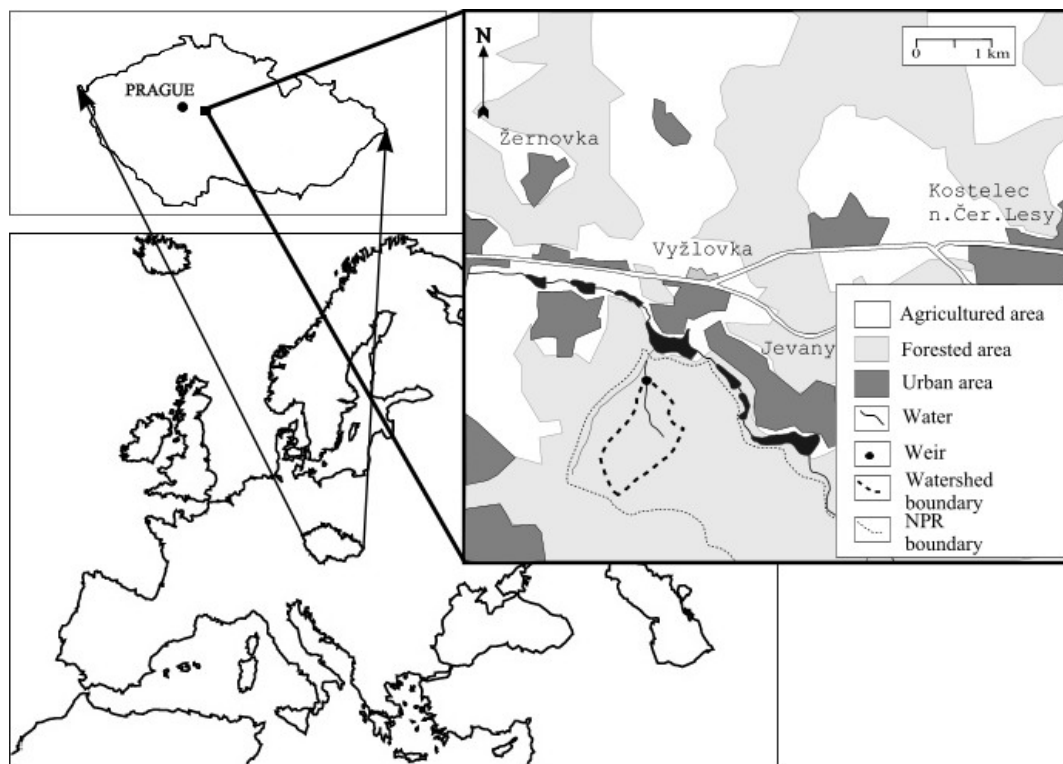


Figure 1 Location of the Lesní potok catchment in Europe, in Czech Republic and in Jevany district

The LP catchment covers an area of 0.765 km². The altitude of the highest point in the catchment is 500 m a.s.l., whereas the Thompson weir is located at 406 m a.s.l.. The three closest villages to the catchment are Louňovice, Vyžlovka and Jevany. The water of the Lesní potok catchment flows directly to the Vyžlovský pond. The pond is part of a cascade of ponds that is drained by Jevanský potok heading to the major river Sázava. The geographical coordinates of the catchment weir are 49° 58' 35" lat. N, 14° 46' 40" long. E, and catchment has a NNE aspect.

3.1.1 Climate and Hydrology

The catchment is located in an area with low precipitation. The average annual precipitation in the period 1994 - 2000 was 600 mm. The highest monthly precipitation amounts are typically in the summer period (June – August). The lowest precipitation amounts are typically in the winter period (November – February).

The annual average temperature at the LP catchment is +7°C. The coldest period at the LP catchment is November – February, January being the coldest month at an average temperature of +0.2°C. The highest average temperature occurs in June (+14.1°C), while the average temperature during April – August is higher than +12°C.

The warm summer coupled with the almost complete afforestation of the catchment causes very high annual evapotranspiration (~80 %), calculated from the chloride budget. The high evapotranspiration rate causes increased concentrations of mobile solutes in stream water (Navrátil et al. 2003). The lowest discharges usually occur during the periods of higher temperature, which correlate with the growing season (Figure 2). The root systems of the vegetation are then able to uptake most of the water due to its slowed movement through the catchment.

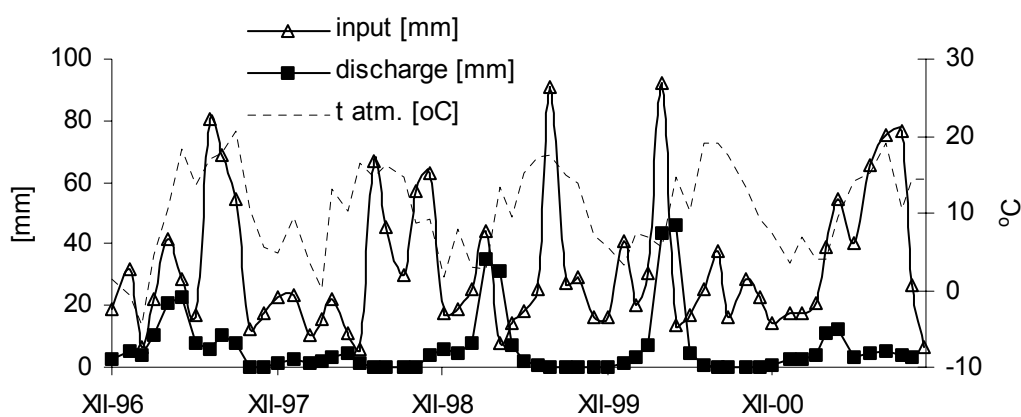


Figure 2 Precipitation input and runoff output depth [mm], temperature [°C]

Two major hydrological pathways are shown on Figure 3. Solid arrows show the major hydrological pathway during the dry periods. During periods of drought, the chemistry of surface water is very similar to the chemistry of shallow groundwater sampled in a well close to the weir. The unfilled arrowheads depict hydrological pathways during periods with increased water table, when the upper zones are saturated. Surface runoff is low at the LP catchment, because of low annual precipitation, low soil porosity (Gleyic Cambisols), relatively high soil thickness and high demand of trees for water.

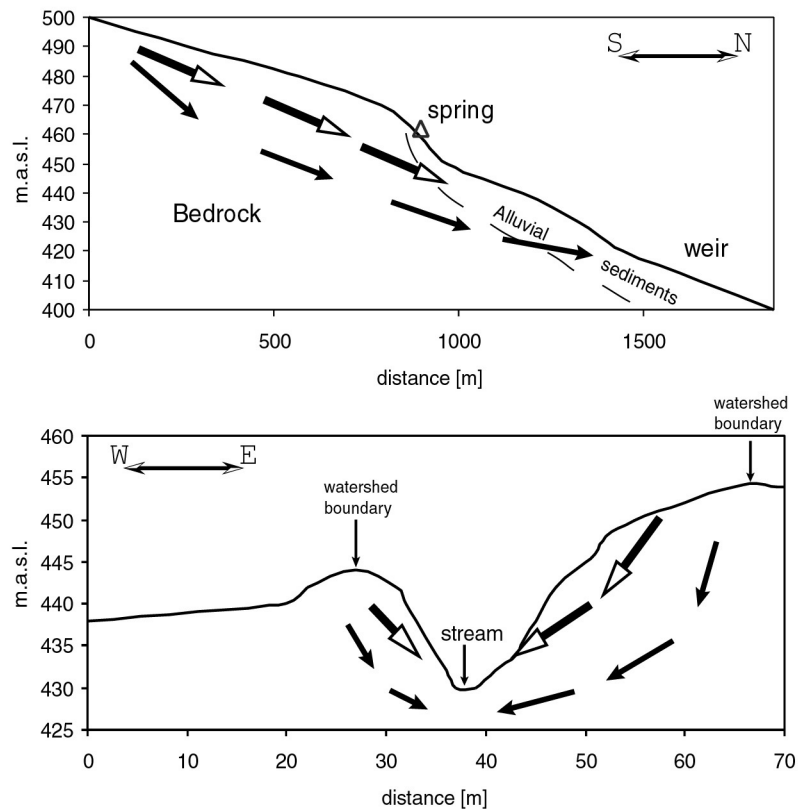


Figure 3 Two profiles with preferential flow pathways (solid arrow low water table, unfilled arrow high water table)

3.1.2 Geology

The catchment is underlain by granite, which belongs to the Říčany Pluton. The Říčany Pluton is a part of a complex mass Central Bohemian Pluton, which is composed of various plutonic rocks ranging from gabbros to granites. The roughly circular Říčany intrusion (ca. 80 km²) is composed of biotite ± muscovite granites. The mineralogy of the granites is monotonous but also structurally variable. The equigranular medium-grained rock forming the centre of the pluton changes gradually to orthoclase porphyry on the edges. The Říčany massif has been extensively studied by numerous authors, because of its enrichment in elements associated with volatile compounds (Sn, W, Li, Be, F etc.) (Vejnar 1974; Němec

1978) and because of its position in the Central Bohemian Pluton (Fiala et al. 1976; Minařík et al. 1986; Janoušek et al. 1995; Janoušek et al. 1997; etc.). Two types of granite are found in the area of the catchment: monzogranitic Říčany type and syenogranitic Jevany type. The coarser Říčany monzogranite surrounds the circular shaped body of the Jevany syenogranite. The mineralogical composition of both types is almost identical: ~27% quartz, ~29% orthoclase, ~35% plagioclase and ~6% biotite (Palivcová 1965; Němec 1978). The trace mineral constituents of both granite types are muscovite, tourmaline and apatite.

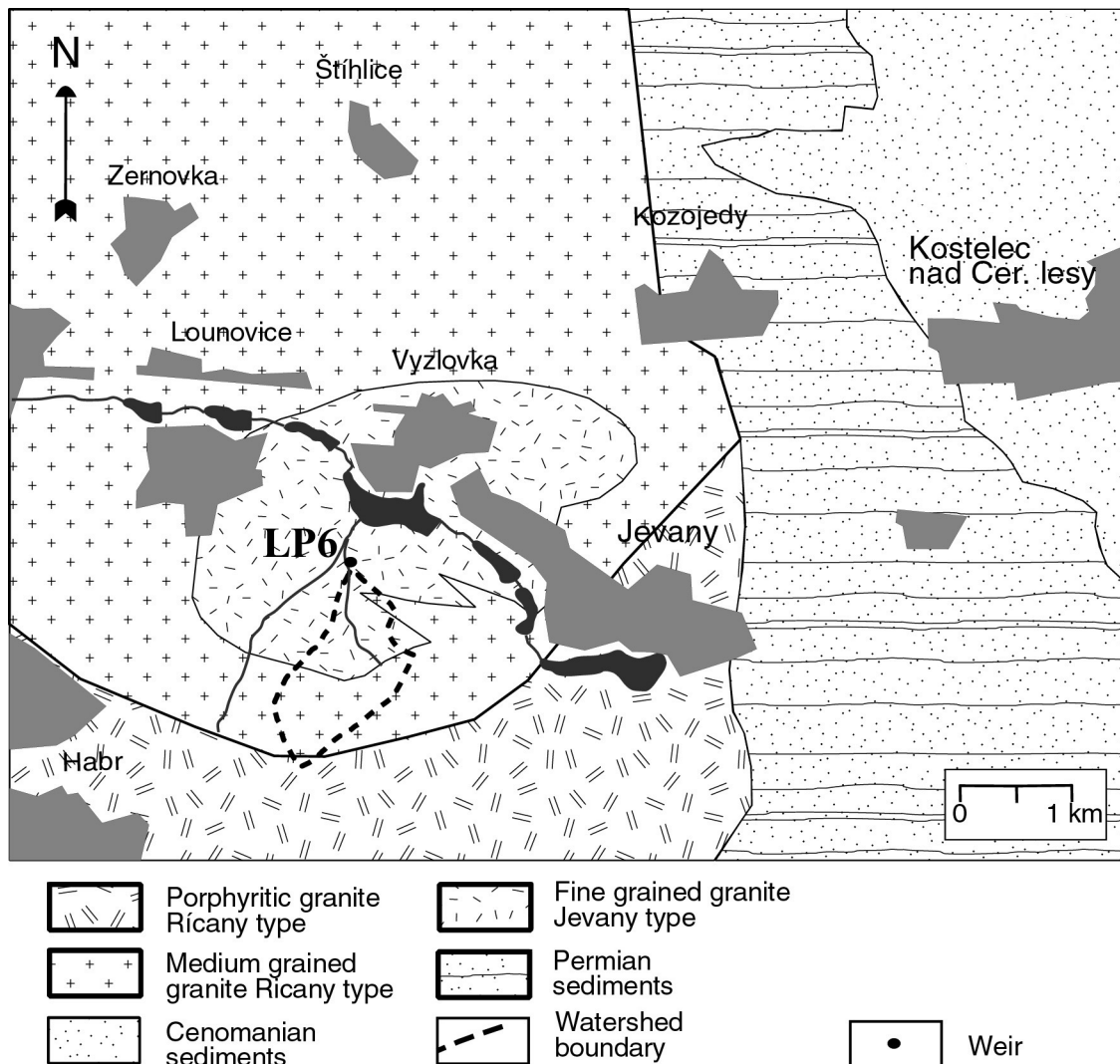


Figure 4 Geological setting of the catchment vicinity

Janoušek et al. (1997) studied the differences between the two types of granites from the Říčany massif. The Říčany granite suite is characterized by high K_2O and low FeO , MgO , CaO , Na_2O/K_2O and FeO/Fe_2O_3 compared to other members of the Central Bohemian Pluton. Trace elements, especially Ba and Sr , show significant ranges in concentration, which is typical for fractionated granites (Janoušek et al. 1997). The orthoclase is usually developed in

the form of microcline and it weathers to clay minerals or sericite. The basic centers of the plagioclases weather preferentially (Janoušek 1991).

The north part of the catchment is underlain by 4 – 5 m of alluvial sediments. A survey well was bored 60 m downstream from the site LP6 (weir) through the alluvial sediments to the bedrock. Hons et al. (1990) describes and discusses mainly the trace element concentrations found in the various depths of the profile. However, the profile was not examined in detail with respect to the elements of the II.A group.

The samples of the sediment were sieved and fractions <0.063 mm and $0.063 - 2$ mm were analyzed. The authors concluded that the alluvial profile was not formed in situ from the Jevany type granite but from the parent material of the Říčany type located in the upper part of the catchment. The indicators for this conclusion are grains of kassiterite found in the profile as the kassiterite is found in the Říčany type, only (Hons et al. 1990). The authors conclude that the geochemical properties of the profile indicate input and/or output of material during the profile evolution. A strong correlation between Ba and Sr was detected throughout the profile. The analytical method OES was used for determination of Be in profile and other elements were determined by X-ray fluorescence.

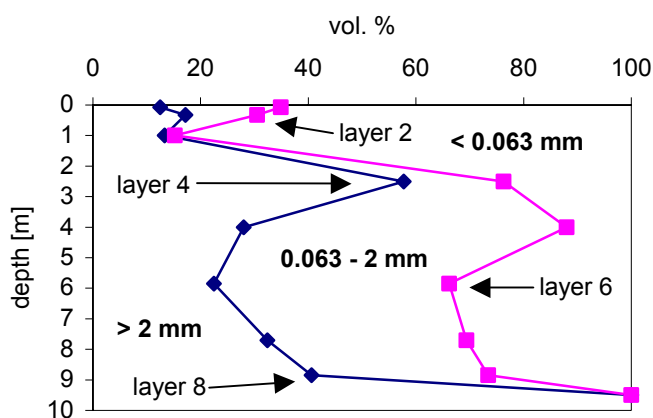


Figure 5 Distribution of the fractions throughout the alluvial profile

The sieving of individual horizons revealed the distribution of three fractions in the profile (Figure 5). The proportion of the coarse material fraction (> 2 mm) decreases towards the top of profile. The only anomaly is found at 3-m depth, where it stands for more than 50%. The fraction of material ($0.063 - 2$ mm) is especially important between depths 3 m – 10 m. The sample from 1-m depth is notable for its absence of the fraction ($0.063 - 2$ mm), which only formed $< 2\%$. The proportion of the finest fraction (< 0.063 mm) increased from the bottom to the top of the profile.

Soils at LP catchment are derived from the Říčany granite, mostly Gleyic or Dystric Cambisols. The soil thickness averages 1 m. The average mineralogical composition of the soil fraction < 0.001 mm is 43% quartz, 13% kaolinite, 12% chlorite, 8% orthoclase, 8% plagioclase, 7% illite, 4% mixed structure of illite and smectite and 2% smectite (Žigová et al. unpublished). The bottom soil horizons often contain boulders and coarse debris derived from the underlying granite. On areas with low slope and high water table level the soils often undergo the processes of gleyfication. The Gleyic Cambisols usually contain increased proportions of the finest fraction material

3.1.3 Vegetation

The stony and locally shallow soils disallowed the land to be agriculturized. Formerly mixed stands were changed to clearly beech stands whereas the fir has almost completely vanished. The composition of the stands was affected by the inaccessibility of the site and difficulties with the transport of the long-timber. The catchment is mainly forested with the deciduous trees (51.4%). However in the upper part of the catchment are prevailingly coniferous trees, which over all cover 46.2% of the catchment. An area of 1% is deforested. The main tree species present in the LP catchment are European beech (*Fagus sylvatica*) and Norway spruce (*Picea abies*). Other tree species that may be found in the LP catchment are European larch (*Larix decidua*), English oak (*Quercus robur*), European hornbeam (*Carpinus betulus*), European black pine (*Pinus nigra*), Silver fir (*Abies alba*) and Common alder (*Alnus glutinosa*). The most typical natural plant communities of the Nature Reserve are: *Fagetum Acidophilum* (4K), *Querceto-Fagetum Acidophilum* (3K) and *Abieto-Fagetum Acidophilum* (5K) (Viewegh, 2000). The composition of the tree species in the area of Voděradské beech stands has changed. The spruce was not the major coniferous specie in the past but fir.

Table 3 The tree species at LP catchment and appropriate covered area in 1998

Tree specie	Area [km ²]	Area [%]
European beech (<i>Fagus Sylvatica</i>)	0.332	43.4
Norway spruce (<i>Picea Abies</i>)	0.280	36.6
European Larch (<i>Larix decidua</i>)	0.048	6.3
Water oak (<i>Quercus nigra</i>)	0.035	4.6
European hornbeam (<i>Carpinus betulus</i>)	0.020	2.6
European black pine (<i>Pinus nigra</i>)	0.018	2.3
Silver fir (<i>Abies alba</i>)	0.008	1.0
Common alder (<i>Alnus glutinosa</i>)	0.006	0.8
other	0.011	1.4
afforested area	0.008	1.0
Total	0.765	100
Coniferous	0.353	46.2
Decidous	0.393	51.4

The expansion of spruce was mostly due to unexplained decline of fir and due to increasing economic demands on the forests. The percentage of area attributed to each tree species is listed in Table 3. The timber supply was evaluated for all the species present at catchment (Sequens 1998). The total timber supply for the spruce and beech on the area of catchment was evaluated as 18454 m³ and 10203 m³ without bark, or 20300 m³ and 11223 m³ including bark, respectively. The values of common annual increment for spruce and beech without and with bark for the catchment were evaluated as 254.9 m³.yr⁻¹ and 174 m³.yr⁻¹, as 280 m³.yr⁻¹ and 174.1 m³.yr⁻¹, respectively. The crop density was reported as 0.88 for spruce and 0.91 for beech. The mass of the fresh foliage was evaluated as 846900 kg for spruce and 171100 kg for beech (Sequens 1998).

Permanent afforestation of the Nature Reserve land conserved some phenomena derived from the ice weathering, soil-ice activity and eolic weathering in the beginning of the Quarternary. These phenomena such as stony seas, stone flows, dry valleys and warps give the impression of former glaciation but were a result of remote (100 km north) presence of glacier (Ambrož 1942).

3.2 Sampling

3.2.1 Rock and mineral samples

The rock samples were disintegrated in an agate mill and totally decomposed by an admixture of super pure HF, HNO₃ and HCl. The chemical analysis of the rock-forming minerals was performed on the polished rock samples with the CAMECA electron scanning microprobe at Institute of Geology - Academy of Sciences, CR (GLI AS CR). The beryllium concentrations in the rock-forming minerals were analyzed on LA-ICP-MS (laser ablation – inductively coupled plasma – mass spectrometer) at Faculty of Science - Charles University, Prague. A detailed description of the calibration is described in Navrátil et al. (2002).

3.2.2 Bulk precipitation and throughfall

Bulk atmospheric precipitation is sampled at site Truba (TR), which belongs to the experimental station of the Czech Agricultural University, Faculty of Forestry. The site TR is located approximately 5.5 km northeast of the catchment (Figure 6). The samples were collected monthly. For the bulk precipitation sampling, 2.5 ml of diluted (22% v/v) HNO₃ (Merck, Suprapur) were inserted in each sampling bottle to prevent the adsorption of dissolved elements onto the walls of the sampling bottle. The analyzed 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 collectors of bulk precipitation consist of a 1 L

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 5 L 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. The collectors are placed inside opaque plastic pipes (to avoid heating and growth of algae), which are attached to metallic rods approximately 1.5 m above the ground. For a detailed description refer to Skřivan et al. (2000).

Throughfall samples are collected in the catchment at sites LP6 (beech) and LP7 (spruce) (Figure 6). Four sampling devices are installed on each site. Throughfall was 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 neck of the funnel is equipped with a nylon sieve and the funnel is screwed with a double PE screw to a 1-L PE sampling bottle. However these sampling devices enabled unwanted contamination by leaching of material (leaves, tree debris and insects etc.) deposited inside the funnel. This leaching of material may overestimate the throughfall fluxes, therefore in this study GCTC throughfall sampling devices were used. The funnel of GCTC device is protected with a glass cone, which protects the sampler against unwanted collection of falling material, but the water droplets deposited on the glass cone are collected. The GCTC sampler was successfully calibrated to the VOSS sampler in order to estimate the effect of glass cone on sample volume. Details of the samplers were described elsewhere (Skřivan et al. 2000, Skřivan and Burian 1996).

3.2.3 Soil solution

Soil solution is sampled by zero tension lysimeters at location LP6 and LP35 (Figure 6). The lysimeters are located at 5 cm and 15 cm depths at both sites, and at 45 cm depth at LP6 only. Both sampling locations are forested with beech trees. The LP6 location is in the vicinity of the stream with Gleyic Cambisol soil type, and LP35 is located on the hillslope with Dystric Cambisols.

3.2.4 Stem wood, roots, bark and assimilatory organs of beech and spruce

Samples of the forest vegetation were collected from beech (*Fagus sylvatica*) and spruce (*Picea abies*). A 1 cm² 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 3 cm long sub-samples, which represented inner- middle- and outer parts of the tree rings. Each subsample was then decomposed and analyzed separately. Roots with diameter > 1 cm were sampled from the top 20cm of the soil profile. The sampled roots and branches were stripped of their bark by means of a quartz glass chip. The consequent treatment and decomposition was done similarly as in case of the bole wood.

The dried samples of assimilatory organs (leaves, needles) were analyzed without any cleaning to avoid losses of the soluble portion of analyzed 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.

All the samples of the vegetation tissue were dried and decomposed in the microwave oven in a PTFE crucible with a mixture of HF and HNO₃ acids.

3.2.5 Soil samples

Soil samples were passed through a 2 mm sieve except for the samples from O horizons were passed through a 5 mm sieve. The fraction < 2 mm (< 5 mm) was then analyzed for total and leachable element concentration. Decomposition of all samples was carried out in the microwave oven in a PTFE crucible with a mixture of HF and HNO₃ acids. Acid-soluble forms of the elements in the individual soil horizons were detected by the extraction of soil samples in 0.1 M nitric acid (Merck, Suprapur) for 24 hours at room temperature (V/m = 200) (Minařík et al. 1998). Exchangeable forms of Ca and Mg in the soil horizons were determined after the extraction of soil samples with 0.1 M BaCl₂ for 24 hrs. at V/m = 200 and room temperature.

The total concentrations of elements in soils were determined on 3 profiles at sites LP33, LP35 and LP36 (Figure 6). The acid leachable and exchangeable concentrations of elements in soils were determined on 8 sites LP33, LP35, LP36, LP50, LP51, LP52, LP53 and LP54 (Figure 6).

The detailed description of soil profiles horizons at LP33, LP35 and LP36 is in Minařík et al. (1998) and Skřivan et al. (2000).

3.2.6 Surface water and shallow groundwater

Samples of surface water and shallow groundwater were filtered in the field through a Sartorius filtering device equipped with the cellulose nitrate filter (pore size 0.45 μm). The filtrate was immediately stabilized with nitric acid (Merck, Suprapur, diluted 1:3 v/v with redistilled water), 1ml of diluted HNO₃ per 100 ml of sample. Unfiltered and unstabilized samples of surface water were collected simultaneously for the determination of bulk

chemical composition and for pH and conductivity measurements. Determination of pH was made by the pH-meters HACH One (USA) and WTW pH 91, WTW 330 (Germany). All the polyethylene (PE) bottles used for the transport of liquid samples to the laboratory were carefully washed (hot distilled water, 0.5% HNO₃, distilled and redistilled water). The sample containers used for analysis of cations were leached with 1:3 HNO₃ at least 24 hours prior to sampling. The bottles were all transported to the laboratory in sealed PE bags.

The surface water of the LP catchment was sampled monthly, directly below the Thompson weir at site LP6 (Figure 6). Air and water temperature were measured in situ. The actual discharge was measured by means of a 4 L vessel. Three aliquots of the streamwater are sampled: filtered, HNO₃ stabilized (cations); unfiltered, HNO₃ stabilized (cations) and unfiltered, unstabilized (anions).

Shallow groundwater was sampled in hydrological years 1999 and 2000 from the well located adjacent to the weir. The well is 5 m deep and made of inert material, and is screened at the bottom 0.5 m. The stagnant water was at first pumped from the well and sample was acquired approximately 3 hours after the water level increased. The initial water level in the well was measured by yardstick. The samples were filtered in field in the same way as the streamwater samples.

3.2.7 Acidification experiment

An acidification experiment was conducted on May 5th, 2001. The air temperature was 20°C and the stream water temperature was 11°C. The discharge at the start of acidification was 2.73 L.s⁻¹ (0.013 mm.h⁻¹). Discharge decreased to 2.43 L.s⁻¹ (0.011 mm.h⁻¹) by the end of sampling. Twenty-two moles of HCl were added to the stream during 4 hours at a point just below the stream weir LP6 (Figure 6). The discharge of acid (4.709 M) from the Mariotte bottle was approximately 20 ml.min⁻¹. Samples of the stream water were taken at points W, B, C and D. Point A and W were located 1 m below and above the acid addition point. Point B, C, and D were 20 m, 45 m and 70 m downstream from A, respectively. Each sampling event included 3 aliquots. The first was unfiltered; the second filtered through 0.45 µm cellulose membrane filter. Both were stabilized with super pure HNO₃ and used for cation analyses. The third aliquot was unfiltered and analyzed for anions. For details refer to Navrátil et al. (in review).

Concentrations of Na, K, Mg, Ca, Al, Mn and Fe were determined with flame atomic absorption spectrometry (FAAS; Perkin Elmer 3100) in all liquid (or digested) samples in this work. Concentrations of F⁻, Cl⁻, SO₄²⁻ and NO₃⁻ in solution were determined by ion

chromatography (HPLC, columns Tessek HEMA-S1000 Q-L 10mm). Concentrations of Be, Ba and Sr were determined by Graphite Furnace AAS (GFAAS, VARIAN SpectrAA 300).

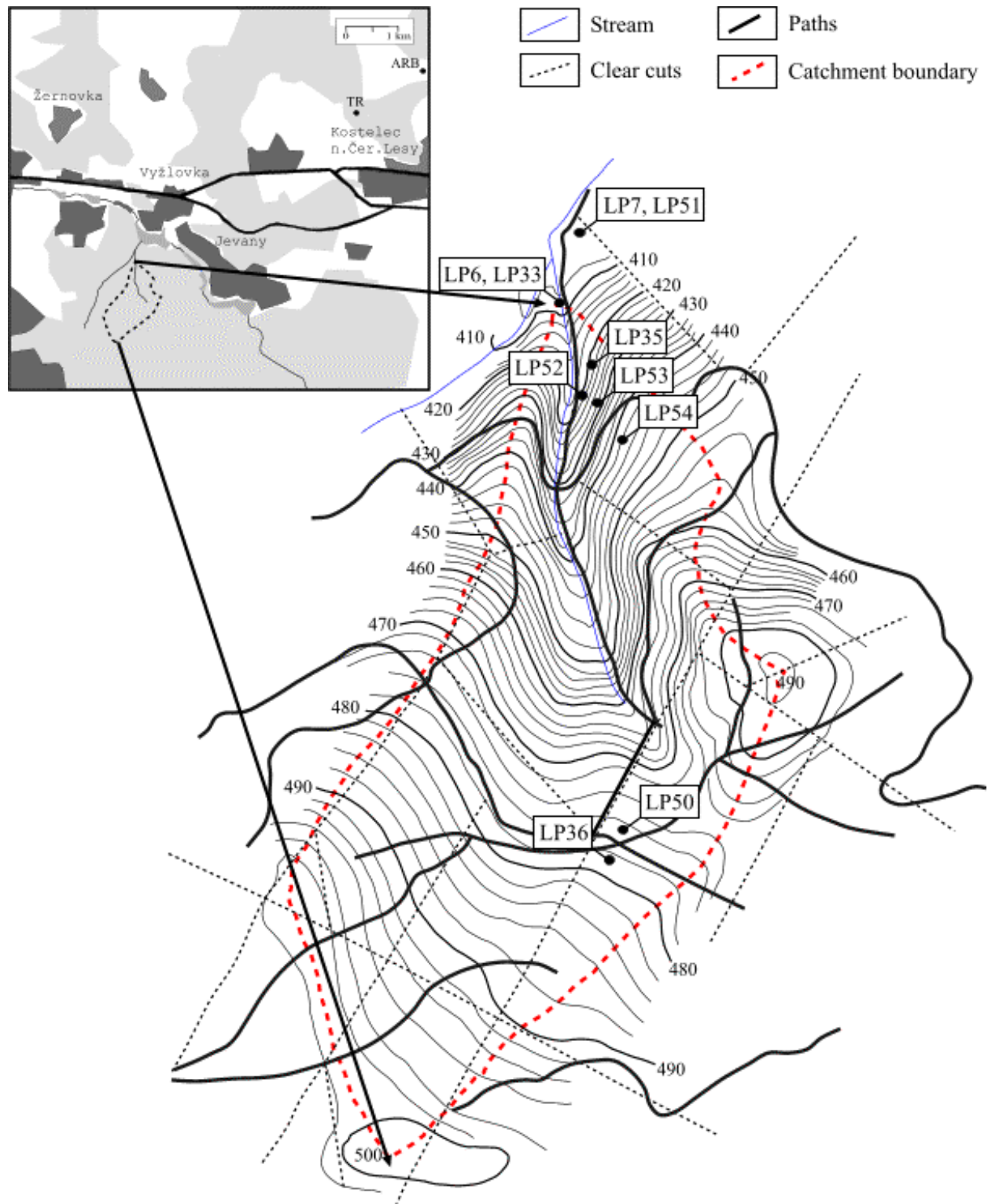


Figure 6 Sampling locations inside and outside of the LP catchment

4 Results

4.1 Bedrock

The sample of Říčany type granite was altered biotitic granite with traces of muscovite. The rock was of gray in color (Figure 7). The biotite was often chloritized. The feldspars were sometimes argillitized or sericitized. Grain size was usually in the range 0.1 – 4 mm, while the xenocrysts were composed of orthoclase and might reach a size of 2 – 3 cm.

The sample of Jevany type granite was from the most weathered suite of the Říčany massif. The fine-grained rock was gray to pink in color (Figure 7). The average grain size was 0.4 mm. The biotite grains were sparsely distributed and reached a maximum size of 1 mm.

Both types of granites exhibit considerably low Ca concentrations, when compared to the average global values for granitic rocks low in Ca (

Table 2, Roessler & Lange 1972). The Říčany and Jevany granites are both significantly enriched in Be and Ba in comparison to the typical low- Ca granitic rocks. In the case of Mg and Sr the Říčany granite contained higher concentrations while the Jevany granite contained lower concentrations than average of low- Ca granitic rocks (

Table 2, Roessler & Lange 1972).

Table 4 Chemical composition of the bedrock

units	Říčany type - monzogranite			Jevany type - syenogranite		
	vol. %		meq.kg ⁻¹	vol. %		meq.kg ⁻¹
SiO ₂	71.24			73.28		
TiO ₂	0.25			0.17		
Al ₂ O ₃	14.18			14.46		
Fe ₂ O ₃	0.46			0.35		
FeO	0.76			0.25		
MnO	0.02			0.01		
MgO	0.76	⇒ Mg	376.4	0.24	⇒ Mg	119.9
CaO	1.17	⇒ Ca	424.4	0.93	⇒ Ca	337.4
SrO	0.04	⇒ Sr	7.5	0.03	⇒ Sr	5.8
BaO	0.17	⇒ Ba	21.7	0.13	⇒ Ba	16.8
Li ₂ O	0.02			0.07		
Na ₂ O	3.72			4.01		
K ₂ O	5.33			5.11		
H ₂ O-	0.19			0.11		
P ₂ O ₅	0.18			0.06		
CO ₂	0.01			0.01		
C*	0.05			0.01		
F	0.15			0.06		
S	<0.005			<0.005		
LOI	0.64			0.38		
Be		-⇒ Be	3.7		-⇒ Be	3.5

The chemical composition of both the Říčany and Jevany granites was generally similar (Table 4). However with respect to the II.A group elements the Říčany type was significantly

enriched in Ca and Mg and comparable in concentrations of Be, Sr and Ba. The Jevany type granite contained greater concentrations of Si, K and Na.

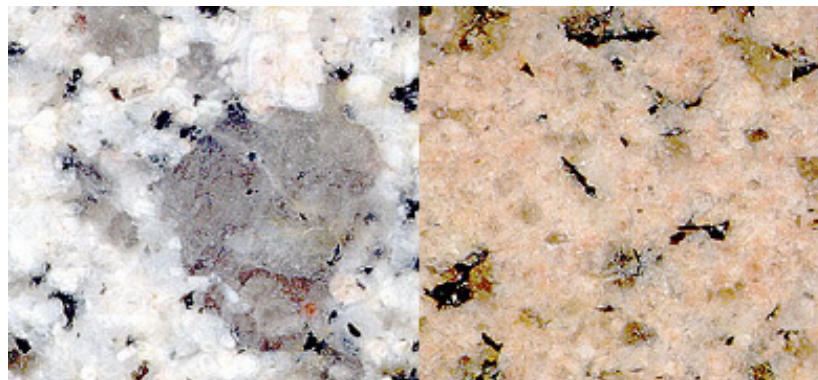


Figure 7 Images of the Řičany type (left) and Jevany type (right) granites

The main rock-forming minerals of monzogranite and syenogranite are quartz, plagioclase, orthoclase and biotite. Plagioclase is the most important mineral containing Be, Ca and Sr in the rock (Table 5). The average concentration of Mg in plagioclase was low. The concentration of Ba in plagioclase was significantly lower than in orthoclase and biotite.

Table 5 Average chemical compositions of the rock-forming minerals

units	Orthoclase		Plagioclase		Biotite	
	vol. %	meq.kg ⁻¹	vol. %	meq.kg ⁻¹	vol. %	meq.kg ⁻¹
SiO ₂	64.18		65.67		41.19	
TiO ₂	0.02		0.01		3.00	
Al ₂ O ₃	18.59		21.91		16.07	
Fe ₂ O ₃	-		-		17.19	
FeO	0.04		0.06		-	
MnO	0.05		0.03		-	
MgO	0.01	2.8	0.01	3.6	12.05	5968.0
CaO	0.03	12.5	2.45	888.0	0.15	53.6
SrO	0.07	13.8	0.08	15.9	0.003	0.5
BaO	0.30	38.9	0.02	2.2	0.13	16.4
Li ₂ O	-		-		-	
Na ₂ O	1.05		9.96		0.43	
K ₂ O	15.59		0.21		10.11	
Be	-	0.2	-	4.0	-	1.8

Orthoclase was the main mineral containing Ba in the rock (Table 5). However the concentration of Sr was significant and comparable to that in plagioclase. The concentration of Be in orthoclase was negligible but its Ca concentrations averaged 12.5 meq.kg⁻¹.

Biotite was the only mafic mineral out of the rock-forming minerals. Thus it contained the highest concentrations of Mg and Fe. The content of Be in biotite was also significant (Table 5). The average concentration of Ba reached 16.4 meq.kg⁻¹, which was smaller than the Ba content of orthoclase. Strontium concentration in biotite was negligible.

Quartz contained very low concentrations of the II.A group elements.

4.2 Alluvial Sediments

The data presented in this chapter (*Alluvial Sediments*) originate in paper of Hons et al. (1990). Hons et al. (1990) sampled a borehole located ca. 60 m north of the location LP6 (Figure 6). The original paper did not discuss this data set with regard to all II.A group elements. For the layout of the profile and the depths of individual layers refer to Figure 5.

The highest Be concentration in the profile was detected in layer 9 above the weathered bedrock (Figure 8). An elevated concentration of Be was also detected in layer 7. Beryllium concentration decreased towards the top of the profile, thus the topmost layers contained the lowest concentrations. The sediments, except layer 9 and 7, contained lower concentrations of Be than the parent bedrock granites (Figure 8).

Magnesium concentration slightly increased from the bottom layers to the top. The concentration of Mg found in layer 3 was higher than the Mg content of the bedrock. In contrast, the lowest Mg content was found in the lowest layer (weathered granite).

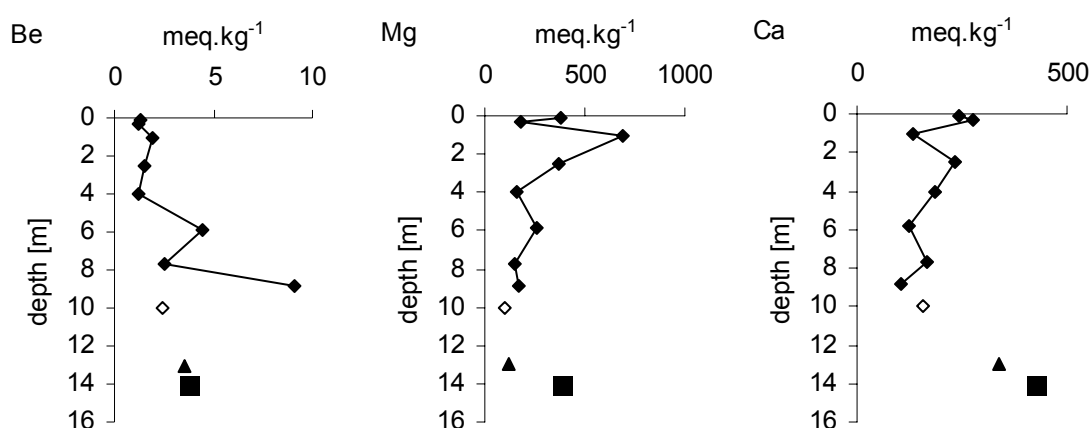


Figure 8 Vertical distribution of Be, Mg and Ca in the alluvial profile, empty diamond represents the weathered rock in 10m depth, triangle represents syenogranite (Jevany), square represents monzogranite (Ričany), filled diamonds represent each layer of profile

The sediments were significantly depleted in Ca when compared to the concentrations in bedrock. Calcium concentration in sediments gradually increased towards the surface. The layer with the highest Mg concentration contained less Ca.

The Sr and Ba concentrations in sediments correlated positively ($R = 0.88$, $p < 0.001$, $n = 8$), as noted by Hons et al. (1990). The topmost layers were depleted in Sr, however Sr content in layers from 2 m downwards were similar to the Sr content of the bedrock.

The Ba concentration in the profile was more or less stable except two anomalous layers. The layers 5 and 7 had elevated Ba concentrations and also the highest Sr concentrations. Sediments were slightly depleted in Ba when compared with the bedrock content.

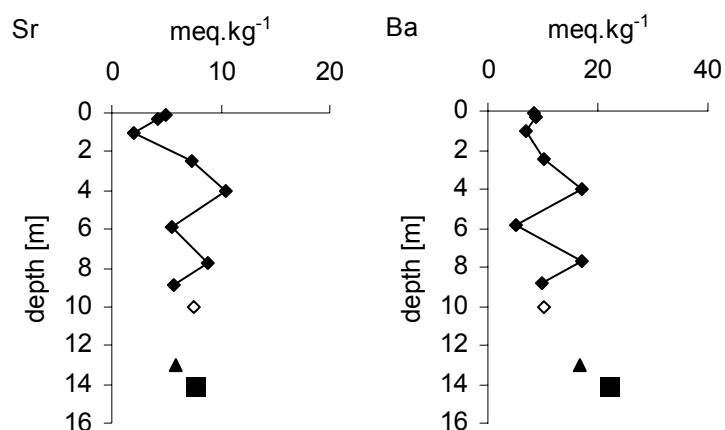


Figure 9 Vertical distribution of Sr and Ba in the alluvial profile, empty diamond represents the weathered rock in 10m depth, triangle represents syenogranite (Jevany), square represents monzogranite (Říčany), full diamonds represent each layer of profile

4.3 Bulk precipitation

Acid deposition on the area of Czech Republic was among the highest in the world between the 1960's and 1990's. A primary cause for the high acid loading was that the Czech Republic was third in the world in the mining of soft coal (lignite). Heavy industrialization was one of the main targets for the former socialistic regime. The heaviest pollution has been reported from the area known as the "Black Triangle". The LP catchment is located 50 km SE but downwind of the Black Triangle. The coal power plant Mělník located approximately 60 km to the northwest also affected the levels of acid deposition at LP.

The volume weighted annual pH of the bulk precipitation gradually increased from 4.17 in 1994 to 4.55 in 2000 (Table 22). This represents a 67% ($26 \text{ meq.m}^{-2}.\text{yr}^{-1}$) decrease in the annual bulk deposition flux of H^+ .

Accordingly, the wet deposition of sulfate has decreased by 60% at LP catchment, from 58 meq.m^{-2} of SO_4^{2-} in 1994 to 23 meq.m^{-2} in 2000 (Table 22). This wet deposition of sulfate at LP ($55 - 60 \text{ meq.m}^{-2}$) from 1994 to 1997 was comparable or occasionally even higher than that for the same period at the Lysina catchment ($42 - 61 \text{ meq.m}^{-2}$) in the area of the former "Black triangle" (1994 - 1997), (Hruška et al. 2002). Since, 1998, wet deposition of sulfate was at least by 10% lower at LP than at Lysina.

The deposition of base cations decreased from $160 \text{ meq.m}^{-2}.\text{yr}^{-1}$ in 1994 to $90 \text{ meq.m}^{-2}.\text{yr}^{-1}$ in 2000, perhaps due to better removal of fly ash from coal power plants emissions.

Beryllium concentrations in bulk precipitation increased greatly during the industrialization of the Czech Republic were a result of uncontrolled release of fly ash from the coal power plants. The annual flux of Be has decreased from $7.4 \text{ } \mu\text{eq.m}^{-2}$ in 1994 to $1.5 \text{ } \mu\text{eq.m}^{-2}$ in 2001

(Table 22). The mean concentration of Be in the bulk precipitation during the years 1994 - 2001 was $0.01 \mu\text{eq.L}^{-1}$. The highest concentration found in the bulk precipitation at the site TR was $0.04 \mu\text{eq.L}^{-1}$. Recent Be concentrations in bulk precipitation have been usually below the detection limit of analyses. The Be bulk fluxes correlated with those of Ba, H^+ , NO_3^- , deposition intensity (DI), F and SO_4^{2-} (Table 23).

Concentrations of Mg in bulk precipitation ranged between 0.8 and $22.2 \mu\text{eq.L}^{-1}$ in years 1994 - 2001, with mean concentration of $6.1 \mu\text{eq.L}^{-1}$. The flux of Mg bulk deposition decreased slightly during the period 1994 – 2001 (Table 22). Magnesium formed about 10% of the cation bulk flux. The Mg fluxes correlated with those of Ca, Ba, SO_4^{2-} , NO_3^- , K and DI (Table 23).

Calcium is the second most abundant cation in the bulk precipitation after NH_4^+ . The concentration of Ca in bulk precipitation ranged between 1.5 and $106.2 \mu\text{eq.L}^{-1}$ in years 1994 - 2001, with a mean concentration of $18.5 \mu\text{eq.L}^{-1}$. Calcium formed about 30% of the bulk cation flux. The Ca fluxes correlated with those of Mg, SO_4^{2-} , NO_3^- , K, Sr and DI (Table 23). The calcium bulk deposition decreased slightly during the period 1994 – 2001 (Table 22).

Strontium is another trace element in the atmosphere, similar to Be and Ba in that concentrations were usually very close to the detection limit of analyses. Concentrations of Sr in the bulk precipitation ranged between 0.01 and $0.15 \mu\text{eq.L}^{-1}$ in years 1996 - 2001. The mean concentration of Sr in the bulk precipitation between 1994 - 2000 was $0.02 \mu\text{eq.L}^{-1}$. The Sr fluxes correlated with those of Be and Ca (Table 23). The annual bulk flux of Sr decreased from 22 to $5 \mu\text{eq.m}^{-2}$ between years 1996 – 2001 (Table 22).

For the concentrations and fluxes of Ba only two years of data were available. The concentration of Ba in bulk precipitation ranged between 0.002 and $0.036 \mu\text{eq.L}^{-1}$ in 2000. The mean concentration of Ba in bulk precipitation was $0.004 \mu\text{eq.L}^{-1}$. Barium annual bulk fluxes were 16 and $15 \mu\text{eq.m}^{-2}$, respectively. The Ba bulk fluxes correlated with those of Be, Mg, K, F and SO_4^{2-} (Table 23).

4.4 Throughfall fluxes

Many studies have demonstrated that tree canopies can capture gases and aerosols from the atmosphere (Mayer and Ulrich 1977; Hosker and Linberg 1982; Lovett and Kinsmann 1990; Linberg 1992; Bytnerowicz and Fenn 1996). Throughfall experiments with artificial leaves showed increased fluxes of dust particles, H^+ , NH_4^+ , Ca^{2+} , Mg^{2+} , Cd^{2+} , Pb^{2+} , Cl^- , NO_3^- and SO_4^{2-} . However, an increase in acid anions exceeded the increase in neutralizing cations, so the precipitation was progressively acidified (Stachurski et al. 2000). The total deposition

determined from bulk precipitation underestimates the real input by as much as several times (Ross and Lindberg 1994). The following components of the input are included in throughfall: wet deposition, dry deposition (dust particles, gases, vapours), interception of water droplets derived from mists, fogs and clouds, and products of leaching of above ground parts of trees. However the methods of throughfall sampling may also overestimate the throughfall fluxes. The overestimation especially takes place when small particles of leaves or needles, insect and debris from the tree crowns fall into the sampler funnel and may be leached until the sample is taken (Skřivan & Burian 1996).

Two types of throughfall are sampled at the LP catchment due to equal afforestation by spruce and beech. It is widely known that spruce throughfall contains higher amounts of solutes, because of the spruce canopy has a high surface area for evapotranspiration and adsorption and leaching processes. Beech throughfall is partly limited due to smaller canopy area for adsorption and also due to seasonality (no leaves in the winter).

The chemical composition of areal throughfall deposited to the catchment was calculated according to afforestation by the various tree species. The most important anions in throughfall deposition flux to the LP catchment during the monitored period were SO_4^{2-} and NO_3^- . The most important cation fluxes in throughfall were potassium and ammonia (Table 22). Throughfall sulfate flux has decreased by 40% from 97 meq.m^{-2} in 1997 to 61 meq.m^{-2} in 2000 (Table 22). The annual deposition of nitrogen to the LP catchment remains relatively stable between 96 – 111 meq.m^{-2} . The deposition of base cations was also decreasing perhaps due to better controls on the emission of solid particles from the coal power plants.

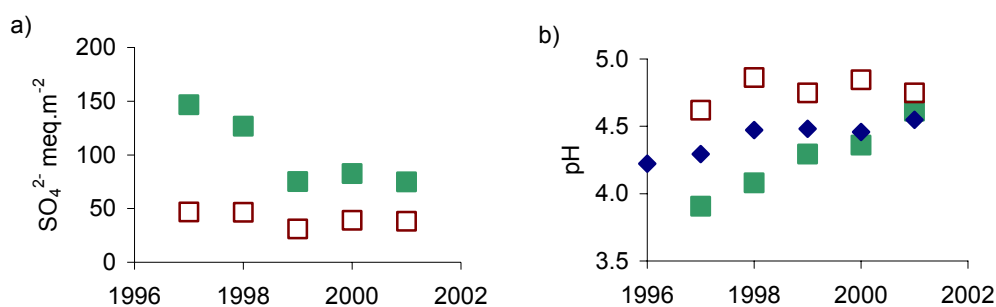


Figure 10 a) The difference in SO_4^{2-} flux below spruce (full squares) and beech (empty squares), b) the differences in throughfall pH below spruce (full squares), beech (empty squares) and bulk precipitation (diamonds)

The monthly deposition volumes were usually higher below the beech trees than below spruce. The higher specific surface area of the spruce canopy causes higher area for evapotranspiration and consequent up-concentration of precipitation solution. During the winter season throughfall volumes under beech may be greater than those under spruce due to

greater canopy retention of snowfall by spruce. Greater canopy interception and evaporation increase the concentration of spruce throughfall, so that most of the solute fluxes under the spruce canopy are higher than their equivalents below the beech canopy. The most significant differences between throughfall fluxes were noted for SO_4^{2-} and NH_4 , which were at least double below the spruce in comparison to beech.

The concentrations of Be in both types of throughfall were usually close to the detection limit of analyses. The highest concentration found in throughfall was $0.05 \mu\text{eq.L}^{-1}$. The mean concentration of Be in the bulk precipitation during the years 1994 - 2001 was $0.04 \mu\text{eq.L}^{-1}$.

The annual fluxes of Be in both types of throughfall were comparable with the bulk deposition fluxes (Table 22). However Be fluxes in beech throughfall fluxes correlated with fluxes of Sr, Ba and Mn (Table 25). The spruce Be fluxes correlated with those of H and Sr (Table 24).

Magnesium fluxes in both types of throughfall were proportionately the most increased elemental fluxes relative to bulk precipitation fluxes. Throughfall fluxes of Mg in the period 1994 – 2001 below the spruce and beech trees were more than 6 - and 5 - fold higher, respectively, than fluxes in bulk precipitation (Table 22). Throughfall fluxes of Mg for spruce and beech were in the range $18 - 24 \text{ meq.m}^{-2}.\text{yr}^{-1}$ and $9 - 30 \text{ meq.m}^{-2}.\text{yr}^{-1}$, respectively.

Throughfall fluxes below the beech were greatest in the period May to November each year. The Mg fluxes in November were usually the highest during each year. Magnesium throughfall fluxes below the beech trees correlated with fluxes of Ca, K, Cl, SO_4^{2-} , F, Na and DI (Table 25).

The Mg throughfall fluxes below the spruce were quite constant except for an elevated flux measured each March in the period 1994 – 2001. The magnesium throughfall fluxes below the spruce correlated strongly with those of Ca, Mn, Na, Cl, SO_4^{2-} , H, K and DI (Table 24).

Calcium fluxes in throughfall were higher in comparison with the bulk fluxes, however only 2.5-fold for both species (Table 22). Overall the Ca throughfall flux was the highest from the II.A group. The throughfall fluxes of Ca below beech were higher than those below spruce during the growing season.

Calcium throughfall flux below spruce and beech was in the range $24 - 36 \text{ meq.m}^{-2}.\text{yr}^{-1}$ and $40 - 22 \text{ meq.m}^{-2}.\text{yr}^{-1}$, respectively.

Throughfall Ca fluxes below the beech increased in the period from July to November each year. Calcium throughfall fluxes below beech correlated with fluxes of Mg, K, Cl, Mn, F, Na, SO_4^{2-} , Sr and DI (Table 25).

Calcium throughfall fluxes below spruce were quite constant except for an extreme flux each March for the period 1994 – 2001. The calcium throughfall fluxes below the spruce trees correlated strongly with those of Mg, Na, Cl, Mn, SO_4^{2-} , H, K, DI and Sr (Table 24).

Strontium fluxes in throughfall were increased relative to bulk precipitation fluxes, however only 2.7-fold for spruce and 1.8-fold for beech (Table 22). The annual throughfall flux of Sr below spruce and beech was in the range 28 - 41 $\mu\text{eq}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$ and 17 - 28 $\mu\text{eq}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$, respectively. The highest throughfall Sr fluxes below beech were detected in June and July. Strontium throughfall fluxes below the beech correlated with fluxes of Ba, F, Ca, Fe, Cl and Be (Table 25).

The Sr fluxes below spruce were quite constant except for an elevated flux usually detected in June. The strontium throughfall fluxes below spruce correlated strongly with those of Be, Al, Cl, Ba and Ca (Table 24).

Barium fluxes in throughfall exhibited enhanced values in comparison with bulk precipitation fluxes, however only 2.4-fold for spruce and 1.5-fold for beech (Table 22). The annual deposition of Ba below the spruce was 31 $\mu\text{eq}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$ in 2000 and 24 $\mu\text{eq}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$ in 2001. The annual deposition of Ba below the beech reached 18 $\mu\text{eq}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$ in 2000 and 17 $\mu\text{eq}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$ in 2001. The highest throughfall Ba flux below beech was detected in the period from May to July. Barium throughfall fluxes below beech correlated with fluxes of Mn, Sr, and Al. The beech throughfall fluxes of Ba were comparable to the bulk precipitation fluxes in the period from November to April, but in the period from May to October the throughfall fluxes were greater.

Barium fluxes below the spruce trees were the highest in period between May and July. The only period when spruce throughfall Ba fluxes were lower than beech was August – October.

4.5 Vegetation

The chemical composition of the spruce and beech roots was variable depending on the sampling site. The most abundant (out of the studied) element in the root mass was usually K (Table 6). The second most abundant element was Ca except for the beech root from LP35 site. The highest concentrations of Ca corresponded to the lowest concentrations of Al in the root mass. The highest concentration of Be was found in beech roots at site LP6.

Table 6 Concentrations of elements in the roots of beech and spruce at LP catchment

species	tissue	loc.	meq.kg ⁻¹								
			Be	Mg	Ca	Sr	Ba	K	Mn	Fe	Al
beech	roots	LP6	0.008	15	25	0.12	0.11	45	1.3	1.3	6
beech	roots	LP35	0.004	11	7	0.08	0.13	68	1.2	4.4	36
spruce	roots	LP35	0.004	10	58	0.23	0.11	41	1.3	1.1	1
spruce	roots	LP7	0.004	13	31	0.12	0.13	28	8.3	0.9	3

The highest concentrations of most elements in the wooden parts of the trees were found in bark, the stem wood contained significantly lower concentrations of elements.

The most abundant element in bark of both spruce and beech was Ca. Bark of the spruce contained lower concentrations of Ca than that of beech (Table 7). The next two most abundant elements in the bark were Mg and K. Similarly as for Ca the spruce bark contained lower concentrations of K. In contrast the spruce bark contained higher concentrations of Mg than the bark of beech. Higher concentrations in the bark of spruce were also detected for Mn, Ba, Al and Be. Higher concentrations of Sr were found in the beech bark similarly as for Fe, Ca and K.

Table 7 Concentrations of elements in the stem wood and bark of beech and spruce at LP catchment

species	tissue	loc.	meq.kg ⁻¹								
			Be	Mg	Ca	Sr	Ba	K	Mn	Fe	Al
beech	bark	LP6	0.015	47.6	649	2.09	1.74	48.5	13.3	2.3	5.8
beech1	stem wood	LP6	0.005	12.8	29	0.11	0.10	20.3	1.3	2.8	0.5
beech2	stem wood	LP6	0.004	10.7	38	0.15	0.11	23.4	1.3	6.1	0.1
beech3	stem wood	LP6	0.005	26.9	37	0.17	0.17	15.2	3.0	1.6	0.3
beech	stem wood	AVG	0.005	16.8	35	0.14	0.12	19.7	1.9	3.5	0.3
spruce	bark	LP7	0.017	64.9	456	1.41	2.64	28.3	50.4	2.0	8.8
spruce1	stem wood	LP7	0.002	8.4	38	0.13	0.26	6.2	6.5	7.1	0.3
spruce2	stem wood	LP7	0.002	7.3	30	0.12	0.19	7.5	6.3	13.3	0.2
spruce3	stem wood	LP7	0.005	8.7	53	0.13	0.19	6.8	7.3	7.0	7.4
spruce4	stem wood	LP7	NA	8.3	26	0.11	NA	9.5	6.1	4.3	0.7
spruce5	stem wood	LP35	NA	6.1	29	0.10	0.23	9.5	1.5	NA	1.0
spruce6	stem wood	LP35	NA	6.3	33	0.12	NA	9.0	1.1	3.1	1.4
spruce	stem wood	AVG	0.003	7.5	35	0.12	0.22	8.1	4.8	7.0	1.8

The most abundant element in the stem wood was Ca. The concentrations of Ca in spruce and beech stem wood are comparable in average 34.7 and 34.6 $\mu\text{eq.kg}^{-1}$. As for K and Mg the

beech stem wood contained significantly higher (over two times) concentrations than spruce. Higher Be and Sr concentrations were also detected in beech stem wood. On contrary spruce stem wood contained increased concentrations of Mn, Fe, Al and Ba.

Average concentrations of Ca in the branches of both beech and spruce were comparable 66 and 61 $\mu\text{eq.kg}^{-1}$, which was double to that in stem wood. The content of K and Mg in branches of beech was over two times of that in spruce branches and for both species these concentrations were elevated when compared to the stem wood. Beech branches contained increased concentrations of Be and Sr in comparison to stem wood, while the spruce branches increased Be but comparable Sr. The branches of spruce were containing increased concentrations of Ba, Mn and Fe.

Table 8 Concentrations of elements in the branches of beech and spruce at LP catchment

species	tissue	diameter	loc.	meq.kg ⁻¹								
				Be	Mg	Ca	Sr	Ba	K	Mn	Fe	Al
beech	branch	3.0cm	LP6	0.007	21	4	0.11	0.13	32	1.9	0.26	NA
beech	branch	2.3cm	LP6	0.008	35	40	0.16	0.39	37	5.8	1.25	NA
beech	branch	1.0cm	LP6	0.036	68	121	0.27	0.18	62	4.8	0.75	NA
beech	branch	3.0cm	LP6	0.013	48	60	0.16	0.14	33	2.1	0.22	NA
beech	branch	1.0cm	LP35	0.016	34	85	0.26	0.22	73	6.1	0.96	NA
beech	branch	1.7cm	LP35	0.008	19	72	0.22	0.45	56	3.3	NA	NA
beech	branch	1.0cm	LP52	0.010	28	82	0.20	0.12	30	8.7	0.44	NA
beech	branch	2.5cm	LP52	0.009	26	65	0.20	0.13	33	6.0	0.36	NA
beech	branch		AVG	0.013	34	66	0.20	0.22	44	4.8	0.61	NA
spruce	branch	2.0cm	LP7	0.006	16	33	0.09	0.46	16	10.1	1.63	NA
spruce	branch	1.0cm	LP35	NA	18	71	0.10	1.09	16	3.3	0.40	NA
spruce	branch	3.3cm	LP35	NA	13	81	0.13	1.12	11	3.3	0.40	NA
spruce	branch		AVG	0.006	15	61	0.11	0.89	14	5.5	0.81	NA

4.5.1 Assimilatory organs

Beech leaves contained higher average concentrations of most of the measured elements than spruce needles (Table 10). The only element that was enriched in spruce needles relative to beech leaves was Al. As for most plant compartments the most abundant element in assimilatory organs was Ca, followed by K, Mg, Mn and Al. The average content of both Ca and Mg in leaves was almost 200% higher than that in needles. The concentrations of Ba and Sr were higher in leaves by 380 and 460%, respectively. Beryllium concentration in leaves was almost double to that in needles. The least relative difference was detected for K, Al and Fe.

The seasonal sampling of assimilatory organs provided information on the accumulation or loss of elements from assimilatory organs according to their age. The assimilatory organs of both tree species exhibited similar trends of chemical composition changes (Table 10). The

concentrations of Mg and K gradually decreased with time during the growing season. Concentrations of all the other elements (Be, Ca, Sr, Ba, Mn, Fe and Al) increased with time. Beryllium accumulated in beech leaves through the growing season (Table 10). The leaves of all three sampled trees from differing sites of the catchment and from different years have shown an increase in Be from May to October each year. The Be concentrations on average increased by more than 80%. The highest Be concentration measured in the beech leaves was $0.086 \text{ meq.kg}^{-1}$. The leaves from location LP6 with soils and soil solution enriched with Be contained elevated Be concentrations when compared to location LP35.

The spruce needles contained on average slightly higher Be concentrations than beech leaves. Similarly to beech, Be concentrations in needles increased with time. The highest concentrations of Be in needles were found at site LP7 perhaps due to high concentrations of Be in soil (Figure 11).

Magnesium was readily lost from the beech leaves (Table 10), as expected from the high Mg concentrations in beech throughfall. Beech leaves lost at least 30% of their Mg from May to October. Leaves sampled at the end of autumn (in December) contained 70% less Mg than in May. Beech leaves from location LP35 contained significantly lower Mg concentrations than leaves from location LP6.

Spruce needles contained lower concentrations of Mg than beech leaves; both were sampled at the same location LP35. The highest Mg concentrations were found in spruce needles from location LP7. Additionally needles from site LP7 were the only assimilatory organs sampled that had increasing Mg content with time.

Concentrations of Ca increased with time in all beech leaves sampled from various trees and various sites. The concentration of Ca increased from May to Oct by 20 - 40% depending on sampling location.

Calcium concentrations in spruce needles were on average lower than in beech leaves (Table 10). Similarly as for Be and Mg, the highest Ca concentrations in spruce needles were found at location LP51. Calcium accumulated in needles of all sampled trees with increasing needle age. The calcium concentration in needles increased by 60 - 80% during 4 years.

Strontium behaved similarly to Ca. However at location LP35 the Sr concentrations in beech leaves remained virtually the same throughout the whole season. In general strontium concentrations were more variable in time than Ca.

The beech leaves contained on average 60% higher concentrations of Sr than spruce needles. A gradual increase of Sr concentration with age was detected in all the sampled spruce needles. The highest concentrations of Sr in needles were again found at location LP51.

Table 9 Concentrations of elements in the assimilatory organs of beech and spruce at LP catchment

sampling date	age class	sample type	loc.	meq.kg ⁻¹								
				Be	Mg	Ca	Sr	Ba	K	Mn	Fe	Al
5.5.1997		beech leaves	LP6	0.014	140	309	0.38	0.21	149	15	3.2	2.0
4.6.1997		beech leaves	LP6	0.023	229	530	1.11	0.48	93	39	5.3	7.1
4.6.1997		beech leaves	LP6	0.015	223	483	1.10	0.55	97	39	4.3	8.5
4.7.1997		beech leaves	LP6	0.036	200	585	1.19	0.34	203	41	5.5	8.5
31.7.1997		beech leaves	LP6	0.044	225	588	1.40	0.45	180	55	5.5	10.6
3.9.1997		beech leaves	LP6	0.059	210	605	1.70	0.60	115	61	4.5	10.6
3.9.1997		beech leaves	LP6	0.058	186	502	1.49	0.64	137	48	6.7	15.7
2.10.1997		beech leaves	LP6	0.054	177	677	1.54	0.69	79	52	6.0	15.3
3.11.1997		beech leaves	LP6	0.042	165	857	1.75	0.75	133	59	6.0	13.6
1.12.1997		beech leaves	LP6	0.077	135	898	2.01	0.82	49	60	10.2	22.3
25.4.2000		beech leaves	LP6	0.006	125	422	0.39	0.70	354	23	3.4	2.6
10.5.2000		beech leaves	LP6	0.005	188	439	0.59	0.71	271	28	3.1	2.9
2.8.2000		beech leaves	LP6	0.026	183	517	0.71	0.88	237	38	3.5	5.0
4.10.2000		beech leaves	LP6	0.045	154	719	0.87	0.99	203	54	6.7	4.1
1.11.2000		beech leaves	LP6	0.049	157	800	0.80	1.15	142	49	5.0	5.9
25.4.2000		beech leaves	LP35	0.003	112	203	0.43	0.39	313	26	2.2	2.6
10.5.2000		beech leaves	LP35	0.004	117	292	0.94	0.57	247	41	2.2	2.6
2.8.2000		beech leaves	LP35	0.008	73	268	0.41	0.50	298	31	3.5	3.0
4.10.2000		beech leaves	LP35	0.017	64	305	0.40	0.53	298	36	4.3	3.6
2.10.2002		beech leaves	LP52	0.006	125	422	0.39	0.70	354	23	3.4	2.6
2.10.2002		beech leaves	LP35	0.005	188	439	0.59	0.71	271	28	3.1	2.9
2.10.2002		beech leaves	LP6-1	0.026	183	517	0.71	0.88	237	38	3.5	5.0
2.10.2002		beech leaves	LP6-2	0.045	154	719	0.87	0.99	203	54	6.7	4.1
1997	5	spruce needles	LP7	0.070	65	275	0.55	0.29	28	63	13.8	40.8
1997	5	spruce needles	LP7	0.067	67	289	0.56	0.30	29	65	13.9	43.0
25.4.2000	0	spruce needles	LP35	NA	83	36	0.02	0.02	354	6	1.1	2.0
10.5.2000	0	spruce needles	LP35	NA	57	62	0.04	0.06	289	8	0.9	2.1
2.8.2000	0	spruce needles	LP35	NA	62	171	0.00	0.00	232	14	0.8	2.2
25.4.2000	1	spruce needles	LP35	NA	42	140	0.09	0.11	98	14	1.0	2.8
25.4.2000	2	spruce needles	LP35	NA	39	182	0.14	0.12	80	16	1.2	3.8
25.4.2000	3	spruce needles	LP35	NA	37	225	0.12	0.15	102	20	1.5	3.6
25.4.2000	4	spruce needles	LP35	NA	26	266	0.14	0.18	108	28	1.8	6.3
2.10.2002	0	spruce needles	LP7	0.008	106	234	0.56	0.54	189	61	0.9	6.0
2.10.2002	1	spruce needles	LP7	0.065	116	448	0.94	0.82	128	99	0.9	7.6
2.10.2002	2	spruce needles	LP7	0.073	132	601	1.12	0.97	92	150	1.3	10.2
2.10.2002	0	spruce needles	LP35	0.016	76	182	0.28	0.20	246	15	1.6	8.3
2.10.2002	1	spruce needles	LP35	0.073	62	266	0.38	0.25	187	18	2.1	12.5
2.10.2002	2	spruce needles	LP35	0.025	46	282	0.38	0.25	165	16	2.3	14.7

Barium concentrations increased with time in both leaves and needles (Table 10). In some samples of leaves and needles Ba concentrations were higher than Sr. Barium concentrations exhibited significant changes in concentration from year to year. The highest Ba

concentrations in needles were found at location LP51 (identical to LP7). The increase of Ba in the needles during 4 years growth was in the range 50-80%.

4.6 Soil

The most frequent soil type at LP catchment was Dystric Cambisol, while around the LP stream and in the north (the lowest) part of the catchment was Gleyic Cambisol. Lithosols covered the highest locations in the catchment. All the soils are acid due to their development from the acidic parent granites. The lowest $\text{pH}_{(\text{H}_2\text{O})}$ values of the soils were found in the top 15 cm of the soil profile, ranging from 3.6 to 4.5. The $\text{pH}_{(\text{H}_2\text{O})}$ lower in the profiles was slightly higher, from 4.0 to 5.2. Soil $\text{pH}_{(\text{H}_2\text{O})}$ was statistically related to total exchangeable acidity (TEA), (Annexes, Table 30).

The surface horizons (O and A) contained the highest content of organic material. The content of organic carbon $\text{C}_{(\text{ox})}$ ranged between 4 and 36% and total nitrogen $\text{N}_{(\text{t})}$ content ranged between 0.2 to 1.6% in the O and A layers. The lower horizons of the soil profiles were reduced in $\text{C}_{(\text{ox})}$ and $\text{N}_{(\text{t})}$, which ranged between 0.02 – 1.5%, 0.01 – 0.08% respectively.

The cation exchange capacity (CEC) of soils in the catchment averaged 160 meq.kg^{-1} . The highest CEC values were found in the O and A horizons (ca. top 10 cm), averaging 294 meq.kg^{-1} , while the CEC progressively decreased to 146 meq.kg^{-1} in the upper B horizons (between 10 - 20 cm) and in lower B or C horizons to 73 meq.kg^{-1} . Elevated CEC values were also determined in some layers enriched in the content of fine particles (e.g. profile LP33 horizons Gr1 and Gr2).

The base saturation (BS) of soils developed on granites is usually low. The highest BS of soils at LP catchment were present in the O and A horizons rich in organic matter with mean BS of 36 % (range 10 – 73%). However, the BS of lower soil layers was significantly lower at 8 % (range 4-15 %). The base saturation of the Gleyic Cambisols was elevated, however proportionally they cover a small area of the catchment, mostly limited to the north (the lowest) part.

The most abundant elements (of those studied) in LP soils were in descending order Al, K, Na and Fe (Table 10). The highest total concentration of Mn (especially in the upper horizons) was found at profile LP36. Elevated total concentrations of Al were found in the riparian LP33 profile.

The acid leachable fraction of Al and Fe is also considerable but the acid leachable fraction of Na and K is minor. The highest acid leachable concentrations of most elements were found at

profile LP51. The soil type at the LP51 profile is Gleyic Cambisol with increased CEC, perhaps as a result of elevated content of fine particles.

The total Be concentrations in 3 soil profiles (LP33, LP35 and LP36) ranged between 0.1 and 2.0 meq.kg⁻¹. Most of the total Be originates in unweathered or partly weathered minerals. The total Be concentrations slightly increased with depth (Table 10) due to increasing occurrence of unweathered mineral particles.

On average 22% of the total Be concentration is acid leachable, and the acid leachable fraction of Be increases significantly with depth. The acid leachable concentrations ranged between 0.01 and 1.41 meq.kg⁻¹ in 8 soil profiles. The concentrations of acid leachable Be correlated positively with those of Mg and Na and also with soil depth (Annexes, Table 30).

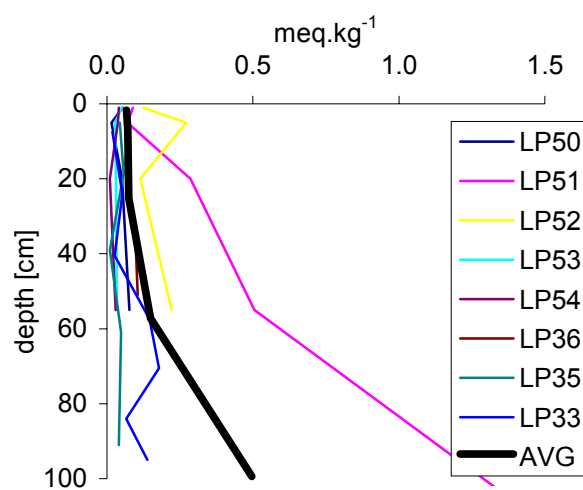


Figure 11 Acid leachable Be concentrations throughout the soil profiles at LP catchment; the average is based on 8 profiles

The total Mg concentrations in 3 soil profiles ranged between 47 and 400 meq.kg⁻¹. The highest concentrations of total Mg were found in LP33 profile (Gleyic Cambisol). Generally the total concentrations of Mg were greatest in the upper horizons of profiles but at riparian profile LP33 some of the bottom layers contained elevated total Mg concentrations (Table 10). The highest total Mg concentrations were found in the upper horizons of LP35 profile with the highest content of organic matter (Table 10). In contrast the bottom layers of LP35 profile contained the lowest total concentrations of Mg.

The acid leachable fraction of Mg in the O and A horizons was slightly elevated (10 to 23 meq.kg⁻¹) in comparison to 7 meq.kg⁻¹ at 25 cm depth. Below 25 cm the acid leachable fraction of Mg increased up to 39 meq.kg⁻¹ in the bottom of the profile. The acid leachable fraction of Mg formed on average 9% of the total Mg concentration. The acid leachable concentrations of Mg in 8 soil profiles ranged between 6 and 1166 meq.kg⁻¹. The

concentrations of acid leachable Mg correlated with Be, Ba, Ca, Fe and $\text{pH}_{(\text{H}_2\text{O})}$ (Annexes, Table 30).

Total Ca concentrations in 3 soil profiles ranged from 14 to 165 meq.kg^{-1} . The concentrations of total Ca were comparable for all 3 profiles. Total Ca concentrations were elevated in the top layers of the soil profile and similarly to Mg the highest Ca concentrations were found in the LP35 O and A horizons (Table 10). The bottom layers of LP35 profile had the lowest observed total Ca concentrations.

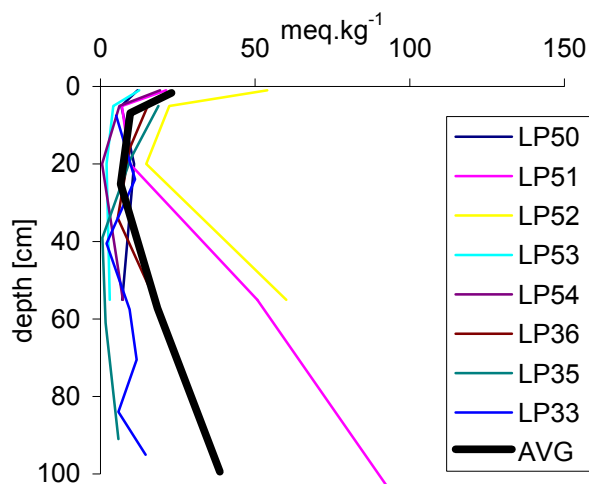


Figure 12 Acid Leachable Mg concentrations throughout the soil profiles at LP catchment; the average is based on 8 profiles

The acid leachable fraction of Ca was the highest in the O horizon of all the profiles, on average 119 meq.kg^{-1} . Deeper in the profile the acid leachable fraction of Ca decreased to 6 meq.kg^{-1} at 25 cm depth. Below 25 cm the acid leachable fraction of Ca slightly increased to 36 meq.kg^{-1} at the bottom of the profile. The acid leachable fraction of Ca formed on average 13% of the total Ca concentration. The acid leachable concentrations of Ca in 8 soil profiles ranged between 0.5 and 218 meq.kg^{-1} . The concentrations of acid leachable Ca correlated with those of Sr, K, C(ox), N(t), Mn, Ba, Mg and Na (Annexes, Table 30).

The total Sr concentrations in 3 soil profiles ranged from 1.2 to 6.3 meq.kg^{-1} . The concentrations of total Sr were comparable for all 3 profiles. The total concentrations of Sr exhibited little variation throughout the profiles (Table 10). Increased total Sr concentrations were found at LP33 profile. Contrary to the total concentrations of Ca, those of Sr were the lowest in layers with the highest organic content.

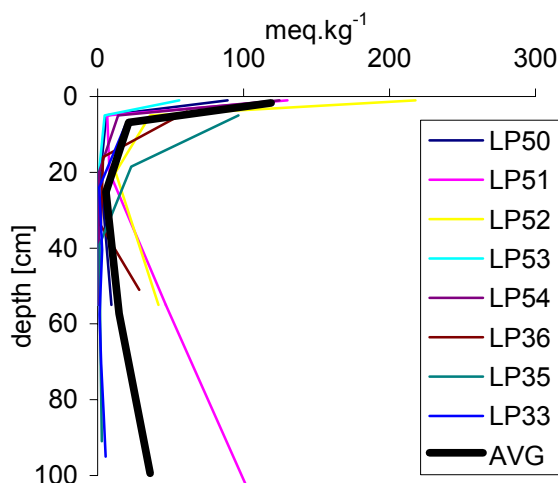


Figure 13 Leachable Ca concentrations throughout the soil profiles at LP catchment; the average is based on 8 profiles

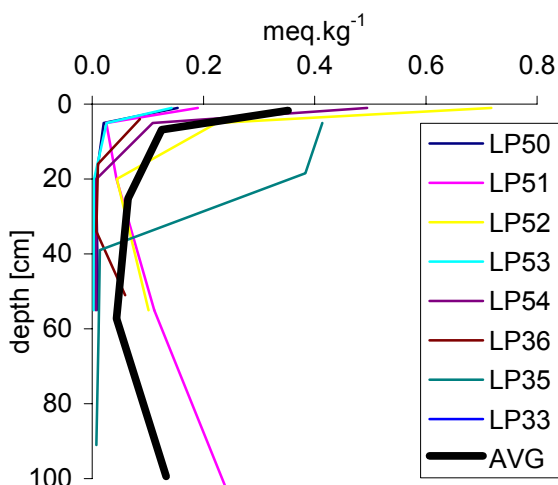


Figure 14 Acid Leachable Sr concentrations throughout the soil profiles at LP catchment; the average is based on 8 profiles

The acid leachable fraction of Sr was the highest in the O horizon of all profiles, on average 0.35 meq.kg^{-1} . Deeper in the profiles the acid leachable fraction of Sr decreased sharply to 0.04 meq.kg^{-1} at 50 cm depth. Below 50 cm the acid leachable fraction of Sr slightly increased to 0.13 meq.kg^{-1} in the bottom of the profile, which was comparable to the Sr leachable fraction in the A horizon. The acid leachable fraction of Sr formed on average 8% of the total Sr concentration. The acid leachable concentrations of Sr in 8 soil profiles ranged between 0.03 and 0.72 meq.kg^{-1} . Statistically the acid leachable concentrations of Sr were correlated with Ca, K, $C_{(ox)}$, $N_{(t)}$, $pH_{(KCl)}$ and CEC (Annexes, Table 30).

The total Ba concentrations in 3 soil profiles ranged from 0.8 to 25.6 meq.kg^{-1} . In general the total concentrations of Ba slightly increased with depth (Table 10). Similarly as in case of Sr,

barium concentrations in the upper horizons rich in organic matter were lower than those in bottom horizons.

The acid leachable fraction of Ba was elevated in the O horizon of all profiles with an average of 0.73 meq.kg^{-1} . Deeper in the profile the acid leachable fraction of Ba sharply decreased to 0.19 meq.kg^{-1} at 25 cm depth. Below 25 cm the acid leachable fraction of Sr increased back up to 0.94 meq.kg^{-1} at the bottom of the profile, which exceeded the Ba leachable fraction in the O horizon. The acid leachable fraction of Ba formed on average 10% of the total Ba concentration. The acid leachable concentrations of Ba in 8 soil profiles ranged between 0.03 and 1.4 meq.kg^{-1} . The concentrations of acid leachable Ba correlated with those of Be, Na, Mg, $C_{(ox)}$, $N_{(t)}$, $pH_{(KCl)}$ and CEC (Annexes, Table 30).

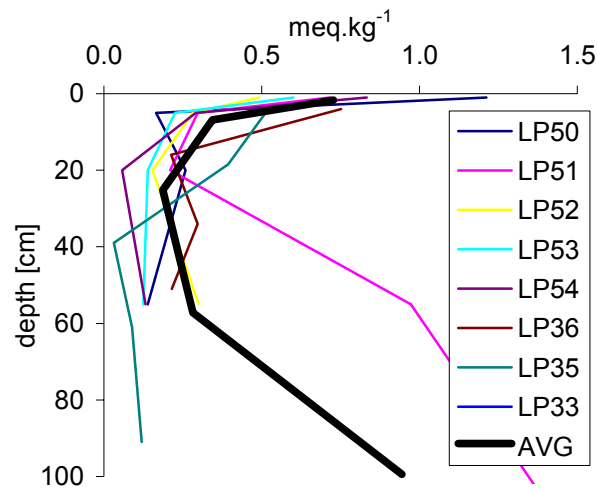


Figure 15 Acid leachable Ba concentrations throughout the soil profiles at LP catchment; the average is based on 8 profiles

Table 10 The properties and element concentrations of LP33, LP35 and LP36 profiles, elements and CEC in meq.kg⁻¹, N(t) total nitrogen, C(ox) oxidable carbon

LP33	depth cm	pH (H ₂ O)	pH (KCl)	N(t) %	C(ox) %	Humus %	CEC	Be		Mg		Ca		Sr		Ba		Na		K		Mn		Fe		Al	
								total	lea.	total	lea.	total	lea.	total	lea.	total	lea.	total	lea.	total	lea.	total	lea.	total	lea.	total	lea.
A	0-15	3.80	3.00	0.32	4.75	8.2	240	0.86	0.03	113	5.1	106	19.2	4.2	0.3	8.0	0.1	447	1.0	564	2.9	4.2	0.7	266	27	6043	143
Bw	15-33	4.04	3.46	0.08	0.45	0.8	137	1.19	0.13	248	11.2	96	1.1	3.6	0.0	6.5	0.3	459	0.7	573	1.8	6.5	0.7	498	31	7892	252
Go	33-48	4.14	3.79	0.03	0.24	0.4	51	1.17	0.12	103	2.0	110	3.0	4.3	0.0	6.2	0.2	668	1.1	789	1.4	2.7	0.3	211	18	6680	104
Gr1	48-67	4.00	3.41	0.04	0.28	0.5	152	1.42	0.24	400	9.4	92	1.4	3.1	0.1	5.0	0.6	385	0.6	557	3.0	6.7	0.2	678	26	10186	259
Gr2	67-74	4.05	3.38	0.04	0.12	0.2	146	1.26	0.32	339	11.7	93	2.4	3.1	0.1	12.1	0.5	433	0.6	586	2.8	4.8	0.2	578	26	8848	237
Gr3	84-87	4.26	3.54	0.02	0.04	0.1	38	1.19	0.13	112	5.8	101	4.2	3.4	0.1	10.5	0.2	658	0.4	751	1.1	3.3	0.1	181	12	5933	90
Gr4	90-100	4.33	3.43	0.02	0.08	0.1	57	2.03	0.27	315	14.6	165	5.5	6.3	0.3	25.6	0.4	853	0.8	976	1.9	4.7	0.1	534	17	11504	126
LP35	depth cm	pH (H ₂ O)	pH (KCl)	N(t) %	C(ox) %	Humus %	CEC	Be total	Be lea.	Mg total	Mg lea.	Ca total	Ca lea.	Sr total	Sr lea.	Ba total	Ba lea.	Na total	Na lea.	K total	K lea.	Mn total	Mn lea.	Fe total	Fe lea.	Al total	Al lea.
Of	0-10	3.65	2.70	1.55	36.61	63.1	926	0.19	0.03	1348	13.3	908	16.2	0.9	0.4	0.7	0.6	151	1.8	175	8.3	2.0	1.0	116	13	993	119
A	10-27	3.00	2.20	0.83	19.03	32.8	812	0.64	0.04	747	7.6	540	4.9	1.3	0.3	1.0	0.5	79	1.9	82	2.5	0.9	0.2	116	8	1314	167
AB	27-51	3.70	2.95	0.05	0.89	1.5	86	1.29	0.06	48	0.7	132	2.6	3.3	0.0	14.2	0.0	559	1.7	292	1.3	1.1	<0.1	124	3	2921	99
Bv	51-71	4.05	3.70	0.04	0.89	1.5	59	1.30	0.04	42	1.6	71	2.0	2.4	0.0	5.6	0.1	40	1.5	63	1.0	1.7	<0.1	286	33	2954	260
Bc	71-111	3.95	3.45	0.02	0.89	1.5	115	1.24	0.03	46	5.3	53	2.2	2.4	0.0	4.8	0.1	158	1.4	116	1.1	2.6	0.2	203	15	2044	111
LP36	depth cm	pH (H ₂ O)	pH (KCl)	N(t) %	C(ox) %	Humus %	CEC	Be total	Be lea.	Mg total	Mg lea.	Ca total	Ca lea.	Sr total	Sr lea.	Ba total	Ba lea.	Na total	Na lea.	K total	K lea.	Mn total	Mn lea.	Fe total	Fe lea.	Al total	Al lea.
A	0-8	3.94	3.22	0.57	10.60	18.3	455	1.22	0.07	690	15.8	516	61.2	1.4	0.1	4.9	0.8	312	1.0	343	10.2	21.3	17.0	307	25	2283	178
Bv1	8-24	4.33	3.93	0.21	1.14	2.0	112	1.63	0.06	207	9.4	213	3.8	2.7	0.0	8.3	0.2	629	1.0	586	1.2	19.9	5.2	328	31	4374	232
Bv2	24-44	4.31	4.12	0.04	0.73	1.3	80	2.16	0.10	229	5.6	247	2.1	1.8	0.0	4.5	0.3	748	0.9	604	1.0	8.6	1.6	217	28	2542	230
BC	44-58	4.83	3.80	0.01	0.16	0.3	46	2.62	0.11	138	15.3	153	28.5	2.9	0.1	4.6	0.2	1041	1.7	510	2.2	5.1	0.9	188	12	2999	85

4.7 Soil solution

Soil solution at both locations of LP catchment (Figure 6) was sampled in beech stands, and thus was derived from beech throughfall (THB); no spruce derived soil solution were sampled. The main difference between two soil solution sampling locations (LP33 and LP35) was the soil organic matter content. The O horizon with elevated organic matter content was absent at LP6 and the A horizon of profile LP35 contained 4 times more humus than the A horizon at the LP6 profile (Table 10).

Table 11 Average values of monitored parameters in soil solutions and THB of the LP catchment in 2000

Parameter	Units	LP6	LP6 soil solution			LP35 soil solution	
		THB	5 cm	15 cm	45 cm	5 cm	15 cm
DOC	mg.L ⁻¹	NA	15	13	12	67	34
Conduc.	μS.cm ⁻¹	60	30	40	62	68	86
pH		4.75	4.55	4.63	4.40	4.05	4.44
H	μeq.L ⁻¹	18	39	31	55	102	72
Be	μeq.L ⁻¹	0.004	0.08	0.12	0.61	0.04	0.08
Mg	μeq.L ⁻¹	47	39	68	145	34	79
Ca	μeq.L ⁻¹	71	93	157	173	79	157
Sr	μeq.L ⁻¹	0.06	0.18	0.32	0.66	0.24	0.45
Ba	μeq.L ⁻¹	0.04	0.38	0.50	1.22	0.36	0.39
Na	μeq.L ⁻¹	10	21	65	80	35	56
K	μeq.L ⁻¹	102	71	45	18	211	112
Mn	μeq.L ⁻¹	9.0	3.4	2.8	4.7	2.2	2.0
Fe	μeq.L ⁻¹	1	32	20	10	34	27
Al	μeq.L ⁻¹	6	140	125	141	146	183
F	μeq.L ⁻¹	2	4	5	11	6	10
Cl	μeq.L ⁻¹	28	19	44	26	49	54
NO ₃ ⁻	μeq.L ⁻¹	56	11	63	6	79	108
SO ₄ ²⁻	μeq.L ⁻¹	95	85	144	356	161	203

Soil solution pH was lower than throughfall pH (Table 11), primarily due to the presence of organic acids in soil solution. The organic matter content in the soil solution is termed dissolved organic carbon (DOC). The average DOC concentration in soil solution decreased with depth (Table 11). This decrease was accompanied by an increase in pH. However, at 45 cm depth at LP6, the pH of soil solution decreased back to 4.40 from 4.63.

Concentrations of Be, Na, Mg, Ca, Sr, F, Ba, Cl and SO₄²⁻ in soil solution increased with depth, contrary to concentrations of K and Fe, which decreased with depth at both profiles (Table 11). Considerably higher concentrations of Cl in soil solution of the LP35 profile

suggested enhanced evapotranspiration, in contrast to Cl at LP6 where the soil solutions were slightly diluted relative to throughfall.

The most significant enrichment in shallow soil solution when compared to throughfall was found for Fe, Al, Be, Ba, H, Sr, Na, F and K (Table 11). Soil solution contained elevated annual average concentrations of K, Fe, Al and Mn in comparison to surface waters (Table 11).

Beryllium entered the soil solution readily, as indicated by the major increase in concentration from throughfall to soil solution. The concentration of Be in soil solution increased with depth. Beryllium concentrations correlated positively with Mg, SO_4^{2-} , Sr, F, Mn, Na, F, Ba and Ca. Beryllium concentrations in soil solution at location LP6 were higher than those at LP35. The concentrations of Be in soil solution were generally lower than those in streamwater.

The soil solution from the upper 5 cm of both horizons had lower concentrations of Mg than throughfall at both profiles. Similar behavior was observed for Mn at both profiles and for K at LP6 only. However in soil solution from 15 cm the concentrations of Mg were higher than those in throughfall. Mg concentrations in soil solution increased gradually with depth. Mg concentrations correlated positively with SO_4^{2-} , Sr, Na, F, Ca, Mn and Be. The Mg concentrations in the soil solution were significantly lower than Mg concentrations in streamwater.

Calcium concentration in soil solution from the upper 5 cm of both profiles was comparable to or slightly greater than throughfall concentrations. The Ca concentration in soil solution increased significantly from 5 to 15 cm. Ca concentrations correlated positively with Sr, Na, Mg, SO_4^{2-} , F, Be and Mn.

Concentrations of Sr increased gradually with depth similarly to Mg. Strontium concentrations were moderately higher than those in throughfall. The concentrations of Sr in soil solution from 5 and 15 cm at location LP6 were lower than those found in soil solution at location LP35. Strontium concentrations correlated positively with SO_4^{2-} , F, Mg, Ca, Na, Be and Cl.

Barium belonged together with Al, Fe and Be to the elements that were most enriched in shallow soil solution. The concentration of Ba in the soil solution was usually higher than the concentration of Sr, in contrast to the pattern in throughfall and surface water. The concentration of Ba increased with depth at both profiles. The barium and Be concentrations were positively correlated. Barium was the only element of the II.A group with a higher annual mean concentration in soil solution than in surface water. In general, the

concentrations of Ba in the soil solution were significantly lower than equilibrium concentrations predicted from the K_{sp} of $BaSO_4$.

4.8 Stream water

The hydrological year at the LP catchment is typical for northern temperate climates with the highest discharge in the spring. The highest discharge measured over the monitored period 1993–2001 was $23 \text{ L}\cdot\text{s}^{-1}$ ($0.108 \text{ mm}\cdot\text{h}^{-1}$) and it occurred during the 2000 spring snowmelt. The high-flow conditions associated with snowmelt in a typical water-year could occur any time during February, March, April or May depending on the time of initiation of snowmelt. High flow may also occur during summer as a result of summer rainstorms but the summer and autumn typically had low mean discharges of $\sim 1 \text{ L}\cdot\text{s}^{-1}$ ($0.005 \text{ mm}\cdot\text{h}^{-1}$).

The months with the greatest average precipitation in the monitored period were June (96 mm), July (91 mm) and August (65 mm). The discharges during the wettest months usually stay low because this coincides with the time of maximum evapotranspiration demand. The fine-grained soils and sediments slow the passage of water through the catchment. There may be up to a one-month lag between a period of increased precipitation and a corresponding response in stream discharge (Figure 2).

Table 12 Discharge weighted average annual values of selected parameters of LP surface water

year	discharge mm	conduc. $\text{mS}\cdot\text{cm}^{-1}$	pH	H $\mu\text{eq}\cdot\text{L}^{-1}$	Be $\mu\text{eq}\cdot\text{L}^{-1}$	Mg $\mu\text{eq}\cdot\text{L}^{-1}$	Ca $\mu\text{eq}\cdot\text{L}^{-1}$	Sr $\mu\text{eq}\cdot\text{L}^{-1}$	Ba $\mu\text{eq}\cdot\text{L}^{-1}$
1994	113	223	4.83	15	2.3	649	997		
1995	122	222	4.86	14	2.1	716	1172		
1996	151	235	4.80	16	2.2	674	1110	4.7	
1997	98	201	5.05	9	1.3	603	832	3.3	
1998	35	193	5.22	6	0.9	554	808	3.0	
1999	73	207	5.04	9	1.0	574	784	3.1	
2000	67	194	4.91	12	1.1	539	757	2.8	0.4
2001	63	195	4.92	12	1.1	557	764	2.7	0.5

year	Na $\mu\text{eq}\cdot\text{L}^{-1}$	K $\mu\text{eq}\cdot\text{L}^{-1}$	Mn $\mu\text{eq}\cdot\text{L}^{-1}$	Fe $\mu\text{eq}\cdot\text{L}^{-1}$	Al $\mu\text{eq}\cdot\text{L}^{-1}$	F $\mu\text{eq}\cdot\text{L}^{-1}$	Cl $\mu\text{eq}\cdot\text{L}^{-1}$	NO_3^- $\mu\text{eq}\cdot\text{L}^{-1}$	SO_4^{2-} $\mu\text{eq}\cdot\text{L}^{-1}$
1994	338	41	3.2	3	117	41	119	94	1771
1995	370	36	2.6	3	115	43	126	76	1890
1996	352	38	1.5	4	124	44	106	43	1900
1997	350	28	1.4	5	102	40	125	41	1641
1998	391	31	1.5	12	65	36	132	44	1439
1999	349	28	2.3	5	101	42	111	66	1521
2000	343	25	4.8	4	91	37	118	140	1336
2001	362	21	1.9	8	97	37	114	56	1431

The chemistry of the LP catchment surface water reflects the high evapotranspiration rate ($\sim 80\%$ annually). The major cations in LP surface water were Ca, Mg, Na, Al and K (Table 12). The most abundant cation in the solution was Ca^{2+} and it usually formed over 40% of the

dissolved sum of cations. The cations Mg, Na and Al followed with 30%, 20% and ~10% respectively. Sulfate made up more than 90% of the strong acid anions (SAA) concentration and the rest was made up by Cl^- , F^- and NO_3^- . The nearly complete afforestation of the catchment caused regular changes of the nitrate (NO_3^-) concentration during the year. The highest concentrations of NO_3^- occurred in the winter and the lowest in the summer as a result of the vegetation uptake. The DOC concentrations in surface water were typically $\sim 8 \text{ mg.L}^{-1}$ (ranging from 5.2 to 13.8 mg.L^{-1}).

The average annual concentration of Be in surface water of the Lesni potok catchment decreased from $2.30 \mu\text{eq.L}^{-1}$ in 1994 to $1.10 \mu\text{eq.L}^{-1}$ in 2000 (Figure 16, Table 12). The mean concentration of $1.20 \mu\text{eq.L}^{-1}$ during the 8 years was high compared to the regional surveys of Czech freshwaters (Veselý & Majer 1998).

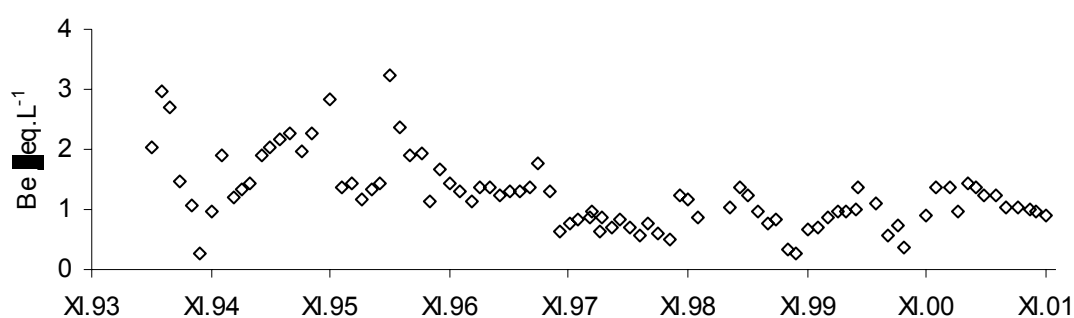


Figure 16 Changes in Be concentration in surface water during period 1993 - 2001

Significant correlations of element concentrations in surface water were found between Be and Al, Sr, H, SO_4^{2-} , F^- , Ca and Mg (Annexes, Table 27).

The most important factors determining Be speciation were Al, F^- , Be concentrations and pH (Navrátil 2000). The main form of Be in the LP surface water was the BeF^+ complex, which formed always $> 50\%$. Under low pH conditions the free Be^{2+} ion was important. But under low discharge and high pH conditions, BeOH^- and BeF_2 dominated over Be^{2+} .

The highest concentrations of Be in the LP surface waters were detected in the early years of monitoring (1994, 1995 and 1996), in periods with increased discharge and decreased pH value. The lowest Be concentrations were associated with dry periods in the LP catchment (i.e. July, August, September), which were accompanied by increased pH. During periods with higher pH the role of uncharged (adsorbed or particulate) Be became more important.

Magnesium is the third most abundant cation in the LP surface water after Ca and Na. Usually it formed approximately 30% of the cation sum. The volume weighted average annual

concentration of Mg in surface water of the Lesni potok catchment decreased from 716 $\mu\text{eq.L}^{-1}$ in 1995 to 539 $\mu\text{eq.L}^{-1}$ in 2000 (Figure 17, Table 10).

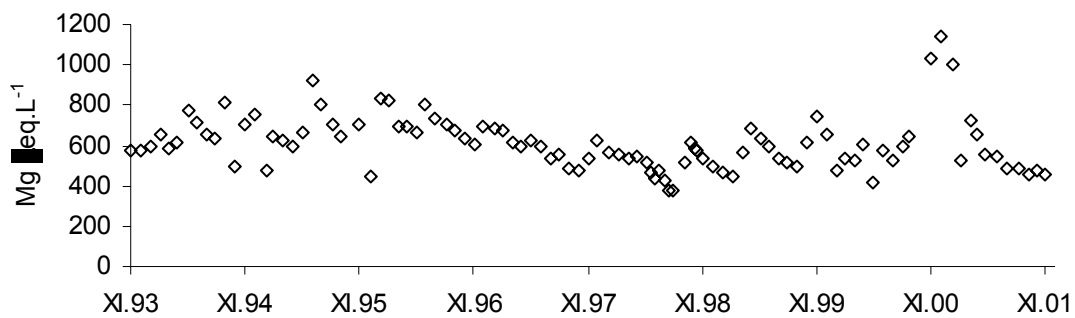


Figure 17 Changes in Mg concentration in surface water during period 1993 - 2001

The mean Mg concentration of 609 $\mu\text{eq.L}^{-1}$ was lower than the average value (765 $\mu\text{eq.L}^{-1}$) for freshwaters on plutonic rocks of the Czech Republic (Veselý & Majer 1998). Magnesium is present as a divalent Mg^{2+} ion almost exclusively. It may also form aqueous complexes with SO_4^{2-} but these species usually make up less than 5% of total Mg concentration. Magnesium concentrations correlated positively with those of Ca, SO_4^{2-} , Sr, F, Ba, Na and Be (Annexes, Table 27). The correlation of the Mg concentrations with sulfate was the highest such correlation out of II.A group elements (Annexes, Table 27).

The highest Mg concentrations occurred together with the highest concentrations of Ca (Figure 25). These periods were typically accompanied by decreased pH and the highest SO_4^{2-} concentrations. The lowest Mg concentrations usually occurred together with low Ca concentrations but not with the lowest discharges.

Calcium is the most abundant cation in the LP streamwater. The volume weighted average annual concentration of Ca in surface water of the Lesni potok catchment changed from 1172 $\mu\text{eq.L}^{-1}$ in year 1995 to 757 $\mu\text{eq.L}^{-1}$ in 2000 (Figure 18, Table 10).

The mean Ca concentration of 933 $\mu\text{eq.L}^{-1}$ at LP catchment was slightly lower compared to the average value (1350 $\mu\text{eq.L}^{-1}$) for freshwaters on plutonic rocks of the Czech Republic (Veselý & Majer 1998). Calcium was present as a divalent Ca^{2+} ion almost exclusively, similarly to Ca, Mg and Sr. According to the speciation calculations it may also form aqueous complexes with SO_4^{2-} but these species usually made up less than 5% of the Ca. Calcium concentration correlated positively with Mg, SO_4^{2-} , Sr, Ba, Na and F (Annexes, Table 27).

The highest Ca concentrations occurred during the same situations as the highest concentrations of Mg (Figure 25). Some of the highest Ca concentrations occurred during the low discharge periods as a result of the groundwater contribution, and also during periods

with high SO_4^{2-} concentration. The lowest Ca concentrations usually occurred together with the low Mg concentrations but not with the lowest discharges.

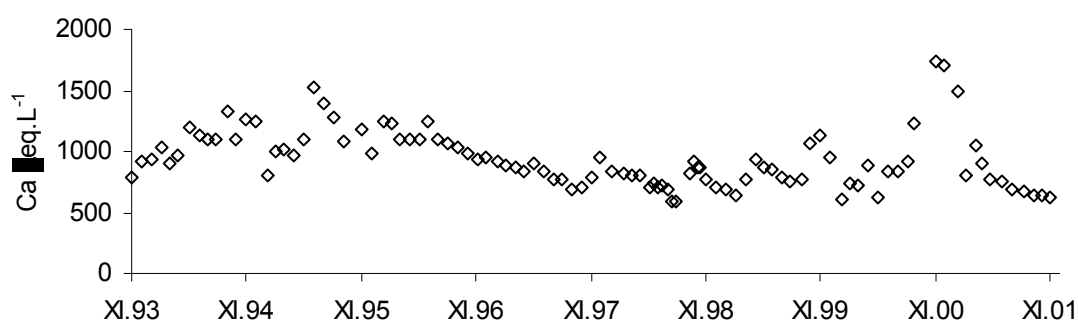


Figure 18 Changes in Ca concentration in surface water during period 1993 - 2001

Strontium in the surface water of the LP catchment has been analyzed since year 1996. Strontium is a trace element and its volume weighted average annual concentration in surface water of the Lesni potok catchment decreased from $4.52 \mu\text{eq.L}^{-1}$ in 1996 to $2.10 \mu\text{eq.L}^{-1}$ in 2000 (Figure 19, Table 10). The mean concentration of strontium $3.40 \mu\text{eq.L}^{-1}$ was in agreement with the average value ($3.42 \mu\text{eq.L}^{-1}$) for freshwaters on plutonic rocks of the Czech Republic (Veselý & Majer 1998).

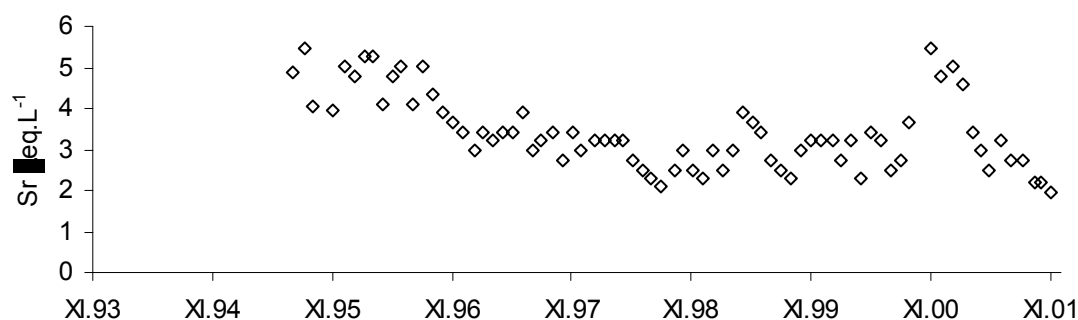


Figure 19 Changes in Sr concentration in surface water during period 1994 - 2001

Strontium was present as a divalent Sr^{2+} ion almost exclusively. Strontium concentrations correlated positively with those of Ca, Mg, SO_4^{2-} , Be and Ba (Annexes, Table 27). The high correlation with Ca was a result of their very similar hydrated radius. The highest concentrations of Sr usually occurred together with elevated Ca concentration and thus during periods of elevated SO_4^{2-} concentrations.

Barium in the surface water of the LP catchment has been analyzed since the year 2000. It is a trace element and the volume weighted average annual concentration of Ba in surface water of the LP catchment was $0.52 \mu\text{eq.L}^{-1}$ (Figure 20, Table 10).

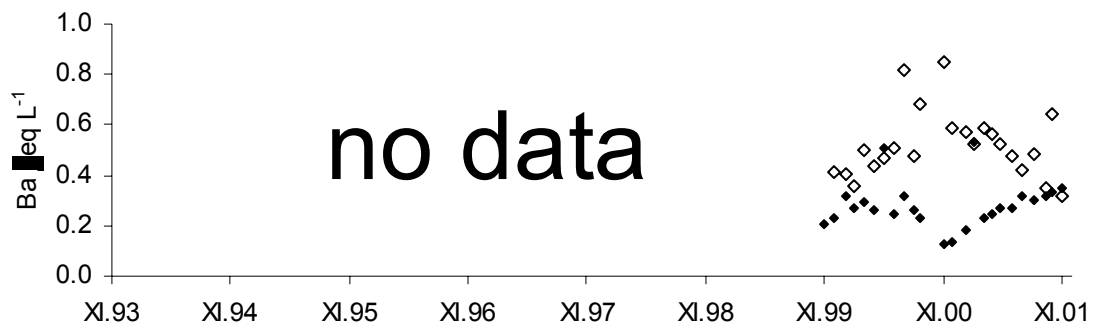


Figure 20 Variations in Ba concentration in surface water during period 2000 – 2001; filled diamonds represent the theoretical Ba concentrations with respect to K_{sp} $BaSO_4$

Barium in the streamwater was primarily present as the divalent Ba^{2+} ion. Barium was the only element of the II.A group with a negative correlation to the concentration of H^+ ions. Barium concentrations further correlated with those of Mn, Fe, Ca, Na, Mg and Sr (Annexes, Table 27).

The highest concentrations of Ba usually occurred during periods with elevated SO_4^{2-} concentration or during low flow periods when the SO_4^{2-} concentrations were elevated due to evaporative concentration of streamwater solution.

The concentrations of Ba were usually higher than predicted equilibrium concentrations calculated from the K_{sp} of $BaSO_4$ (Figure 20). However during periods with decreased SO_4^{2-} concentration the measured and theoretical values were very similar.

4.8.1 Streambed material

A large proportion (> 50%) of the sampled stream sediment mass was organic matter. From the inorganic part of the stream sediment were macroscopically (binocular) identified quartz and feldspars. The qualitative X-ray analysis of the finest mineral fraction revealed also the presence of quartz and feldspars but no other minerals.

The most abundant element in the streambed material (out of measured elements) was Al, followed by Na, K and Fe. The total concentrations of Mg and Ca were also considerable but concentrations of other elements were low (Table 13).

The stream substrate contained high concentrations of labile (acid leachable) Al (262 meq.kg^{-1}) and Fe (284 meq.kg^{-1}). The increased amount of labile Fe was due to the presence of Fe-precipitate in the LP streambed, which forms during low discharge periods (Figure 21).

High concentrations of labile Al were probably due to the presence of amorphous precipitate (i.e. gibbsite) or Al bound in organic matter. The leachable concentrations of base cations decrease in the order $Ca > Mg > K > Na$ (Table 13). The leachable fractions of Na and K were

minor (Table 13). The concentration of labile Beryllium was 1.3 meq.kg^{-1} , which exceeded the concentrations of labile Sr (0.9 meq.kg^{-1}) and Ba (0.8 meq.kg^{-1}) in the stream sediment. The stream sediment contained 12 meq.kg^{-1} of labile Mn.

Table 13 Chemical compositions of the streambed material and soil (calculated as average weighted by layer thickness)

element	unit	STREAMBED MAT.		SOIL	
		total	acid leachable	total	acid leachable
Be	meq.m^{-2}	2.8	1.4	0.7	0.1
Mg	meq.m^{-2}	160	44	233	8.1
Ca	meq.m^{-2}	267	151	179	8.4
Sr	meq.m^{-2}	2.8	0.5	2.9	0.1
Ba	meq.m^{-2}	6.4	0.6	5.4	0.3
Na	meq.m^{-2}	530	2	622	1.2
K	meq.m^{-2}	494	3	577	2.0
Mn	meq.m^{-2}	15	12	4.9	0.9
Fe	meq.m^{-2}	470	262	244	18
Al	meq.m^{-2}	3565	284	4343	151



Figure 21 Iron precipitate at the LP streambed

Most of the elemental total concentrations in the streambed material were comparable to their mean total concentration in soils. The stream sediments had higher total concentrations of Be (4x), Mn(3x), Fe(2x), Ca(1.5x) and Ba(1.2x). The leachable concentrations of all measured elements were higher in the streambed material than in soils. The most significant differentials in the labile fraction were for Ca (18x), Fe(15x), Mn(14x) and Be(13x). The smallest differences between soil and sediment acid leachable concentrations were found for Al, Na and K. Their leachable concentrations in sediment were approximately double to those in soils.

4.8.2 Experimental acidification

Lesni potok stream was artificially acidified with HCl during a 4 - hour period to assess the role of stream substrate in acid neutralization and to evaluate the difference in behavior among II.A group elements during acidification. The pH of the surface water above the acid addition was 4.80 but after 3.5 hours it decreased to nearly 3.20 at points A and B, 3.48 at point C and 3.75 at point D (Figure 22). It required 3 hours to acidify the first 20 m of the stream to pH value ~ 3.2 . At 4.25 hours (15 minutes after the end of the addition) the pH at point A recovered to 4.62, and after 30 minutes was almost back to its initial value. At point B the pH increased during the first 15 minutes of the recovery to 3.9. After 4 hours of recovery, pH increased to 4.55. The recovery was a slower process than the acidification (Figure 22).

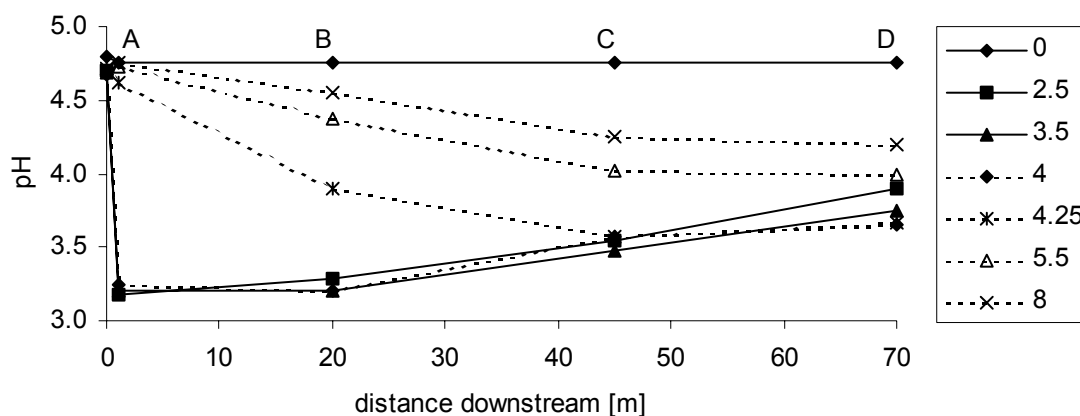


Figure 22 Streamwater pH value at sites in the experimental stream reach. Solid lines represent changes during the acidification phase; dashed lines represent changes during the recovery. The number in the legend is time (hours) from the beginning of experiment.

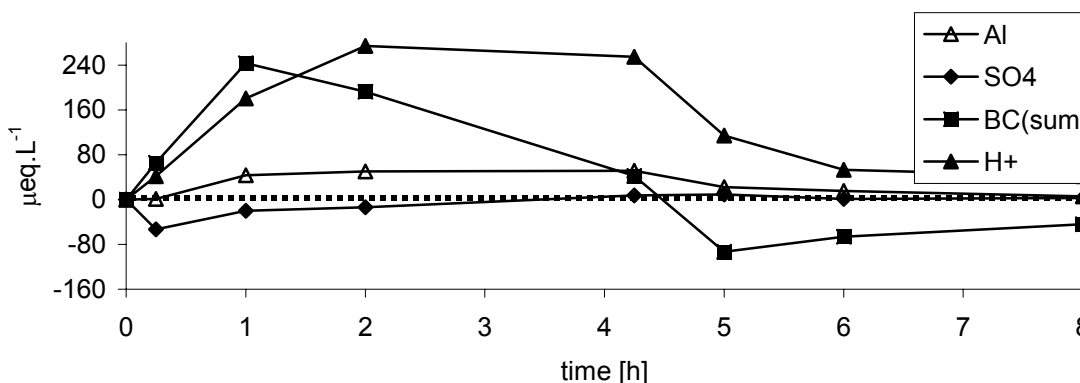


Figure 23 The change in solute concentrations ($c_t - c_0$) at point C, 45 m below the point of acid addition. The dashed line represents no change. BC = the sum of base cations (Ca, Mg, Na, and K)

After 1 hour Cl^- concentration reached $536 \mu\text{eq.L}^{-1}$ and remained at $\sim 540 \mu\text{eq.L}^{-1}$ until the end of the acidification phase. Ten minutes after the end of the acid addition (4.17 hours from the

start), Cl^- concentration at point C decreased to $403 \mu\text{eq.L}^{-1}$. Three hours later, the concentration of Cl^- had decreased to its initial value, $\sim 110 \mu\text{eq.L}^{-1}$ at point C (Table 14).

The concentration of SO_4^{2-} , the most abundant anion, decreased by 4% ($51 \mu\text{eq.L}^{-1}$) at point C during the first 15 minutes of the experiment (Table 14, Figure 23). After reaching its minimum value ($1400 \mu\text{eq.L}^{-1}$) at first 15 minutes of acidification, SO_4^{2-} started to gradually increase. During the recovery stage SO_4^{2-} reached its maximum concentration ($1463 \mu\text{eq.L}^{-1}$) at 6 hours after the start of the acid treatment (Table 14). Thereafter it remained virtually constant until the end of experiment (Figure 23). The SO_4^{2-} concentration normally increases during high discharge events at LP.

The F concentration increased from 35 to $44 \mu\text{eq.L}^{-1}$ (Table 14), 1 hour after the acidification started and then decreased to slightly above background values even as the pH declined. Some Cl^- may have exchanged with the F^- explaining some of the missing Cl^- . Nitrate varied erratically (Table 14).

The concentration of Na did not vary significantly during the experiment. The maximum increase of Na concentration at point C was 2% ($8 \mu\text{eq.L}^{-1}$). The maximum increase for K concentration was 5% but its contribution (ca. $20 \mu\text{eq.L}^{-1}$) to the sum of cations was negligible. The concentration of K increased during the first hour and then decreased.

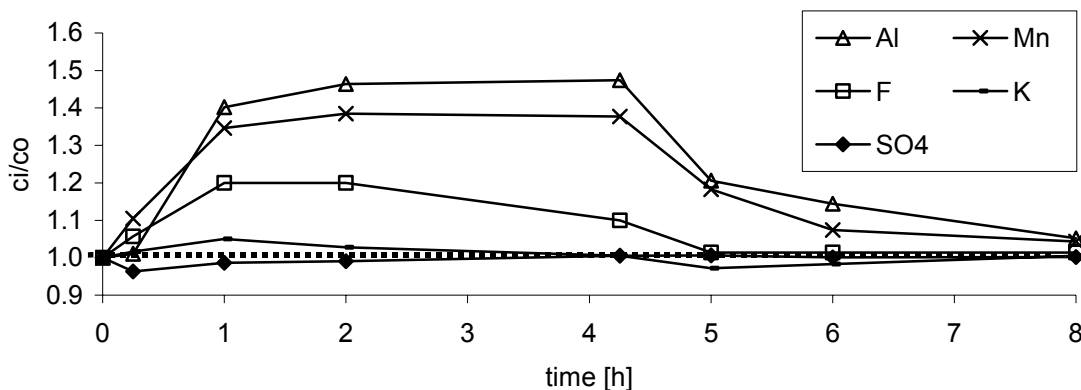


Figure 24 The relative change (c_i/c_0) of various analyte concentrations in time at point C, 45 m below the acid addition point

The Al concentration did not change significantly during the first 15 minutes of the acidification but then increased by about 50% (Figure 24), the most of all metals plateaued for three hours. The Al concentration was still increasing at 4 hours. After the acid addition stop, the concentration of Al decreased, but after 4 hours did not recover to the initial concentration.

Manganese concentration was low (ca. $4 \mu\text{eq.L}^{-1}$) and it increased only by 1 to $2 \mu\text{eq.L}^{-1}$ at the lowest pH. Manganese concentrations correlated strongly ($R = 0.95$; Annexes, Table 28) during the experiment with Fe and Al. Iron concentrations were low and increased only by $\sim 2 \mu\text{eq.L}^{-1}$ during the acidification. During the recovery stage Fe concentration remained higher than their initial concentration.

The Be concentration increased by up to $0.5 \mu\text{eq.L}^{-1}$ (25%, Figure 26) at the peak of acidity and then decreased during recovery. The correlation of Be with Al was significant ($R = 0.88$; Annexes, Table 28), as it was with concentrations of Mn and Fe.

Table 14 Data on changes of concentrations at points W, B, C and D during the acidification experiment

W	time min	pH	$\mu\text{eq L}^{-1}$														
			H	Be	Mg	Ca	Sr	Ba	Na	K	Fe	Mn	Al	F	NO_3^-	SO_4^{2-}	Cl
0	4.95		11	1.52	510	706	3.8	0.62	364	23	5.0	5.0	108	35	23	1456	109
	480	4.76	17	1.57	514	712	3.4	0.60	359	23	4.8	4.3	108	39	21	1450	105
B	15	3.60	251	1.72	542	797	4.2	0.75	372	24	5.9	5.5	123	NA	NA	NA	NA
	60	3.38	417	1.67	527	760	3.9	0.76	372	23	6.1	5.5	128	39	36	1448	556
	240	3.20	631	1.65	508	727	3.7	0.71	361	23	6.1	5.3	125	39	23	1448	578
	480	4.55	28	1.54	503	709	3.6	0.61	355	23	4.7	4.4	107	37	21	1456	107
C	15	4.25	56	1.59	533	753	4.0	0.74	361	23	6.1	5.2	109	39	27	1400	258
	60	3.71	195	1.90	571	884	4.4	0.92	370	24	7.2	6.3	152	44	32	1433	536
	120	3.54	288	1.88	551	856	4.2	0.93	368	24	7.2	6.5	158	44	24	1440	547
	250	3.57	269	1.89	508	751	3.8	0.80	365	23	6.8	6.4	159	41	22	1460	403
	300	3.89	129	1.68	478	651	3.3	0.65	361	22	6.1	5.5	130	37	16	1463	134
	360	4.17	68	1.59	488	670	3.4	0.63	358	23	6.4	5.0	124	37	22	1454	123
	480	4.25	56	1.56	493	689	3.5	0.62	357	23	6.1	4.9	114	37	10	1456	111
D	270	3.73	186	1.89	532	803	4.0	0.92	365	23	6.8	7.6	173	44	20	1458	426
	360	4.08	83	1.70	482	660	3.3	0.66	369	22	6.1	6.3	129	37	18	1448	125

Concentrations of Ca and Mg increased significantly and rapidly. Calcium release neutralized the most acid; its concentration increased by 25% ($175 \mu\text{eq.L}^{-1}$) at its maximum. Magnesium concentration increased rapidly but only to a maximum of 11% ($58 \mu\text{eq.L}^{-1}$). In the first 20 m of the stream, sources of Ca and Mg were depleted after the first hour of the acidification, and their concentration in solution gradually decreased (Figure 26).

Fifteen minutes after the acidification ceased ($t = 4.25$ hrs), Ca and Mg concentrations decreased below the initial values ($t = 0$) and then started to increase slowly. The correlation of Ca and Mg for all samples was $R = 0.97$ (Annexes, Table 28). However at $t = 4.25$ hrs the pool of Mg was depleted or nearly depleted (Figure 26). The individual Ca and Mg peak concentrations did not exceed values from the long-term monitoring data (Figure 25).

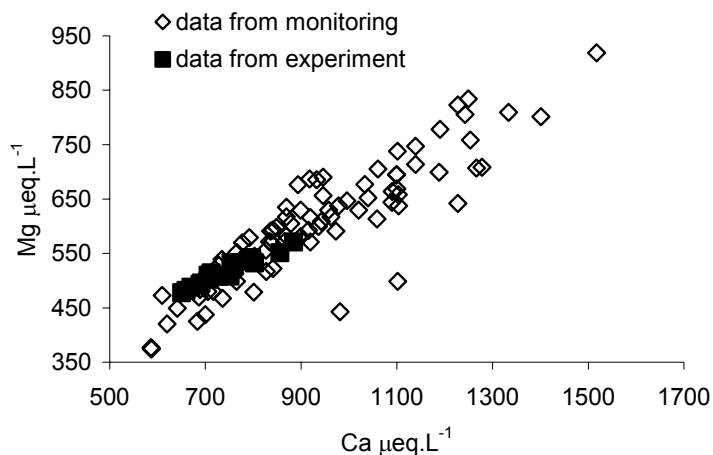


Figure 25 Relationship of Ca and Mg concentrations in the LP streamwater

Strontium concentrations correlated positively with Mg, Ca, Ba and K during the experiment (Figure 26). Strontium concentration increased by 15% or $0.5 \mu\text{eq.L}^{-1}$. Sr behaved similarly to Ca or Mg during the recovery stage of the experiment.

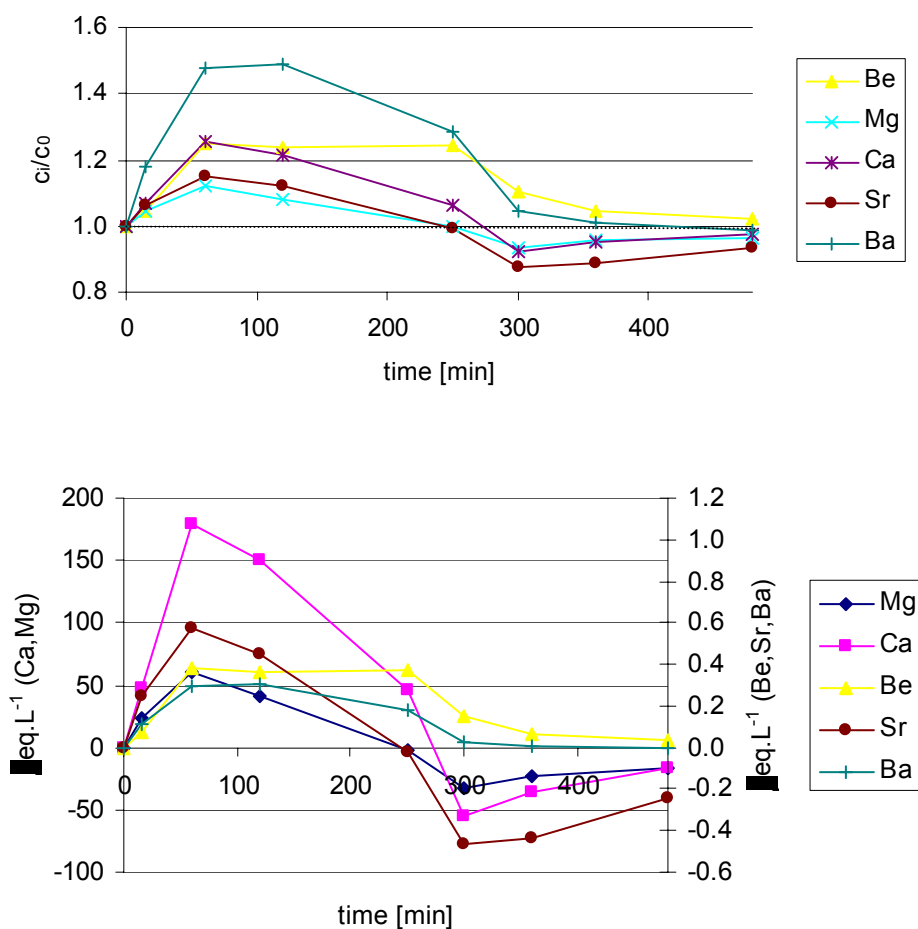


Figure 26 The relative change c_i/c_0 and absolute concentration changes ($c_i - c_0$) of the II.A group elements during the acidification experiment

Barium concentration increased by 49% (Figure 26), which makes it the most mobile element of the II.A group. However this change represents an increase of only $0.3 \mu\text{eq.L}^{-1}$. Concentrations of Ba correlated positively with F, Be, Ca, Al, Fe and Mg. During the recovery stage Ba concentration did not decrease below the initial value.

4.9 Shallow Groundwater

Shallow groundwater was sampled from a 5 m deep well (site LP6 at Figure 6). The chemistry of the shallow groundwater was influenced by a reducing environment at 5 m depth. The shallow groundwater is the "oldest" water in the catchment and has followed deeper hydrologic flow paths compared to most of the water making up streamflow. The mean pH value 6.69 of the shallow groundwater during the monitored period was higher than the stream water mean pH of 5.25. The mean concentrations of Ca, Na, Cl, Mn and Fe were higher in shallow groundwater than in streamwater (Table 15). Concentrations of other measured solutes were lower in the groundwater than in the surface water (Table 15). Increased Ca, Na and SiO_2 originate from plagioclase weathering. High concentrations of Fe and Mn were due to low redox potential of the groundwater.

In contrast, the concentrations of Al and Be were low because of the high pH value. During the low discharge periods, usually during the summer and autumn, the surface water chemistry was very similar to that of shallow groundwater (Table 15).

Table 15 Mean concentrations of solutes in groundwater and surface water during year 1999

year		pH	Be	Mg	Ca	Sr	Ba	Na	K	Mn	Fe	Al	F	Cl	SO_4^{2-}	NO_3^-
		$\mu\text{eq.L}^{-1}$														
1999	groundwater	6.69	0.05	416	1205	2.4	0.43	653	25	31	246	0.9	16	126	930	5.2
	stream low flow	5.56	0.76	578	937	3.2	0.77	445	45	20	50	40.5	37	189	1529	14.2
1999	stream	5.25	0.82	566	826	2.9	NA	395	29	10	17	83.0	38	121	1460	48.0

The concentration of Be was very low in the subsurface water and it usually was in range of $0.0X \mu\text{eq.L}^{-1}$. The highest concentration of $0.36 \mu\text{eq.L}^{-1}$ was recorded during the 2000 spring snowmelt in association with a decrease in pH. Beryllium concentrations in the groundwater correlated positively with stream discharge, H, and Al, and negatively with groundwater level, Mg, Ca, K, Na, Cl^- , SiO_2 , Mn and Fe (Annexes, Table 29).

Magnesium concentrations in the shallow groundwater were usually about 30% lower than those in surface water. The mean concentration of Mg in the groundwater was $\sim 416 \mu\text{eq.L}^{-1}$, and as in other waters Mg and Ca were strongly positively correlated. Magnesium

concentrations correlated positively with groundwater level, Ca, K, Na, SiO₂, Mn, and Fe, and negatively with stream discharge Be, and SO₄²⁻ (Annexes, Table 29).

Calcium was the only element from the II.A group whose mean concentrations in the groundwater were higher (by 50%) than in the surface water. The mean concentration of the Ca in the groundwater during the monitored period was ~1205 µeq.L⁻¹. The calcium concentrations correlated positively with groundwater level, Mg, Sr, K, Na, SiO₂, Mn, and Fe and negatively with stream discharge, H, Be, and SO₄²⁻ (Annexes, Table 29).

The mean concentration of Sr in groundwater during the monitored period was ~2.4 µeq.L⁻¹, which was moderately lower than that in surface water. The strontium concentrations correlated positively with Ca, K, Na, and SiO₂ (Annexes, Table 29).

The mean concentration of Ba in the groundwater during monitored period was ~0.43 µeq.L⁻¹. The barium concentrations did not correlate with any of the measured parameters. Barium concentrations in the shallow groundwater were very similar to the theoretical equilibrium concentrations of Ba calculated from the K_{sp} of BaSO₄ (Figure 27).

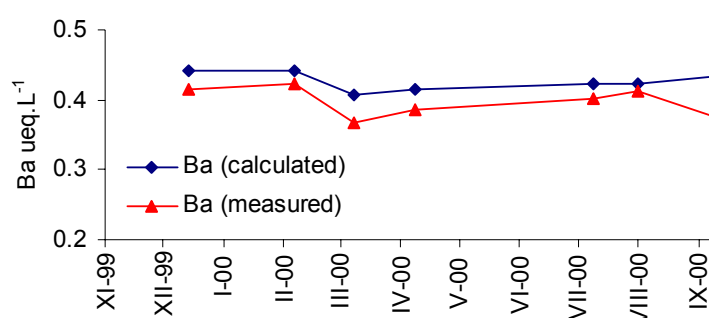


Figure 27 Measured and calculated Ba concentrations in the LP shallow groundwater

4.10 Fluxes and seasonal variations

The annual export of most solutes was directly related to water output. This relationship of the water mass makes the mass fluxes of elements highly predictable at the LP catchment, as has been reported for other catchments (Likens & Bormann 1995).

The seasonal changes in bulk deposition fluxes of most elements were affected mainly by the amount of precipitation. This was especially true for changes in the flux of Be, H⁺ and SO₄²⁻. The deposition of Ca and Mg in summer months (June – August) was not significantly elevated when compared to spring fluxes. The opposite was typical for Be, H⁺ and SO₄²⁻.

The comparison of throughfall H⁺ deposition fluxes with the bulk H⁺ deposition fluxes indicated significant neutralization of precipitation by the forest canopy in the period April –

December. In the period November – March the H fluxes in throughfall and bulk deposition were approximately the same. The H fluxes increase in June and July only.

The export of most elements from the catchment was affected above all by the spring snowmelt, which usually occurred in March or April (Figure 28). A minor peak in output fluxes curves was also observed in July and it was attributed to summer rainstorms.

Half of the annual exported mass of Be, Ca, Mg and Sr typically left the catchment in the period March – May. In the case of Ba the exported mass between March – May comprised 76% of the annual Ba mass export. It is necessary to notice that during the same period usually occurred 50% of the annual water runoff (Figure 28).

Of the II.A group elements, Ca had the greatest mass export from the LP catchment. However the mass exports of Mg, Sr and Be were also considerable especially relative to their atmospheric inputs. Barium had the least mass export in the group (Table 22).

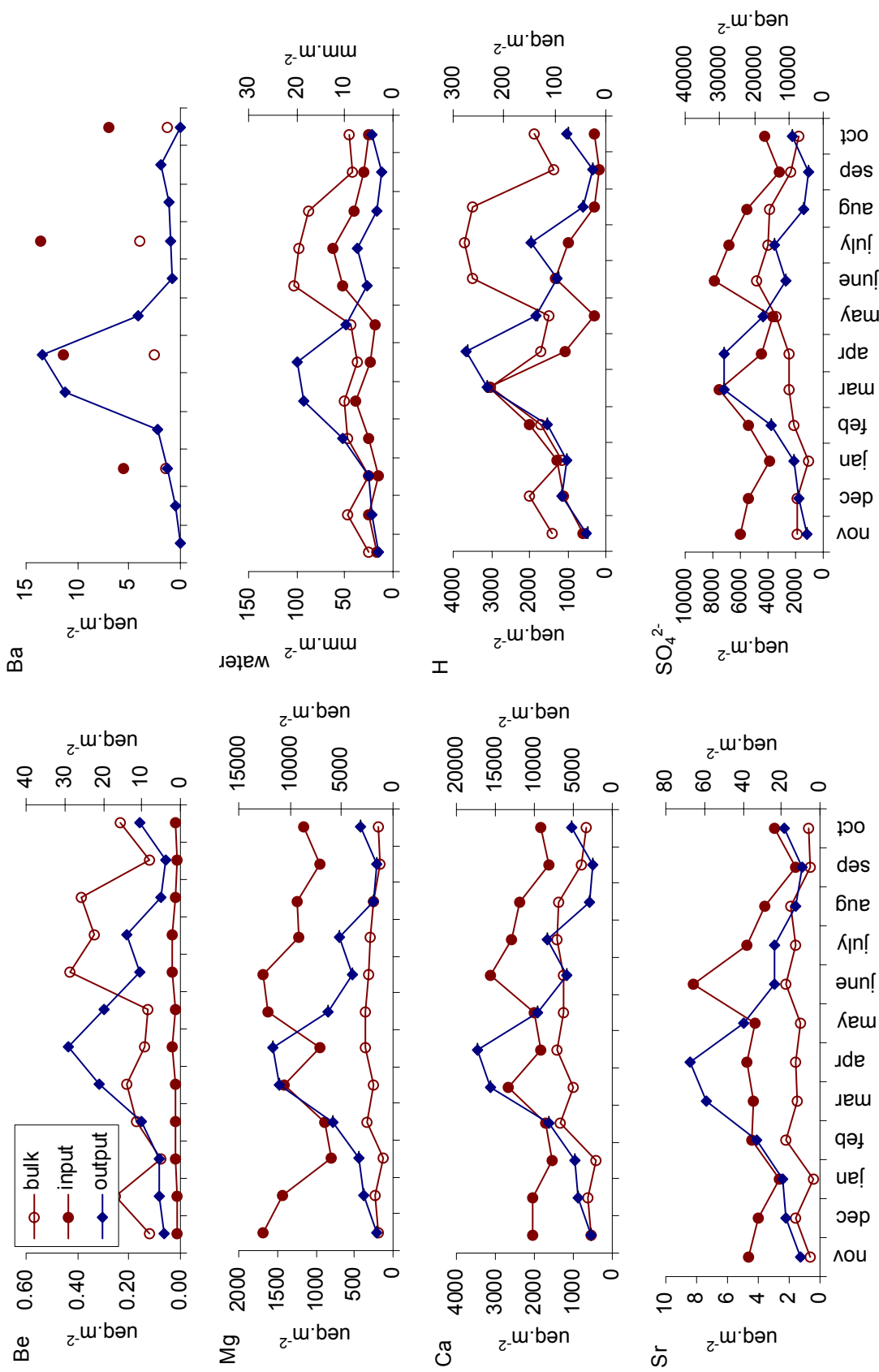


Figure 28 Average seasonal changes of selected fluxes in and out of LP catchment (secondary Y axis attributed to output, if included)

5 Discussion

5.1 Fluxes and cycling in forest ecosystem

5.1.1 Sources for the watershed system

5.1.1.1 Bedrock and alluvial sediments

The average composition of the LP bedrock was calculated from the analyzed compositions of Jevany and Říčany types of granites. This composition is considerably lower in Ca than typical low-Ca granitic rocks (Roessler & Lange 1972). On the other hand, the Sr concentration of the bedrock is average for low-Ca granitic rocks, while concentrations of Be, Mg and Ba are elevated. The most significant differences with respect to typical low-Ca granitic rocks are the 3 times higher concentration of Be, almost double concentration of Mg and more than 50% lower concentration of Ca.

The elevated concentrations of beryllium found in plagioclase and biotite (Table 5) imply that these minerals are the most important sources of Be for weathering. The lower modal content of biotite makes plagioclase the major source of Be. The position of Be in plagioclase and in biotite has not been clearly explained. It is anticipated that Be substitutes (together with Si) for Al in the silicate crystal lattice. Beryllium is easily released from the solid materials, especially in an acidic environment. Under circumneutral conditions it remains bound to solid phases, e.g. clays or other secondary minerals. Weathered rock just above fresh unweathered rock contains the highest concentrations of Be (Figure 8). The increased Be concentrations at the bottom of the alluvial profile were most probably due to higher pH and thus decreased Be mobility. Beryllium concentrations in the profile decreased toward the top of the profile (Figure 8) as a result of acid leaching and enhanced chemical weathering in the upper parts of profile.

Biotite was likely the most important source of Mg. It is the only mafic rock-forming mineral in the Říčany granites. The biotite of the Říčany granites is typical with high Mg content and its chemical composition was close to phlogopite modification. Magnesium enters the weathering solution but some Mg is bound in secondary minerals, e.g. chlorite. Chlorite was among the secondary minerals found in LP soils (Žigová - unpublished). The anomalously high Mg concentration of 695 meq.kg^{-1} at 1-m depth in the alluvial sediments (Figure 8) coincides with the layer that has the highest proportion of finest particles (Figure 5) and with the lowest Ca concentrations (Figure 8). This elevated magnesium concentration may indicate enrichment of secondary chlorite. Feldspar weathering may release small amounts of Mg. Concentrations of Mg in the sediments and regolith were comparable to those in the

unweathered bedrock, while the slight enrichment towards the top of profile may indicate favorable conditions for the formation of secondary minerals – possibly chlorite or others.

Calcium is a substantial structural component of plagioclase, which is the most important source of Ca for weathering. Calcium depletion of the regolith (Figure 8) is a result of its rapid leaching and high weathering rate (Skřivan et al. 1994). The calcium concentrations available in biotite or orthoclase are unimportant relative to its concentration in plagioclase. The lowest Ca concentrations were found in the same sediment layer as the highest Mg and Fe concentrations. This pattern, coupled with the low Na and K concentrations in this layer, may indicate greater leaching, preferential flow paths, or other processes that create favorable conditions for the formation of secondary Mg rich chlorite. The lower concentrations of Ca at the bottom of the profile result from its high mobility, consistent with high Ca concentrations in the groundwater (Table 15).

Due to the similar Sr concentrations found in both orthoclase and plagioclase (Table 5), it appears that both feldspars are important sources of Sr in Říčany granites, which is in agreement with many previous studies. As noted by Wedepohl (1969), Mg-Fe minerals usually have less than 10% of the Sr content of feldspars; for the biotite of the Říčany granites this amount was 3 – 4%. The nearly unchanged Sr concentration at the bottom of the alluvial profile is perhaps due to stronger binding of Sr to secondary minerals than is the case for Ca. The volume of unweathered minerals (especially K feldspars) is also anticipated to be the highest in the bottom layers of profile (White et al. 2001). The lowest Sr concentration in 1 m depth coincided with the lowest Ca concentration.

The high concentrations of Ba found in orthoclase and biotite correspond to the high K concentrations as crystallo-chemical properties of Ba and K enable their substitution (Wedepohl 1969). The least important rock-forming mineral with respect to Ba was the plagioclase due to its very low content of Ba. Weathered material and sediments contained slightly lower concentrations of Ba than the parent rock. The strong correlation of Ba and Sr in sediments (Hons et al. 1990) may result from the significant amounts of both elements in orthoclase. Also orthoclase is more resistant to weathering than biotite and plagioclase (White et al. 2001).

5.1.1.2 Atmospheric inputs in bulk precipitation

The decrease of II.A element bulk input fluxes between 1994 and 2001 (Table 22) most likely resulted from better controls on emissions from Czech Republic coal burning power plants. The lowest bulk fluxes for most of the elements occurred in 1999 when the desulphurization of all Czech power plants was completed (Hruška et al. 2002). The proportional decreases of

elemental fluxes were calculated from the average fluxes in 1997 - 1998 (before desulphurization) compared to the average fluxes in 1999 – 2001 (after desulphurization).

The decrease of bulk input fluxes was very sharp for Be, Al, H^+ , SO_4^{2-} and F^- , while the decrease was modest for Ca and Mg (Table 22). The decrease in bulk fluxes of Be and Sr was comparable to the sharp decrease of H^+ , SO_4^{2-} and F^- , which suggests a common source - the coal burning emissions. The decrease of Ca and Mg may have been smaller because these elements have numerous other sources aside from the power plant emissions. Other sources of Ca and Mg in bulk precipitation include natural eolian dusts, oceanic spray, and anthropogenic dusts (from various construction, production and agricultural activities). An especially important factor in the deposition of dusts and ashes is the proximity of the LP catchment to Prague (Figure 1).

The burning of lignite from the NW coal basin containing up to 13 meq.kg^{-1} of Be was the main source of Be in atmospheric inputs. The decline in Be fluxes has already been reported at the LP catchment (Skřivan et al. 2000, Skřivan et al. 2000a). The recent annual fluxes (years 2000 and 2001) were precisely analyzed by means of sample preconcentration to 2.3 meq.m^{-2} .

The bulk input fluxes of Ca at LP catchment were comparable to those at other sites in more polluted parts of the CR (Krám et al. 1997). The mean annual bulk flux of Ca (12.7 meq.m^{-2}) between 1994 and 2001 observed at LP in the central Czech Republic was much higher than the 4.4 meq.m^{-2} found at the more pristine and unpolluted HBEF catchments in the northeastern USA (Likens et al. 1998). The mean Ca bulk input flux (10.1 meq.m^{-2}) from the 1999 to 2001 should remain constant, as no further emission controls will be applied.

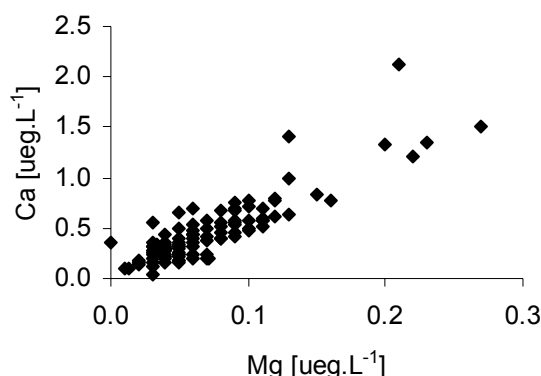


Figure 29 The relationship of Ca and Mg concentrations in the bulk precipitation

Similarly to Ca, the average bulk input fluxes of Mg at LP were comparable to those in the western part of the CR in 1994 (Krám et al. 1997). The linear relationship between Ca and Mg

concentrations in bulk precipitation was maintained (Figure 29), which eliminated sea aerosols as their possible source at LP catchment. It seems that the important sources of elevated fluxes of Ca and Mg beyond the alkali fly ash also maintain a linear relationship for Ca and Mg in precipitation solutes. Calcium and magnesium in bulk precipitation had the strongest correlation among the measured parameters (Annexes, Table 23).

The mean concentration of Sr in bulk precipitation was $0.03 \mu\text{eq.L}^{-1}$ in the period 1994 – 2001, similar to the mean Sr concentration in bulk precipitation of Switzerland (Atteia 1994). The annual bulk flux of strontium decreased during the period 1996 – 2001 but remained well within the range $5.5 - 59.3 \text{ meq.m}^{-2}$ (Table 22) determined at the Swiss sites (Atteia 1994). Elevated bulk Sr inputs in Norway were usually attributed to marine sources (Berg et al. 1994). However, the higher Sr bulk fluxes in 1996, 1997 and 1998 (compared to 1999 – 2001) at the central CR site can be attributed to elevated emissions of coal ashes, as there was no shift of the Mg:Ca ratio towards that of oceanic spray.

The two-year monitoring period of Ba fluxes in bulk precipitation was too short to make conclusions on the trends of Ba input flux. However it enabled a comparison of Ba bulk input fluxes and concentrations at the LP catchment with those from marine and continental sites. The concentrations of Ba in bulk precipitation were comparable to those from Switzerland (Atteia 1994). Also some marine sites in Norway (Berg et al. 1994) exhibited annual Ba input fluxes similar to those at the LP catchment. The main source of Ba at the central Czech Republic were perhaps the dusts or ashes (in keeping with the constant Mg:Ca ratio).

5.1.2 Internal cycling

5.1.2.1 Throughfall

The throughfall fluxes of most solutes were higher than the bulk precipitation fluxes. The excess flux of elements originated in wash-off of particles from dry deposition to the aboveground parts of trees, dissolution of atmospheric gases adsorbed to foliar surfaces in the canopy, as well as canopy leaching of solutes originating internally from the trees.

The beech canopy was more effective in the neutralization of acid precipitation especially due to greater canopy leaching, which was especially evident from the pH increase in beech throughfall relative to bulk precipitation (Figure 10). In contrast the spruce canopy appeared to be very effective in scavenging of aerosols and gases containing S and N, which resulted in further acidification and a considerable decrease in pH of the throughfall solution.

The throughfall fluxes of most elements in both types of throughfall decreased during the period at the LP catchment, similar to the trend in bulk precipitation inputs. For most solutes

this decrease was more evident in the spruce throughfall due to the greater effectiveness of the spruce canopy in scavenging aerosols and particles from the atmosphere during the whole year. The decrease of element input fluxes was evaluated from the difference in the average flux from years before (1997 - 1998) versus after (1999 - 2001), the complete desulphurization of Czech power plants. The most significant flux decrease occurred for H^+ , Be, Mn, Al, F^- and SO_4^{2-} in spruce throughfall, and for Mn, Fe, Al and F^- in beech throughfall. The decrease of SO_4^{2-} flux in beech throughfall was surprising small at 23%. The corresponding proportional decreases of SO_4^{2-} flux in bulk precipitation and spruce throughfall were 61% and 43%, respectively. The most significant seasonal decrease in mean sulfate flux from before (1997 - 1998) to after (1999 - 2001) power plant desulphurization was observed in bulk precipitation and throughfall for the period June – August. The most dramatic decrease in this seasonal sulfate flux occurred in bulk precipitation, followed by spruce throughfall. In contrast, this seasonal sulfate flux remained almost constant for beech throughfall through the period.

Increased fluxes of Be in throughfall relative to bulk precipitation were reported from LP as well as other catchments (Skřivan et al. 2000, Veselý et al. 2002, Neal et al. 1992). The sampling method is of special concern due to the possible ready leaching of Be from litter, which was accidentally caught in funnels of the typical VOSS samplers. This was eliminated by usage of the GCTC samplers (see *Methods*). The first results this artifact of increased Be fluxes detected in VOSS samplers compared to GCTC samplers (Skřivan et al. 2000). The higher Be fluxes in VOSS throughfall fluxes were attributed to Be leaching or washout of the scavenged particles from the litter trapped by the collector.

The Be concentrations in throughfall collected with GCTC samplers were comparable to those in bulk precipitation. The similarity is especially evident from precisely evaluated deposition fluxes in 2000 and 2001 derived from analysis of preconcentrated samples. Generally, it was inconclusive whether Be throughfall fluxes were higher or lower than those in bulk precipitation. The uncertainty during 1994 – 1998 resulted from the high percentage of monthly samples that had Be concentrations below the detection limit. In 1999 – 2001, when samples were preconcentrated, throughfall Be fluxes were higher than bulk precipitation fluxes with the exception of beech throughfall in 1999. It is not clear from the results of this study whether Be is lost or gained as precipitation passes through the canopy.

The flux of Mg was generally much higher in throughfall than in bulk precipitation (Annexes, Table 22), and generally greater in spruce throughfall than in beech throughfall. The average annual Mg flux in spruce throughfall of $19.4 \text{ meq.m}^{-2}.\text{yr}^{-1}$ was comparable to that reported

from the Mg- poor (granitic) catchment Lysina in the western part of the CR, but less than half of that at the Mg-rich (serpentinite) Pluhův Bor catchment in the same area (Krám et al. 1997). The greater proportional enrichment of Mg fluxes compared to Ca fluxes in throughfall was a result of major internal leaching of Mg from the canopy (Figure 30).

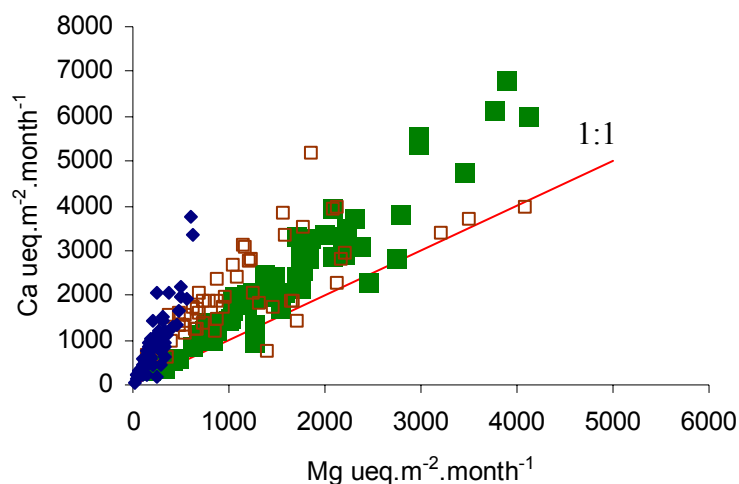


Figure 30 Relationship of Ca and Mg fluxes in bulk precipitation (diamonds), beech (empty squares) and spruce (filled squares) throughfall

The composition of beech throughfall during the winter season was very similar to the bulk precipitation (Figure 30). This was caused by the absence of the beech canopy in the winter. The spruce canopy is present whole year and thus modifies the Mg fluxes in throughfall most of the time. In some cases the beech throughfall fluxes had a Mg:Ca ratio close to 1:1, (red line on Figure 30) usually in the period from May to November. The lowest throughfall fluxes of H⁺ occurred during this same period (May to November), suggesting ion exchange of Mg from the canopy by H⁺. The enhanced magnesium throughfall fluxes in May might also be a result of the undeveloped cuticular protection of young foliar surfaces, while in the period August to November the beech canopy is senescing. Hydrogen fluxes in throughfall are elevated in June and July, as a result of the highest monthly precipitation and potential depletion of Mg exchange sites in the canopy, and faster passage of water through canopy (Figure 31). The similarity of changes in monthly Mg and K fluxes in beech throughfall (Figure 31) indicate that the reason for the enhanced H⁺ fluxes is the ion exchange of Mg and K with H⁺ from the canopy.

The excess Mg enrichment (relative to Ca) observed in beech throughfall generally did not occur in spruce throughfall, except in October. This suggests that Ca and Mg were perhaps leached from the spruce canopy in similar fashion. The highest peak of Mg throughfall flux accompanied by increased fluxes of K and Ca occurred in March (Figure 32).

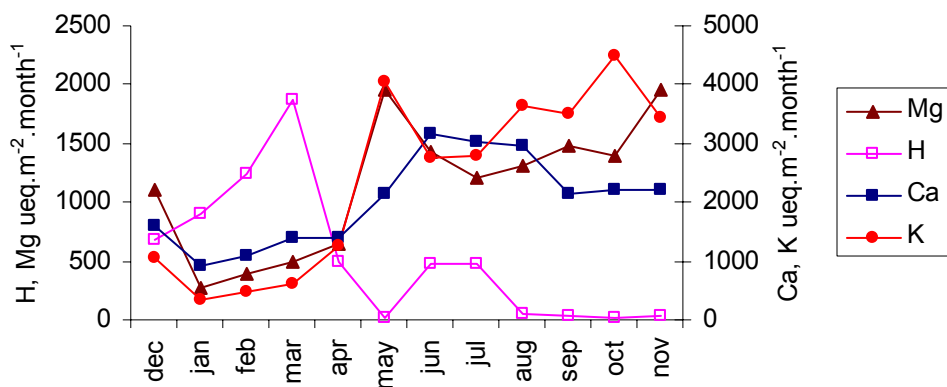


Figure 31 Seasonal changes in the flux of Ca, Mg and K in beech throughfall, data are 4-year monthly averages

The average annual beech and spruce calcium throughfall fluxes 28.7 and 29.3 meq.m^{-2} at the LP catchment were nearly similar. The average annual spruce throughfall Ca flux at the granitic Lysina catchment in the more polluted western part of the CR was much higher at 68.8 meq.m^{-2} (Krám et al. 1997). Moreover, the spruce Ca throughfall flux at LP 29 meq.m^{-2} was lower than that at serpentinite catchment Pluhův Bor in the same part of the CR as Lysina, where it annually averaged 36.6 meq.m^{-2} (Krám 1997).

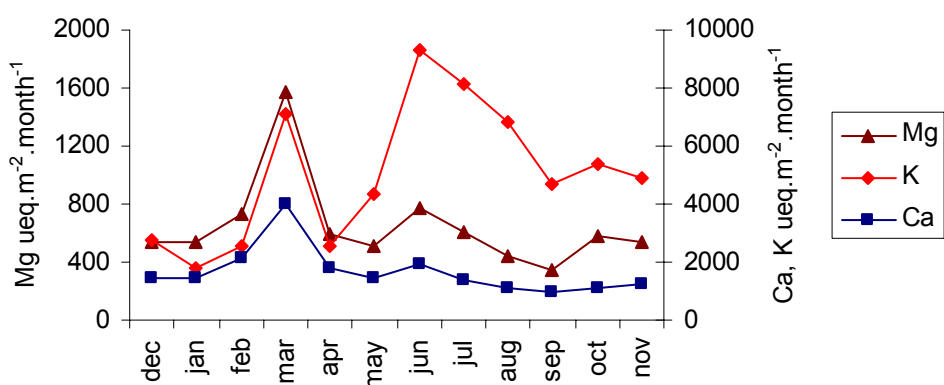


Figure 32 Seasonal changes in flux of Ca, Mg and K below the spruce, data are 4-year monthly averages

The enhanced throughfall fluxes of Ca at granitic catchment Lysina may be a result of its greater foliar leaching and/or enhanced uptake of Ca, as Lysina catchment soils are very poor in Mg (Krám 1997). In contrast, lower fluxes of throughfall Ca from Pluhův bor perhaps result from low abundance of Ca in the serpentinite or inhibited uptake of Ca because of a toxicity effect from excess Mg.

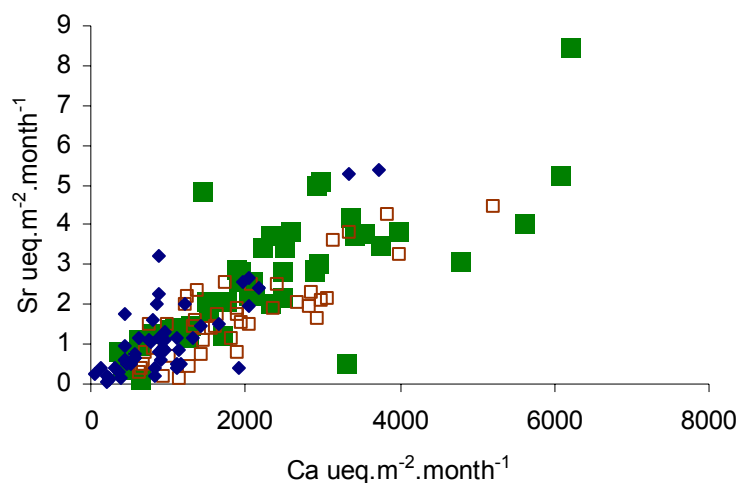


Figure 33 Relationship of Sr and Ca fluxes in bulk (diamonds), beech (empty squares) and spruce (filled squares) throughfall

A similar proportional decrease of Sr fluxes in both types of throughfall was detected at LP catchment. Average throughfall Sr fluxes before 1999 were 15% higher than those in 2000 and 2001. The relationship of Ca to Sr concentrations and fluxes was linear (Figure 33) and it implies similar behavior of Ca and Sr in throughfall. Similar relationships of Ca and Sr were reported from a granitic catchment Aubure for both beech and spruce throughfall (Poszwa et al. 2000 etc.). The (Sr:Ca)*1000 ratio from Aubure (beech and spruce, 1.03 and 0.99) was comparable to those from LP catchment (beech and spruce, 1.10 and 1.05). The slight difference in (Sr:Ca)*1000 ratios in the two catchments can be attributed to presence of fly ash as well as to different (Sr:Ca)*1000 ratios in soil solutions or in soils.

Only two years of data on Ba throughfall fluxes were available from LP. The scarcity of reports on Ba throughfall fluxes precluded comparison to other monitored sites. At LP it was possible to conclude that Ba fluxes in spruce throughfall were at least 50% higher than bulk precipitation fluxes.

5.1.2.2 Biomass processes, pools and sinks through accretion

The content of elements in the pool of bole wood per m² of the catchment is considerable (Table 16). The available pool of element below one m² of soil calculated using the acid leachable concentrations is overestimated with respect to potential plant uptake. It would be more precise to calculate the available pool out of exchangeable concentrations, but this was not possible with available data. However, it was possible to conclude that the exchangeable pool of BC is about 33% of the acid leachable fraction (Navrátil unpublished).

The pool of calcium, potassium and manganese in bole wood per m² composed approximately 13% of the acid leachable pool of these elements in the soil per m². This amount of essential

elements would compose much higher proportion of the exchangeable concentrations (in fact it is 29, 34 and 59%). The importance of this pool is thus essential as it might be potentially removed and lost from the catchment. Natural processes, such as wood and bark degradation, may form a pool of elements readily available for new young plants. However, this process is strongly impacted by forest harvesting and at areas with intensive forestry the exchangeable pools of elements in soils may be significantly depleted.

Table 16 The pools of elements (meq.m⁻²) in biomass at LP catchment and annual loss by wood and bark accretion

unit		acid leachable pool below m ² of soil	pool in wood and bark per m ² (no canopy)	pool in canopy per m ²	annual sink in wood and bark accretion per m ²		
					beech	spruce	total
Be	meq.m ⁻²	139	0.12	0.005	0.001	0.002	0.002
Mg	meq.m ⁻²	14311	396	17	4.6	6.3	5.3
Ca	meq.m ⁻²	16733	2097	58	9.8	37.1	21.7
Sr	meq.m ⁻²	94	7.0	0.077	0.039	0.119	0.074
Ba	meq.m ⁻²	344	9.7	0.053	0.033	0.222	0.115
Na	meq.m ⁻²	1611	23	NA	0.50	0.20	0.37
K	meq.m ⁻²	3057	370	38	5.4	4.6	5.1
Mn	meq.m ⁻²	1306	172	7.0	0.53	4.47	2.24
Fe	meq.m ⁻²	28926	123	1.0	0.97	2.82	1.77
Al	meq.m ⁻²	208958	44.6	2.7	0.08	1.15	0.55

The highest annual mass sink of element into wood and bark was that of calcium. Annually 22 meq.m⁻² of calcium is sequestered in the wood biomass, as calcium is the most important inorganic structural element of woody cells. The annual sink of Ca through biomass accretion per m² at LP catchment was greater for spruce than for beech. The primary reason for this is the higher annual increment of wood (faster growth) by spruce and also its significantly higher annual bark accretion compared to beech. Bark contains the highest Ca concentrations out of all the tree compartments (Table 7). Magnesium and strontium exhibit the same patterns of sinks as Ca, although the differences between the pools are more significant for Ca. The annual sink of Mg is lower (Table 16) compared to Ca, especially due to the low abundance of Mg in bole wood.

Contrary to Ca and Mg and despite the differences in annual increments the annual sink of K is greater in beech than in spruce (Table 16). The concentrations of K in beech wood and bark were double those in spruce (Table 7). Uptake of Na is insignificant in comparison to the rest of BC, and in biogeochemical studies it is usually considered to be zero.

The wood and bark of spruce had higher concentrations of toxic elements such as Be, Ba and Al compared to beech. It is known that Al toxicity is fatal more to spruce than to beech trees.

Because soil properties are similar across the catchment, spruce trees must be more vulnerable to Al uptake than beech trees. The highest concentrations of Al were found in the canopy and bark of spruce, but in the roots of beech. Spruce had a greater uptake of Be and Ba, which are reported to be toxic for plants under specific conditions, but their physiological functions were not been fully explained. Similarly to previous studies (Lotspeich and Markward 1963), high concentrations of Ba were found in spruce branches.

The uptake of Mn is much greater by spruce than beech due to its high Mn metabolism. The higher leachable concentrations of Mn in soil below the spruce trees and significantly elevated Mn spruce throughfall fluxes support the idea of spruce enhanced Mn metabolism (Table 22). Magnesium and beryllium were distributed similarly in the tree compartments of both spruce and beech. The highest concentrations of Mg were present in the canopy and bark due to its physiological importance for tree. The exact mechanisms of beryllium toxicity to plants are not fully understood (Anonymous 1962). It seems that Be does not accumulate in roots as was generally reported by Anonymous (1962), but that a considerable amount is translocated to the canopy. The reason for this may be substitution of Be for Mg (Anonymous 1962), although potential positive effects of this substitution were limited to soils with $\text{pH} > 7$ (Anonymous 1962). The continuous translocation of Be to leaves may also represent a possible detoxification mechanism of the tree. The contamination of bark and assimilatory organs may also be of a concern based on occasionally lower Be fluxes in throughfall compared to bulk deposition. The higher concentrations of Be in the foliage of beech may be a result of concurrent higher Mg concentrations in soil solution from deeper horizons and/or due to the deeper rooting system of beech in comparison to spruce. The similar distribution of Be and Mg in soil and soil solutes may support this idea (see *Soil* and *Soil solution*).

Beech trees contained higher concentrations of Mg than spruce in all the tree compartments except bark. This may result from greater uptake due to the deeper rooting system of beech, or a lower ability of spruce to transport Mg to the canopy.

The concentrations of Mg found in tree compartments at LP catchment were generally lower than those reported from the serpentinite catchment Pluhův Bor (Krám 1997), which has an extreme abundance of Mg in soils and soil solution. In most tree compartments the Mg concentrations were ca. 2 times higher but in the canopy Mg concentrations were 4 times higher at Pluhův Bor. In comparison to the magnesium deficient Lysina catchment (Krám et al. 1997) the Mg concentrations at LP in all tree compartments except foliage were comparable. Differences between the Mg content of roots and branches were a result of bark removal for analysis used in this work. The foliar Mg concentration (analyzed the same way

at both sites) was 2 times higher at LP catchment than at Lysina. These points lead to the conclusion that Mg saturation status is especially evident on canopy.

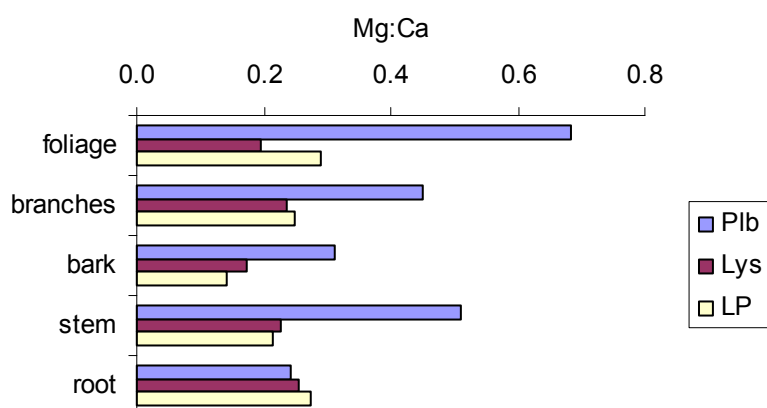


Figure 34 The Mg:Ca ratio in spruce compartments at Lesni Potok (LP), at Lysina (Lys) and at Pluhův Bor (Plb) catchment (data on Lys and Plb from Krám 1997)

The branches and stems of both spruce and beech contained similar concentrations of calcium at LP catchment (Table 7 and Table 8). The foliar and bark concentration of Ca at LP catchment were higher in beech than spruce, again probably as a result of the deeper rooting system of beech in comparison to spruce. Note also that the Ca concentrations in soil solution increased with depth in the beech stand (see *Soil solution*).

The Ca concentrations were comparable at all three sites: serpentinite catchment Pluhův Bor and granitic catchments Lysina and LP. The lowest concentration of Ca in spruce stem wood was found at Pluhův Bor (Krám 1997). A surplus of Mg in soils is probably blocking the uptake of Ca and possibly other nutrients. The toxic effects of Mg are observed on serpentinite catchments due to slower tree growth or as mutations of vegetation called nanisms. However, the approximately double foliar concentrations of Ca at Pluhův Bor in comparison to low-Ca granite catchments (Lysina and LP) suggest that trees were able to translocate Ca to the canopy.

Magnesium deficiency or over-saturation may be observed through assessing the Mg:Ca ratio in tree compartments (Figure 34). The lowest Mg:Ca ratio was found in the foliage of the Mg deficient catchment Lysina (Krám 1997) but all the ratios in other compartments of spruce were comparable to those from LP. The highest Mg:Ca ratios were found in above ground compartments of spruce trees at the Plb catchment, which may indicate over-saturation of the tissues with Mg.

The ratio Mg:Ca decreased with time in both types of canopy as the assimilatory organs accumulate Ca and lose Mg through time (Table 9).

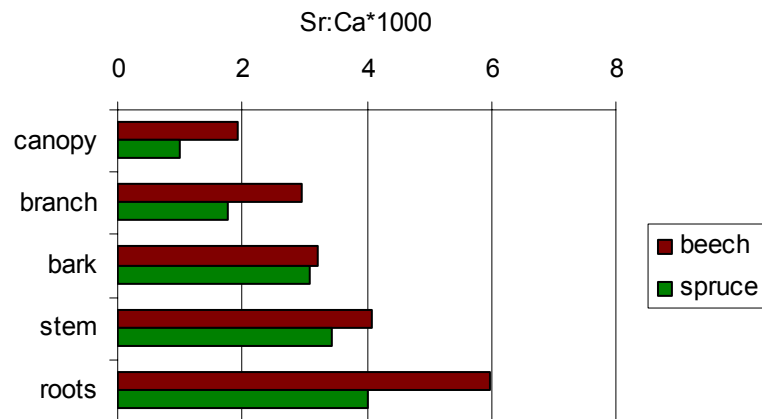


Figure 35 The (Sr:Ca)*1000 ratio in tree compartments of beech and spruce at LP catchment

Similarly to calcium, the strontium concentrations were higher for beech than for spruce in the majority of tree compartments, except the roots. The reasons for enhanced uptake of Sr by beech should be similar to the case of Ca. The concentrations of Ca, Sr and Ba in the case of both spruce and beech were higher in bark than in foliage.

Although Ba was reported to be a toxic element to terrestrial plants (Wang 1986), beech and spruce trees at LP catchment contain significant amounts of Ba. Moreover some tissues, especially of spruce contain more Ba than Sr, which is known to be an essential element. The greater concentrations of Ba compared to Sr were perhaps due to higher concentrations of Ba in soil solutions at LP catchment (see *Soil solution*). The increased Ba concentrations in foliage may suggest that beech is probably more efficient in detoxifying the Ba. The greater concentrations of Ba in stem wood, bark and branches of spruce relative to beech indicate slight accumulation of Ba in its tissues.

The (Sr:Ca)*1000 ratios in beech and spruce followed similar trends as those reported from the granitic Aubure catchment (Poszwa et al. 2000). The values of the ratios were considerably higher at LP catchment (Aubure 0.36 – 2.91; LP 1.01 – 5.96). The difference in values of the ratio (Sr:Ca)*1000 result from different ratios found in other catchment compartments such as the soil exchange pool and soil solution (see *Soil* and *Soil solution*). Beech compartments at both catchments had higher (Sr:Ca)*1000 ratios than spruce (Figure 35). The difference between spruce and beech may be attributed to uptake of solutes by beech from deeper soil horizons, which also have increased (Sr:Ca)*1000 ratios (see *Soil* and *Soil solution*).

The concentration of a given element in the canopy reflects the physiological role of that element in the plant as well as the abundance of that element in soil and/or soil solution.

Particles from canopy samples were not removed prior to analysis in this work. The literature reported a low contribution of dusts to foliar concentrations in the case of Ca, Sr, Ba and Mn (<2%), however the authors note that for elements with low concentration in needles, dust may be of concern (up to 20%) (Wytttenbach et al. 1995).

The highest concentrations of Be, Ca, Sr and Ba in the canopy were found at site LP51 (close to site LP7, see Figure 6). The soil at LP51 contains a high proportion of clay so it is very poorly permeable. The increased base saturation of soils at location LP51 as well as increased concentrations of Be, Sr and Ba (Figure 11, Figure 14 and Figure 15) together with an elevated water table might comprise favorable conditions for their uptake.

Significantly higher concentrations of II.A group elements in the assimilatory organs of beech were detected at site LP6 in comparison to site LP35 (Table 9). This pattern (especially in case of Mg) cannot be attributed to soil or soil solution chemical differences due to similar concentrations of the selected solutes (Table 11). The difference may result from lower soil solution availability at site LP35.

The insignificant differences in concentrations of II.A group elements between years 1997, 2000 and 2002 suggest no significant changes in uptake within that period of time.

The proportional increases of Ca, Sr and Ba over time in leaves and needles were very similar. This was especially interesting with respect to essentiality of Ca and Sr, but for Ba it is remarkable as Ba is reported to be toxic for flora (Wang 1986). Beryllium together with aluminum was proportionally the most enriched element in the assimilatory organs with respect to their age. Its concentrations in beech leaves increased between May and Oct by at least 70%, while the same rate of increase was detected when comparing the 1-yr and 4-yr old needles.

The mean (Sr:Ca)*1000 ratios in spruce needles (1.44) and in beech leaves (1.88) at LP catchment were considerably higher than those found at Aubure granitic catchment for the same tree species 0.36 and 0.62 (Poszwa et al. 2000). The original data from Aubure suggest enhanced uptake of Ca when compared to LP. The needles contained 200 - 500 meq.kg⁻¹ of Ca at Aubure but only 40 - 200 meq.kg⁻¹ at LP. The LP values correspond to significant differences of (Sr:Ca)*1000 ratios, as was also observed in the soil solution (see *Soil solution*).

5.1.2.3 Litterfall

The concentrations of elements entering the forest floor through litterfall were calculated from the average concentrations of elements in fresh leaves in autumn for beech and in the 4-year-old needles for conifers.

The annual input of all monitored elements through litterfall to the forest floor was generally of similar magnitude to their throughfall fluxes (Table 17). The annual throughfall flux represents the majority of the total annual elemental flux to the forest floor in the case of K, Mg, Al and Fe as it amounts for 75, 66, 63 and 55%, respectively.

Table 17 Elemental fluxes to the forest floor through the litterfall

element	unit	litterfall beech	litterfall spruce	litterfall input	avg. throughfall input
Be	meq.m ⁻²	0.003	0.009	0.006	0.002
Mg	meq.m ⁻²	9	10	9	18
Ca	meq.m ⁻²	37	48	42	29
Sr	meq.m ⁻²	0.065	0.074	0.069	0.029
Ba	meq.m ⁻²	0.046	0.053	0.050	0.022
K	meq.m ⁻²	12	14	13	39
Mn	meq.m ⁻²	3.0	9.1	6.0	5.2
Fe	meq.m ⁻²	0.3	0.8	0.6	0.7
Al	meq.m ⁻²	0.8	3.4	2.1	3.5

The litterfall elemental flux represented more than 70% of annual flux to the forest floor in the case of Be, Sr and Ba (Table 17). Litterfall also made up the majority of the input to the forest floor for Ca (59%) and Mn (54%).

The domination of throughfall flux over litterfall in case of K and Mg was due to intensive leaching of these elements from the canopy. The decreasing concentrations of K and Mg with time in the living (fresh) tissues support this idea (Table 9).

The elemental flux in spruce litterfall exceeded that in beech throughfall for all measured elements. Although the litterfall fluxes of Mg, Ca, Sr, Ba and K were nearly comparable in the two canopy types the litterfall fluxes of Al, Mn, Be and Fe were considerably greater in the spruce stands. Previously reported annual litterfall Be fluxes (Veselý et al. 2002) of beech (39 $\mu\text{eq.m}^{-2}$) and spruce (30 $\mu\text{eq.m}^{-2}$) at LP were reevaluated using a more robust dataset. Significantly lower annual litterfall fluxes (3 and 9 $\mu\text{eq.m}^{-2}$) of Be were determined in this study, in part through the use of dry weight instead of fresh weight for the canopy.

The increased litterfall flux of Al in spruce may result from the replacement of exchangeable Ca by toxic Al on the cation exchangeable complex of the forest floor (Miller et al. 1993).

5.1.2.4 Forest floor and mineral soil pools

The soil pools (Table 16) of the II.A group elements are by far the largest pools in the ecosystem. The average concentrations of the elements in soil were calculated from weighted averages in individual horizons. The average concentration of total Be in the soils of LP catchment (1.50 meq.kg^{-1}) was slightly higher than the world average for soils (Drury et al. 1978). Beryllium must thus be readily mobilized from LP soils, which were derived from Be-rich bedrock (3.50 meq.kg^{-1}). The average concentration of total Mg (233 meq.kg^{-1}) in soils of LP catchment was 2.5 times lower than the typical Mg content in soils on granites (Beneš 1994). Similarly the average total concentration of Ca (179 meq.kg^{-1}) in LP catchment soils was 2.5 times lower than the usual Ca content in soils on granites (Beneš 1994). Total concentrations of Sr (2.9 meq.kg^{-1}) and Ba (5.4 meq.kg^{-1}) were 1.4 and 2.2 times smaller than typical concentrations for soils on granites (Beneš 1994). With respect to concentrations of the II.A group in LP bedrock the soil was depleted in Be (2.4 times), Ba (3.6 times), Ca (2.2 times) and Sr (2.3 times), whilst the total concentrations of Mg were comparable.

The concentrations of elements in labile or mobile forms are more important with respect to studies of fluxes and forest dynamics than the total concentrations. The acid leachable (0.1 M HNO_3) concentrations for each element of the II.A group were determined at 8 locations in the LP catchment (Figure 11 - Figure 15). The main differences between patterns of the II.A group element concentrations in these profiles were found in top 20 cm of the soil profiles.

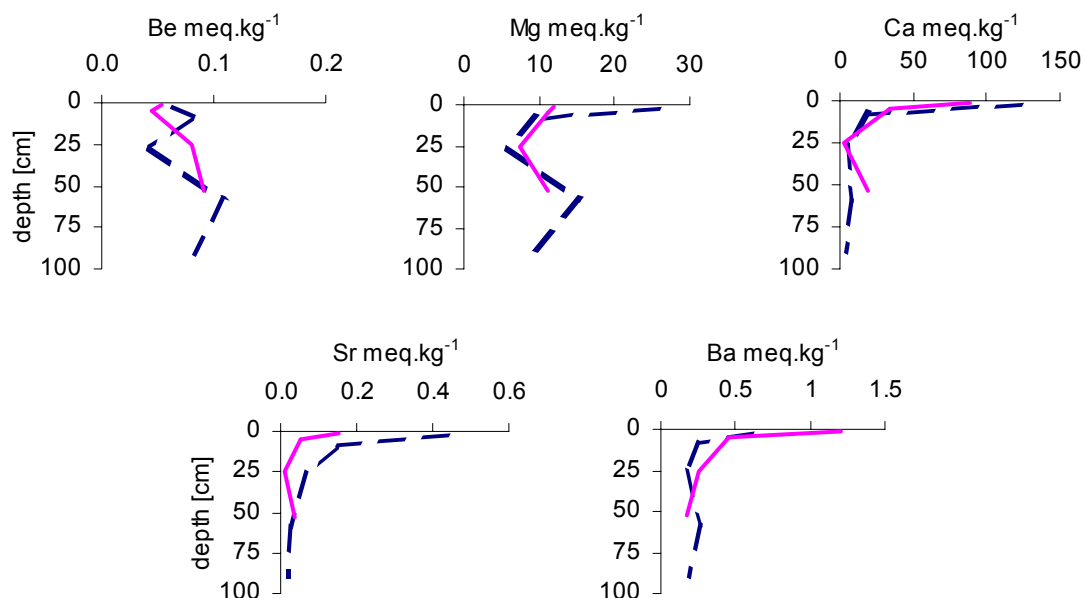


Figure 36 Differences of II.A leachable concentrations in soil below beech (dashed) and spruce (solid) canopies

The acid leachable fraction of Be was in the range of 4 to 50% of its total content in soils of the LP catchment. The acid leachable fraction of Be in topsoil horizons of LP catchment were lower than those found in Ap horizons of Czech agricultural soils (Podlešáková et al. 1994). Lower leachable Be concentrations in the forested ecosystem (LP) topsoil are due to its lower soil pH as well as the increased acidity of throughfall relative to bulk deposition. Additionally removal of Be may also be enhanced by the low pH of soil solutions in upper horizons, which favors Be mobilization. Another possible explanation for the rapid removal of Be from the O and A horizons stems from the solubility product of Be oxalate (Table 18), which may be the highest of the II.A group oxalates. Acid leachable concentrations of beryllium increased with soil depth, similarly to those of Na and Mg (Annexes, Table 30). The positive correlation of Be with Na leachable concentrations is perhaps a result of their similar main weathering source – plagioclase. This increasing acid leachable Be concentration with depth suggests a rapid mobilization of Be from top to bottom of soil profiles and consequential export from the catchment in streamwater. There was no significant difference in leachable Be concentrations or trends in soil below beech and spruce canopies (Figure 36). There was a strong positive correlation of Be and Mg (Annexes, Table 30) probably due to their similar incorporation in secondary minerals, and also due to minor enrichment of Mg in the O horizons. The acid leachable Al and Be concentrations were statistically unrelated similarly to the exchangeable concentrations of Al and Be reported by Veselý et al. (2002). Additionally the weak correlation of acid leachable Be and soil depth was similar to the weak correlation of exchangeable Be and soil depth (Veselý et al. 2002).

Table 18 Solubility constants of the II.A group oxalates

	formula	K_{sp}
beryllium oxalate	BeC_2O_4	freely soluble
magnesium oxalate	MgC_2O_4	9.6×10^{-5}
calcium oxalate	CaC_2O_4	1.9×10^{-9}
strontium oxalate	SrC_2O_4	6.0×10^{-8}
barium oxalate	BaC_2O_4	1.6×10^{-7}

Sources: James & Lord (1992)
Fairhall (1960)

The slightly increased Mg concentration at the top of the soil profile may originate in the freshest litterfall material. The concentrations of Mg in the O horizon are lower than those at the deeper horizons, contrary to the pattern for Ca and Sr. Lower concentrations of Mg in the topsoil indicate that Mg is perhaps mobilized faster than Ca, Sr and Ba from the O and A horizons to lower soil horizons. Moreover, magnesium is leached throughout the growing season from the tree canopy (see *Assimilatory organs*). During and after decomposition of the

organic material the residual Mg in litter becomes available for uptake or transport throughout the soil profile. The O horizon of soil below spruce canopy contains significantly lower acid leachable concentrations of Mg (Figure 36), than that below beech, possibly due to significantly lower Mg concentrations found in the spruce canopy (Table 9) or due to slower decomposition of the spruce litterfall.

The leachable concentrations of Ca are similar to those of Mg from 25 cm depth to the bottom of the soil horizon. Calcium content is greatly enriched in the O layer. This enrichment is due to the high abundance of Ca in the organic material (mainly assimilatory organs) in the upper soil horizons and also due to Ca immobilization. Calcium, Sr and Ba are present in the canopy predominantly as oxalates (Wytenbach et al. 1995, Skřivan et al. 2002). Calcium oxalate is the least soluble oxalate of the II.A group (Table 18), thus it is significantly retained in the O horizon. The leachable Ca concentrations in soil below beech and spruce canopies were comparable, except for a slightly higher concentration in the O horizon of beech (Figure 36). This similarity is probably a result of low Ca mobility due to the low solubility of Ca oxalate (Table 18). The positive correlation of leachable Ca concentrations with Sr, K, C(ox), N(t), Mn and Mg (Annexes, Table 30) is a result of the linkages of these parameters with biogeochemical recycling and decomposition of organic material in the soil.

A significantly higher proportion of Mg is non-mobile in the O and A layers than that of Ca. This was implied from the higher total Mg:Ca ratio in soil relative to the Mg:Ca ratios in the leachable and exchangeable fractions (Figure 37). This surplus of Mg in total soil demonstrates its depletion and preferential removal from leachable and exchangeable Mg soil pool (probably in the upper soil layers) as also reported by Norton et al. (1999).

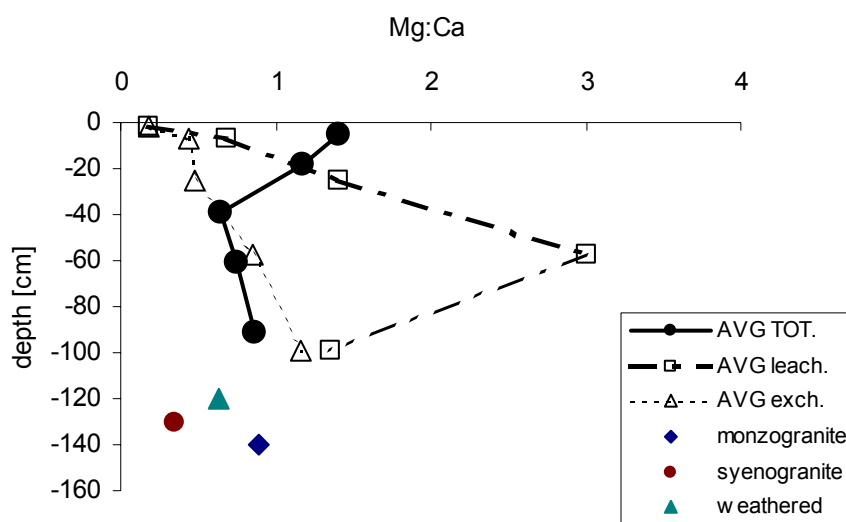


Figure 37 The Mg:Ca ratios in the LP catchment soil profile

The slight increase of the Mg:Ca ratio from weathered bedrock (0.63) to the deepest soil horizon (0.87) indicates preferential release of Ca from the bedrock.

The increased ratios of Mg:Ca (>1) in soil are primarily a result of higher Mg leachable concentration over that of Ca. This surplus of Mg is perhaps due to formation of chlorite or some other secondary mineral. At three analyzed profiles chlorite was the most abundant secondary mineral between 20 and 50 cm depth (Žigová – unpublished data). The Mg:Ca ratio is lowest in the O and A horizons of the soil because of the low ratios in litterfall (beech leaves in October had Mg:Ca ~ 0.25, and 4-year old spruce needles had Mg:Ca ~ 0.19). The increasing exchangeable Mg:Ca ratio toward the bottom of the profile is a result of gradual Ca depletion with depth. At the bottom of the profile the exchangeable and leachable fraction ratios were similar (Figure 37) perhaps because both fractions were governed by the CEC.

The concentrations of leachable Sr followed very similar patterns throughout the soil profile as Ca. The differences in distribution of Ca and Sr throughout the soil profile were evaluated by means of the ratio (Sr:Ca)*1000 (Poszwa et al. 2000). The soil profile LP35 (Figure 38) was selected for comparison of the (Sr:Ca)*1000 ratio distribution due to the availability of a complete dataset on total (this work), acid leachable by 0.1 M HNO₃ (this work) and exchangeable with 0.5 M NH₄NO₃ (Skřivan - unpublished) Sr and Ca concentrations. The soil profile can be divided into two stages. The first stage includes the O and A horizons which have the characteristic sequence of (Sr:Ca)*1000 ratios total < acid leachable < exchangeable. Low total (Sr:Ca)*1000 ratios in the O and A horizons result from the high Ca concentration in the fresh organic material. The (Sr:Ca)*1000 ratio in the O horizon of 1.07 is controlled by the ratio in leaves (1.31) at site LP35. A very slight increase of the total (Sr:Ca)*1000 ratio in the A horizon is due to increased mixing with soil particles from the lower horizons with increased ratio values. The difference between (Sr:Ca)*1000 ratio in the leachable fraction was lower than that in the exchangeable fraction due to the higher Ca concentration in the leachable fraction; the Sr concentration was similar in each. This suggests that nearly all of the available Sr is present on the cation exchange complex, and that Ca may have an additional source (apart from the cation exchange complex) in leaching of the organic material or other soil particles (i.e. secondary or unweathered primary minerals).

The second stage of the soil profile typically has the sequence of (Sr:Ca)*1000 ratios exchangeable < acid leachable < total, opposite that of the first stage. Values of the total (Sr:Ca)*1000 ratio in horizons AB and Bv may be derived from mixing of material from the top and bottom layers. The possible depletion of Ca in these layers arises from the preferential mobilization of Ca during mineral weathering. The total ratio (Sr:Ca)*1000 found in the

bottom Bc horizon is controlled by the (Sr:Ca)*1000 ratio of the weathered bedrock (Figure 38). The gradual increase of the total (Sr:Ca)*1000 ratio with depth was caused by a gradual decrease in total Sr but a much more rapid decrease in total Ca concentrations. The excess Sr concentration over Ca is perhaps due to a higher proportion of unweathered orthoclase over partly weathered plagioclase or due to its slower leaching. The gradual decrease of leachable and exchangeable (Sr:Ca)*1000 towards the bottom of the profile was especially due to increasing Ca concentrations on the CEC supplied from weathering but constant or decreasing Sr concentrations.

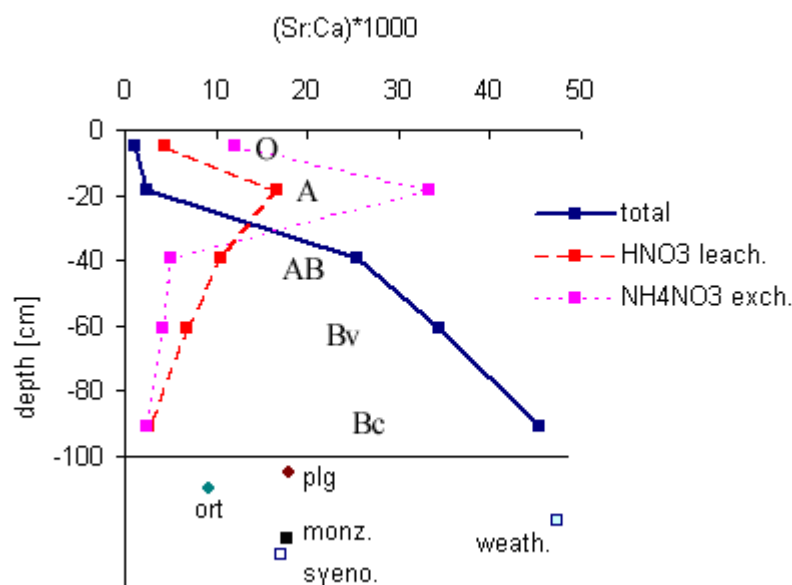


Figure 38 Ratio (Sr:Ca)*1000 through LP35 profile and in the LP bedrock

The lowest variation and lowest mean values (2.9) of the leachable (Sr:Ca)*1000 ratio were found in the O horizon of 8 profiles throughout the catchment. The mean leachable (Sr:Ca)*1000 ratio increased significantly from between 0 and 10 cm of the profile primarily due to preferential leaching of Sr from decomposing organic matter. This preferential leaching of Sr is caused by higher solubility of Sr oxalate (Table 18) relative to that of Ca oxalate. The acid leachable (Sr:Ca)*1000 ratio stays almost constant to the depth of 30 cm and then progressively decreases with depth to the bottom of the soil profile (Figure 39).

The leachable (Sr:Ca)*1000 ratios found in soil in beech stands was significantly higher than those found in spruce stands (Figure 39). This is consistent with the (Sr:Ca)*1000 ratios found in the tree compartments, where beech contained higher (Sr:Ca)*1000 ratios than spruce (see *Biomass*). This is due to significantly higher leachable concentrations of Sr found in soils in beech stands (especially in the upper horizons) (Figure 36).

The positive correlation of leachable Sr concentrations with Ca, K, C(ox), N(t) and Mn (Annexes, Table 30) is a result of the linkages of these parameters with biogeochemical recycling and decomposition of organic material in soil, as in the case of calcium.

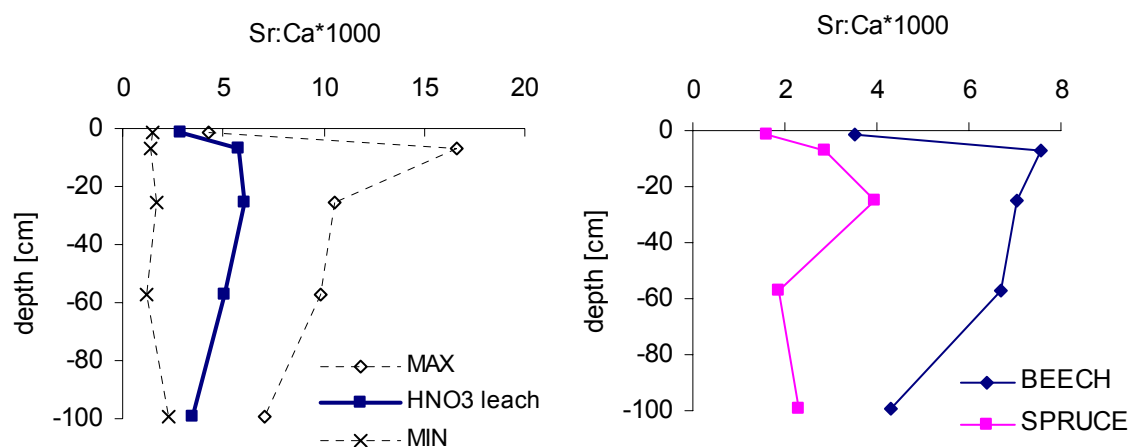


Figure 39 Ratio of average acid leachable (Sr:Ca)*1000 in soils of LP catchment and for sites with various afforestation

The pattern of Ba throughout the soil profile followed similar patterns as the essential elements of the II.A group - Ca and Sr. The high concentrations of leachable Ba in the top horizons of the soil were due to supplementary Ba in the assimilatory organs. Beech stand soils contain on average less leachable Ba than soils in spruce stands (Figure 36), perhaps due to the high concentrations of Ba in litterfall (Table 17). The enrichment of Ba in the O horizon was not as pronounced as in case of Ca and Sr, a result of the higher Ba-oxalate solubility in comparison to the oxalates of Ca and Sr. Thus barium may be mobilized more rapidly from decomposing organic material and its higher concentrations in soil solution (see *Soil solution*) in comparison to those of Sr support this idea.

5.1.2.5 Soil solution chemistry

Soil solution chemistry was studied only in beech stands (sites LP35 and LP6 see Figure 6). The most important difference between the two sampling sites was soil organic matter content (Table 10), which caused contrasting soil solution DOC concentrations. The throughfall solutions deposited to the forest floor undergo a number of processes after infiltration into the soil. Usually the soil solutions become more concentrated due to evaporation but they may also be affected by adsorption, ion exchange reactions, and other processes.

The most significant difference in the average concentration of elements sampled at the same depth at each site was found for H, K and NO_3^- (Table 11). The concentration of H^+ was greater at the high-organic profile LP35, due to increased production of organic acids. The lower K and NO_3^- concentrations at site LP6 may be explained by lower biological activity

associated with the lower organic content at this site. Manganese concentration was considerably greater at location LP6 because of higher acid leachable Mn concentrations at that site. Aluminum concentration in soil solution was greater at site LP35 because of significantly higher DOC concentrations. A high concentration of DOC in soil solution induces a lower pH, which enhances Al complexing with organic acids (Hruška et al. 2001).

The differences in mean concentration of elements in throughfall and O horizon soil-water at both sites followed similar patterns. The elements with the greatest positive concentration change from throughfall to soil solution were Fe, Al, Be and Ba. The concentration of these elements increased by at least 800% after the throughfall infiltrated the top 5 cm of soil. The concentrations of Sr also increased sharply (500%) in soil solution when compared to throughfall. Calcium concentrations remained the same from throughfall to soil solution at the LP6 profile poor in organic material while Ca concentration approximately doubled at the organic-rich profile LP35.

The concentrations of most elements in soil solution increased with depth, except for K and Fe, which decreased with depth. High concentrations of K in shallow soil solution were caused by the high content of organic material, which contains high concentrations of labile K. The concentration of K at both profiles decreased with depth perhaps due to adsorption of K onto the cation exchange complex or due to loss of K on behalf of the secondary minerals. The decrease of Fe with depth is most probably due to precipitation of Fe hydroxides in the B horizon and related loss of DOC (which complexes Fe) from solution.

Beryllium concentrations in soil solution increased with depth, in keeping with the increasing concentrations of leachable Be with depth in soil profiles at the LP catchment. Similar patterns of increasing Be concentrations with depth were also detected at Lysina catchment in the western part of CR (Krám et al. 1998). Beryllium concentrations in soil solutions at Lysina were lower than those at LP mainly due to the lower abundance of Be in soils and bedrock (Navrátil 2000). Contrary to Al, higher Be concentrations were observed at a profile with lower DOC concentrations in soil solution, which suggests that Be and DOC may not be correlated (Annexes, Table 26).

Magnesium concentrations found in soil solution from all horizons of LP catchment were higher than those reported from base poor Lysina catchment in the western part of CR (Krám et al. 1997). Magnesium concentrations at LP were two fold higher in the O horizon and nearly 4 fold higher in the B horizon than those at Lysina, as a result of significantly lower Mg concentration (10 times) in the Lysina bedrock. Throughfall solutions contain significantly elevated Mg concentrations from canopy leaching (see *Throughfall*) and due to

this some Mg may be lost to the topsoil cation exchange complex which is significantly unsaturated in exchangeable Mg (Figure 37). The increased Mg:Ca ratio in the lower A horizon suggests a slight increase of Mg on the cation exchange complex of A horizon soils (Figure 37). A similar decrease of concentration from throughfall to O horizon soil solution at both sampling sites was noted for Mn, but unlike Mg, Mn concentration continued to decrease with increasing depth in the profile.

Calcium concentrations in throughfall increased slightly after infiltrating the first 5 cm of soil and then more sharply after passage through another 10 cm of soil (Table 11). The cation exchange complex of the top 5 and 15 cm of soil is more saturated with Ca in comparison to Mg so there is more Ca available for leaching. In spite of their contrasting behavior in soil solution with respect to throughfall, Mg and Ca concentrations in soil solution had a strong positive correlation (Annexes, Table 26). The relationship of Ca and Mg concentrations (Figure 40) was clearly affected by the loss of Mg from solution in the first 5 cm of the soil profile. However at 45 cm depth at site LP6 the concentrations of Ca and Mg had a ratio close to 1:1 (solid line).

This ratio was perhaps affected by the extreme Mg:Ca ratio (10.2) in the B layer of the LP33 profile, which is significantly enriched in acid leachable Mg (Table 10). The low acid leachable Mg concentrations in layer Go of the LP6 profile suggest that favorable conditions exist for Mg leaching and its consequent mobilization into deeper layers of the LP6 profile. This mobilization of Mg towards the bottom of the profile may have caused an enrichment of acid leachable Mg concentrations in layers below G₀ (Table 10).

Calcium concentrations in soil solution from 5 cm depth at LP catchment (beech stand) were comparable to those at Lysina (spruce stand). However, calcium concentrations in the lower horizons of the LP catchment were approximately 3 fold higher. This difference is attributed to the virtually complete depletion of exchangeable BC (mainly Ca) of the extremely base poor soils (especially the lower horizons) at Lysina. The major decrease of soil base saturation with depth to ~ 5% at Lysina (compared to ~ 14% at LP) had several possible causes: lower content of BC in the bedrock, spruce monoculture (highly acidic throughfall, slow decomposition of litterfall), almost double annual precipitation (greater flushing of soils), and lower annual average temperature (slower weathering rates to re-supply cations).

The upper horizons are supplied with Ca from the litterfall and dry atmospheric deposition. Toward the bottom of the profile, Ca is usually lost from soil solution due to biological uptake or leaching and may be replaced in solution by soluble Al. The increase of Ca concentration

in soil solution with depth at LP catchment is probably due to the larger pool (2 times bigger) of Ca in the soils and bedrock and the less intensive acidification of LP soils.

The increasing concentrations of Sr in soil solution with depth are a result of the increasing acid leachable Sr concentration in LP catchment soils with depth (Figure 14). A linear relationship of Ca and Sr concentrations (Figure 40) was found in LP soil solution, similar to observations from other sites with granitic bedrock (Poszwa et al. 2000). The mean ratio of (Sr:Ca)*1000 (2.84) in soil solution at LP catchment was much higher than the ratio at the Aubure granitic catchment (Poszwa et al. 2000). This work reported a comparable ratio to LP soil solution from the site Lutry (planted with spruce) on calcareous quaternary sediment ('molasse') (Poszwa et al. 2000). The difference between the two granitic sites (Aubure and LP) is a result of lower Ca concentration and higher Sr concentration in the LP soil solution. The concentrations of Sr and Ca in soil solution are comparable to those from Lutry, however due to lack of data (Poszwa et al. 2000) on bedrock and soil composition it was not possible to make detailed conclusions.

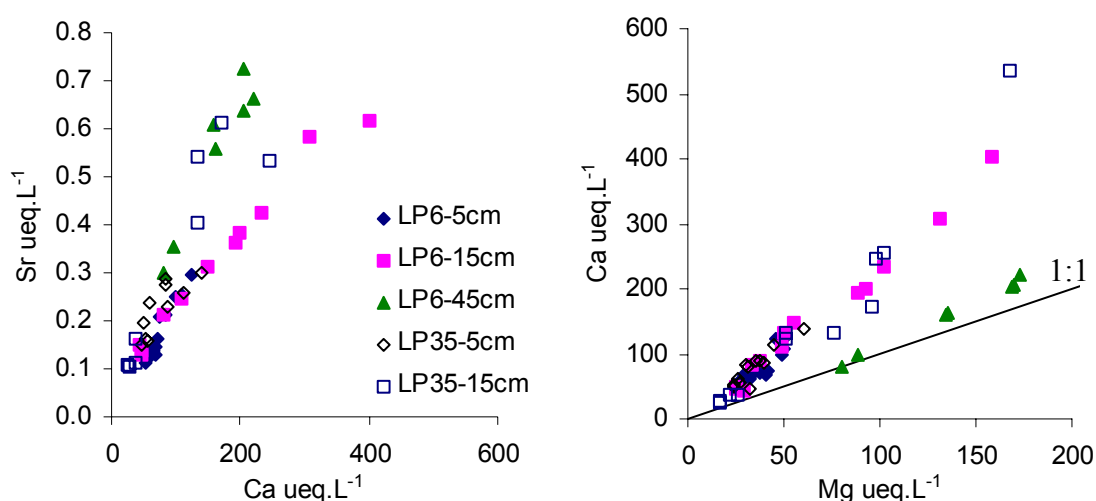


Figure 40 Relationship of Ca vs Sr concentration and Mg vs Ca concentration in soil solution at LP catchment

Barium concentrations in soil solution were significantly lower than theoretically calculated equilibrium Ba concentrations with respect to $K_{sp}(\text{BaSO}_4)$. This was perhaps due to a different solid phase controlling the solubility and/or adsorption of Ba. There probably is no solid phase of Ba less soluble than BaSO_4 in the LP soils, so Ba concentration is probably controlled by ion exchange and sorption reactions (Palmer 1999). The mean Ba concentrations in soil solution were greater than those of Sr, suggesting that Sr concentration is controlled by oxalate. Barium oxalate is more soluble than Sr oxalate (Table 18), which explains the higher concentrations of Ba over Sr.

5.1.3 Losses from watershed ecosystem

5.1.3.1 Losses in stream water – concentrations, trends and patterns

The categorization of discharge conditions according to the actual stream discharge was potentially misleading in terms of the stream chemical response. For example, a summer rainstorm with initial discharge $0.05 \text{ L}\cdot\text{s}^{-1}$ and peak discharge $0.25 \text{ L}\cdot\text{s}^{-1}$ would be considered a low discharge condition in the context of the annual hydrograph, however its chemistry corresponds to an episodic event situation. For this reason, the concentration of Fe was selected as an indicator of high flow, low flow or base flow in the LP stream. Streamwater chemistry at low discharge was very similar to shallow groundwater chemistry (Table 19). The episodic events mask the groundwater signal in the surface water with more surficial flow. During events pH decreased and concentrations of Ca, Mg, Al, Be, SO_4^{2-} , F^- , and NO_3^- increased. Concentrations of Na, Cl^- , SiO_2 , Fe and Mn decreased as a result of dilution. The increase of Be and Al concentrations during the episodic events was reported by Navrátil 2000.

Table 19 Average pH and solute concentrations of LP surface water at three flow regimes determined according to Fe concentrations during the monitored period 1994 - 2001

		data for 1994 - 2001			groundwater
		lowest 25%	central range	highest 25%	
Q	$\text{L}\cdot\text{s}^{-1}$	4.84	2.11	0.09	
pH		4.77	4.90	5.56	6.69
H^+	$\mu\text{eq}\cdot\text{L}^{-1}$	17.1	12.5	2.8	0.2
Be	$\mu\text{eq}\cdot\text{L}^{-1}$	1.51	1.33	0.76	0.05
Mg	$\mu\text{eq}\cdot\text{L}^{-1}$	666	620	578	416
Ca	$\mu\text{eq}\cdot\text{L}^{-1}$	1026	921	937	1205
Sr	$\mu\text{eq}\cdot\text{L}^{-1}$	3.9	3.4	3.2	2.4
Ba	$\mu\text{eq}\cdot\text{L}^{-1}$	0.59	0.53	0.77	0.43
Na	$\mu\text{eq}\cdot\text{L}^{-1}$	349	377	445	653
K	$\mu\text{eq}\cdot\text{L}^{-1}$	43	43	45	25
Mn	$\mu\text{eq}\cdot\text{L}^{-1}$	6.5	8.5	20.2	31.3
Fe	$\mu\text{eq}\cdot\text{L}^{-1}$	2.5	7.3	49.7	246.4
Al	$\mu\text{eq}\cdot\text{L}^{-1}$	73.6	62.3	40.5	0.9
F^-	$\mu\text{eq}\cdot\text{L}^{-1}$	41	39	37	16
Cl^-	$\mu\text{eq}\cdot\text{L}^{-1}$	161	172	189	126
SO_4^{2-}	$\mu\text{eq}\cdot\text{L}^{-1}$	1700	1639	1529	930
NO_3^-	$\mu\text{eq}\cdot\text{L}^{-1}$	94.7	51.4	14.2	5.2

The concentration of SO_4^{2-} in the LP surface water is decreasing rather slightly over time. During the last 4 years the total output of SO_4^{2-} was two times the input. Much of the sulfate deposited during the period of heavy acid deposition (until 1999), which was adsorbed on the acid soils due to the enhanced adsorption in acid conditions (Nodvin et al. 1986), is more

recently being exported from the catchment. The enhanced export of sulfate from the catchment over time (with respect to its decreasing inputs to the catchment) is a result of decreasing pH of the throughfall deposition and consequent increase of soil solution pH.

The LP surface water has a relatively high ionic strength due to a combination of chemical weathering and high evapotranspiration in the catchment. The hydrological situation of the catchment has a direct influence on the water chemistry (Table 19). Concentrations of Be, Mg, Ca and Sr were higher during situations with increased discharge (Table 19). The reasons for such increase of each element are different.

The enhanced mobility of beryllium reflects the presence of unbuffered H^+ ions (decreased pH), whose concentration in surface water increases with increasing discharge. The concentrations of metals including Al and Be increase during high flows (Table 19, Figure 41) and their export is enhanced.

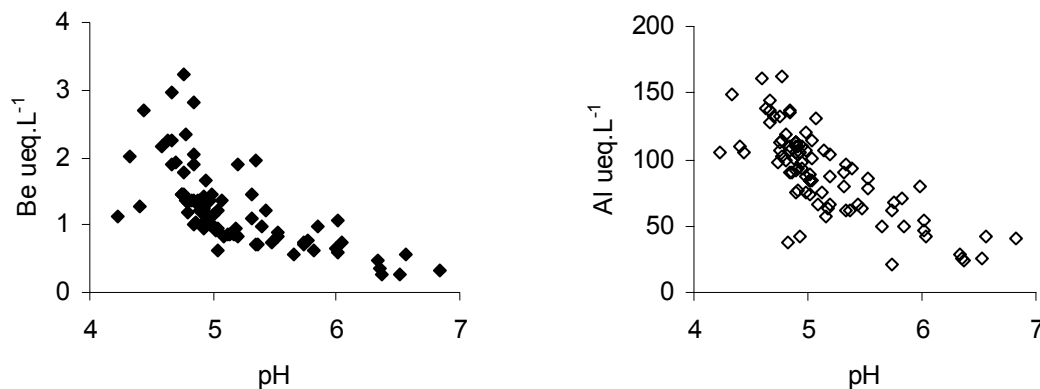


Figure 41 The pH dependence of Be and Al concentration in LP surface water

The acidification of catchments results in enhanced Be export. This result is consistent with other experimental studies (e.g. Kaste 1999, Navrátil 2000, Veselý et al. 2002). Beryllium correlated strongly with concentrations of Al, probably due to the similarity of their charge-to-ionic radius ratio (64.5 and 60.0 nm^{-1}) (Krám et al. 1998), their similar behavior under decreased pH conditions, and their similar tendency to bond with F^- in the aquatic environment.

Calcium and Mg in surface water effectively neutralize H^+ ions. Less Be is exported as more H^+ that is neutralized by Ca and Mg. The slight increase of Ca concentration during low flow situations is a result of the shallow groundwater signal in the stream. The shallow groundwater contains lower concentrations than streamwater in all flow classes for all of the II.A group elements except Ca. Decreasing values of the Mg:Ca ratio (Figure 42) through

time possibly represent lower export of Ca due to decreased acid deposition or increased adsorption of Mg in the cation depleted soils of the LP catchment.

Strontium in surface water behaves in a manner very similar to Ca, due to their similar hydrated ionic radii (Table 1). However, the correlation of Ca and Mg in surface water is stronger than that of Ca and Sr (Annexes, Table 27).

The high barium concentrations in LP surface water were a result of its high solubility, which was greater than the theoretical concentration corresponding to the K_{sp} of $BaSO_4$. The elevated Ba concentrations may be explained by streamwater acidity, as K_{sp} is calculated for circumneutral pH. An example of an environment where $BaSO_4$ solubility controls Ba concentrations is the shallow groundwater with pH ~ 7 . The positive correlation of Mn and Fe concentrations in surface water with those of Ba (Table 27) may be due to the adsorption of Ba onto Mn or Fe hydroxides. The dissolution or mobilization of Fe and Mn under appropriate conditions (low flow, low Eh) from these hydroxides would also enhance Ba concentration and mobility.

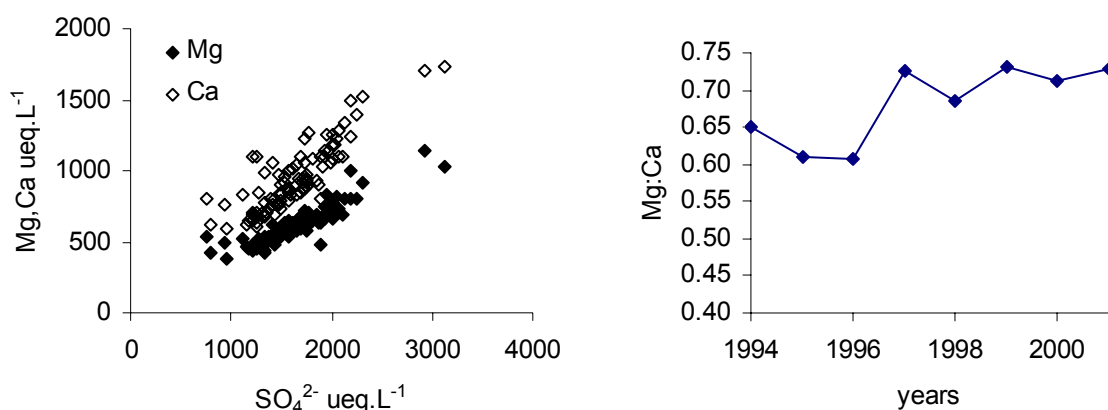


Figure 42 The relationship of Ca and Mg with SO_4^{2-} in LP streamwater and the Mg:Ca ratio through time in LP streamwater

The annual volume weighted concentrations of Be, Mg, Ca and Sr have decreased during the monitored period (Table 12). It was impossible to evaluate the trend for Ba concentration due to short duration of monitoring. The reason for the observed decrease of concentrations differs for each element, although the general reason is the decrease in acid deposition. Mean beryllium concentrations decreased annually according to the change of mean streamwater pH. The strong correlation of Ca and Mg with SO_4^{2-} concentrations demonstrates their neutralizing role (Table 27), as sulphuric acid is still the main acidifying agent of the atmospheric input.

5.1.3.2 Implications from the acidification experiment

The results of the acidification experiment suggested that an increase in stream acidity might simulate long term processes, e.g. sulfate adsorption during the acidification and its subsequent release or the depletion of base cations, leading to catchment acidification (Norton et al. 1999) (Figure 23).

The SO_4^{2-} behavior is dominated by pH-related changes in anion exchange capacity, with adsorption increasing at lower pH. During the recovery stage, desorbed SO_4^{2-} was released from the stream substrate (Figure 43). This experiment supports the conclusions from Hruška et al. (2002) who examined the release of SO_4^{2-} from other catchment in CR. In general, atmospheric deposition rates of SO_4^{2-} have decreased in Europe and North America. Excess SO_4^{2-} in soils and stream sediment is now being desorbed and exported from many catchments. At LP catchment the export of SO_4^{2-} did not increase after the decrease of atmospheric acidity in 1999. This may be due to variable loading (in contrast to the constant loading in the experiment), but the output of SO_4^{2-} from the catchment is higher than its current input in throughfall (Annexes, Table 22).

Sodium behaved contrary to Ca, Mg, and K. The long-term concentration of Na correlates negatively with discharge (Table 19) but was unaffected in the experiment. High discharge events normally slightly enhance the export of K from the catchment but the difference between the mean K concentrations for low and high discharge is small (Table 19). The concentration of K changed less than $1 \mu\text{eq.L}^{-1}$ from the background value. Sodium and K were relatively unaffected by in-stream processes during the acidification experiment due to low exchangeable concentrations on the stream substrate (Table 13).

Beryllium, relatively to its streamwater concentration, was one of the most mobilized metals during the acidification experiment. Its concentration increased throughout the experiment, in contrast to all other II.A group elements, which decreased in concentration between 120 and 250 minutes of the experiment. The contribution of Be to neutralization was trivial. The long-term correlation of Be and Al in streamwater was retained during the experiment (Annexes, Table 28).

The typical positive correlation of Ca and Mg with concentrations of SO_4^{2-} was not present during the acidification experiment. Instead, Ca and Mg were positively correlated with Cl^- , which became the main acidifying anion (Annexes, Table 28). The long-standing positive correlation of Ca and Mg in streamwater was retained during the experiment (Figure 25, Table 28).

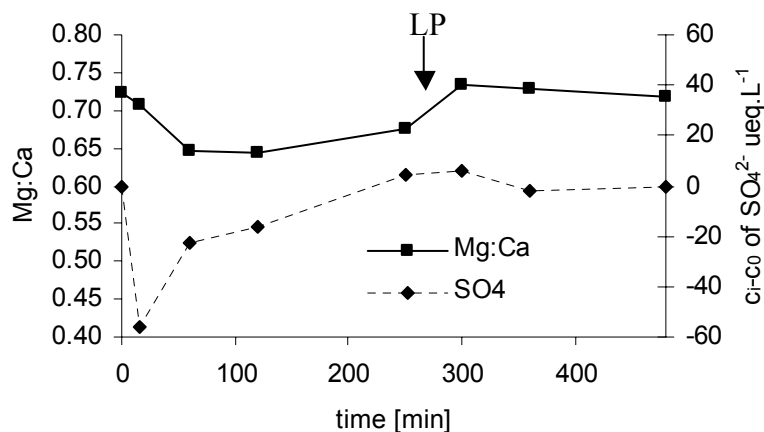


Figure 43 Changes of Mg:Ca ratio and SO_4^{2-} concentration at point C during the acidification experiment

The range of the Mg:Ca ratio (0.64 – 0.73) during the experiment is within the range of the Mg:Ca ratio (0.45 – 0.78) determined during the 7 years of monitoring the LP catchment. During the initial phase of the experiment, release of the divalent base cations Ca and Mg was the most important component of the acid neutralization. As this reservoir became depleted, release of Al contributed more to the neutralization of the acid input. This mechanism is typical for chronically acidified streams draining catchments with low buffering capacity of the bedrock or stream sediment. The Mg:Ca ratio was the lowest at 1 to 2 hours, indicating Ca desorption in greater proportion than Mg from the stream substrate (Figure 43).

The highest Mg:Ca ratio occurred at 5 hrs, representing the start of the Ca and Mg re-adsorption during the recovery stage. At 5 hrs (Figure 43), Mg was re-adsorbed in greater proportion to its stream concentration than was Ca. Two hours after the acid addition stopped, Ca and Mg concentrations started to slowly increase (Figure 26). Although the Mg:Ca ratio recovered to its original value by the end of the experiment, the concentrations had not. The rate of recovery was slower than the rate of mobilization of base cations during the acidification phase.

Barium was most likely associated with the dissolution of phases rich in Al, Mn and Fe. The correlation of Ba and Be supported this idea (Table 28). No re-adsorption of Ba and Be was detected during the recovery stage (Figure 26) contrary to Ca, Mg and Sr. A possible explanation for this is the differing sources of solutes released from the stream substrate. The released Ca, Mg and Sr were mostly bound to the cation exchange complex sites of the stream substrate, where they started to re-adsorb during the recovery stage (Figure 26). But release of Be and Ba was most probably associated with dissolution of some solid phase, a process that is generally not reversible, thus no re-adsorption was observed. The correlation of both Be

and Ba with concentrations of Fe, Mn, Al and F^- suggests that the dissolving solid phase may be Mn, Al or Fe oxy-hydroxides. The affinity of Ba to Mn hydroxides is well known (Puchelt 1967) but association of Be with Al hydroxides is anticipated due to their similar behavior during the experiment and in the long-term streamwater chemistry.

5.1.4 Comparison of biogeochemistry of the II.A elements

The enrichment factors enable comparison of the relative abundance of elements in each solution, solid phase or tree compartment present in the studied ecosystem.

Beryllium starts enriching after infiltrating the soil column (Table 20). The most significant increase in the Be enrichment factor occurred at 45 cm depth in the soil. Be has the greatest EF in surface water due to chronic acidification of the LP catchment. Beryllium becomes rapidly mobilized in an acidified environment, as has been demonstrated by both long-term and short-term acidification experiments (Kaste 1999, Norton et al. 2000, Veselý 2002, Navrátil et al. 2003).

Magnesium has the highest enrichment factors in both types of throughfall (Table 20) as a result of Mg leaching from the canopy. Loss of magnesium during the first 5 cm of soil infiltration may be a result of selective Mg loss from the CEC of the litter horizon (Norton et al. 1999 and this work). The enrichment factor of Mg at 45 cm is comparable to those of Sr and Ba. The large enrichment factor of Mg indicates that it has a significant export from the catchment.

Table 20 Enrichment factors of elements in solutions of the LP catchment, calculated as mean $c_{\text{(solution in ecosystem)}}/c_{\text{(bulk)}}$ (data 2000 – 2001)

	Enrichment Factor				
	Be	Mg	Ca	Sr	Ba
bulk	1	1	1	1	1
throughfall beech	1	11	4	4	1
throughfall spruce	1	14	5	5	2
soil solution 5cm	8	8	5	10	9
soil solution 15cm	14	14	8	19	11
soil solution 45cm	87	30	9	33	30
surface water	157	112	41	140	13

The significantly increased EFs of Ca (Table 20) in both types of throughfall (similar to those of Sr) suggest a contribution of dry deposition and/or canopy leaching. Slightly increased EFs for Ca in soil solution are a result of soil depletion of Ca. Although calcium is the most exported cation from the LP catchment, its EF in surface water is lower than those of Be, Mg and Sr. The reasons for this may be: a) chronic removal of Ca from the catchment, b) the high concentration of Ca in bulk deposition and c) significant uptake of Ca by biomass.

The significantly increased EFs of Sr (Table 20) in both types of throughfall are similar to those of Ca. The progressive enrichment of Sr in the upper horizons of the soil profile is due to the high solubility of Sr oxalates as the upper horizons contain significant amounts of organic material.

Table 21 Depletion factors of elements in bedrock derived compartments of the LP catchment, calculated as mean $C_{(\text{compartment of ecosystem})}/C_{(\text{bedrock})}$

	Depletion Factor				
	Be	Mg	Ca	Sr	Ba
bedrock	1.0	1.0	1.0	1.0	1.0
soil total	0.2	0.6	0.5	0.4	0.3
soil acid leachable	0.03	0.03	0.02	0.01	0.01
stream sediment total	0.8	0.6	0.7	0.4	0.3
stream sediment leach	0.4	0.2	0.4	0.1	0.0

Although Ba is significantly enriched in soil solution of the LP catchment (Table 20), its enrichment in the surface water is the lowest. Barium is the least exported element of the II.A group from the LP catchment due to the control of dissolved Ba ions by the low solubility product of BaSO_4 in deeper horizons.

The depletion factors (DFs) of catchment solid phases for II.A group elements are < 1 , which suggests gradual exhaustion of the elements with respect to bedrock, and simultaneously ascribes low importance to their atmospheric inputs (Table 21). Depletion factors of total element content in soils imply depletion of II.A group in the order: $\text{Be} > \text{Ba} > \text{Sr} > \text{Ca} > \text{Mg}$. The lowest DF values (the highest depletion) of total soil concentration were found for Be due to its rapid leaching and export from the catchment. Very low DF values were found for leachable soil concentrations as these represent only a small part of the total concentrations.

Considerable DFs of II.A (with the exception of Be) were found for the total stream sediment. Because stream sediment is partly derived from soils, DFs for soils and sediment were similar (Table 21). However DFs of the leachable fraction were significantly higher for the elements that had high export (Be, Mg, Ca and Sr). These increased DFs of the mobile fraction of II.A group elements (except Ba) in surface water were reflecting (or controlling) the concentrations of elements in surface water. The lowest DF of the mobile Ba fraction was due to its low concentration in surface water.

6 Conclusions

The comparative biogeochemical study of II.A group elements has proved to be a convenient and useful tool to understand their *relative* dynamics in a selected experimental landscape. The advantage of this approach is the ability to carry out the research simultaneously at identical physicochemical conditions of the particular ecosystem. The biogeochemical behavior of a chemical element is strongly dependent on numerous factors including the chemistry of the bedrock, precipitation height, precipitation chemistry, mean annual temperature, and type of vegetation cover.

Another advantage of the study was the study site, which is characterized by several convenient features, including a relatively well-defined hydrologic area, bedrock sensitive to acidification, bedrock rich in trace elements (Be, Ba), typical rural site with historically high acid deposition rates, and a simplified forest cover with two dominant tree species.

Bedrock

The abundance of II.A group elements in the bedrock decreased in the order $\text{Ca} > \text{Mg} > \text{Ba} > \text{Sr} > \text{Be}$. The most important source of Be, Ca and Sr is plagioclase. Orthoclase is equally important as a source of Sr and it is the major source of Ba. The highest concentrations of Mg were found in biotite, the only mafic rock-forming mineral present.

Weathered rock was depleted in II.A elements in the following descending order: Ca (54% lower concentration), Ba (40%), Be (31%) and Mg (17%). Surprisingly the concentration of Sr was maintained perhaps due to resistance of orthoclase to weathering and/or the incorporation of released Sr into secondary minerals.

Bulk precipitation

The most abundant cation in bulk precipitation was Ca followed by Mg. The mean bulk fluxes of Ca and Mg decreased after 1999 probably due to lower emissions of Czech industrial dusts into the atmosphere. A strong correlation was present between the fluxes of Ca and Mg in bulk precipitation had a strong positive correlation.

The concentrations and fluxes of Be, Sr and Ba in precipitation were low, especially after the completion of desulphurization of all Czech power plants in 1999.

Throughfall

The concentrations and fluxes of II.A group elements in precipitation change as a result of interaction with tree canopy. The most significant difference between bulk and throughfall fluxes was detected in the case of Mg as it was readily leached from the canopy. This vigorous leaching of Mg is possible due to a different position of Mg (i.e. chlorophyll

molecules) in comparison to other II.A group elements in the canopy. In the case of beech, Mg was the element with the greatest contribution to neutralization of the throughfall solutes. In the case of spruce, the leaching of Mg and other elements was less than the contribution of acidificants (N, S), which resulted in additional acidification of spruce throughfall. Calcium, strontium, barium, and beryllium were leached to a lesser extent due to different position and bonding in the assimilatory organs of the beech and spruce trees. Their concentration and fluxes in throughfall were increased by evapotranspiration and/or washout of scavenged particles, and also by leaching, though leaching was minor in comparison to that of Mg.

Vegetation

The most important flux to the forest floor for all II.A group elements except Mg was litterfall. Because of its high leaching rate, more than 60% of the annual flux of Mg to the forest floor occurs as throughfall. However in the case of Be, Sr and Ba litterfall represents more than 70% of the annual flux to the forest floor. In case of Ca the litterfall flux represents almost 60% of the annual flux to the forest floor.

Significant uptake of toxic Ba was detected, especially in spruce trees. As in the bark and especially the branches of spruce, Ba concentrations (similarly to the soil solution) were higher than those of essential Sr.

Soil

The acid soils at LP catchment are depleted most notably in Ca with respect to the bedrock composition. Elevated leachable (0.1M HNO₃) concentrations of Mg, Ca, Sr and Ba occurred in the organic horizon as a result of biological recycling. The absence of a similar accumulation of Be in the organic horizon suggests its rapid mobilization from the organic material during and after its decomposition. Beryllium leachable concentrations increased downwards in the soil profile due to its rapid mobilization under acid conditions. The leachable concentrations of Mg, Ca, Sr and Ba decreased in the middle part of the profile, then increased just above the bedrock due to weathering inputs.

Lower enrichment factors suggest depletion of II.A group elements in soil (total) with respect to bedrock. The most significant (the lowest EF) is the depletion of Be due to its enhanced mobility in an acidified environment. The least significant depletion was determined for Mg, possibly due to the formation of secondary minerals (e.g. chlorite).

Soil solution

Concentrations of all II.A group elements in soil solution increased with depth. The increase from mean throughfall to soil solution concentrations of the II.A group elements indicated

that Be, Ba and Sr enter soil solution readily. The significant increase of Be and Ba in the first 5 cm of the soil profile was especially due to rapid dissolution or leaching of decomposing organic matter, which is supplied to the forest floor by litterfall. Beryllium, Ca, Sr and Ba are stored in the assimilatory organs of trees in the form of oxalates. The solubility of Be and Ba oxalates is the highest which explains their rapid leaching. Soil solution was the only solution in the catchment that had higher concentrations of Ba than Sr.

Concentrations of Ca in soil solution remained relatively unchanged in comparison to those in throughfall, while Mg concentrations decreased in soil solution. The decrease of Mg was probably caused by cation exchange or biological uptake.

The highest EF of Be found in soil solution from 45 cm suggests rapid leaching of Be in the bottom part of the soil profile due to increasing Be soil leachable concentrations. Low EF values of Ca in soil solution are possibly a result of CEC depletion with respect to Ca or its rapid biological uptake.

Streamwater

The mean annual concentrations of Be, Ca, Mg and Sr in streamwater of LP catchment gradually decreased due to differing reasons. The mean Be concentrations decreased as a result of lower levels of acid deposition and consequential increased pH of streamwater. Concentrations of Ca and Mg decreased due to the decrease of SO_4^{2-} concentration in the streamwater.

The decrease of SO_4^{2-} concentration in turn is due to the decreased acid deposition loading to the catchment.

The concentrations of Be, Mg, Ca and Sr increase during episodic events especially due to concurrently increasing SO_4^{2-} concentration.

Barium concentrations in the streamwater were higher than theoretical equilibrium concentrations calculated with respect to the K_{sp} of BaSO_4 . The excess Ba in the streamwater is probably the result of decreased pH, which has the effect of increasing the K_{sp} of BaSO_4 . The solubility product of BaSO_4 seems to limit the Ba concentrations in the LP circum-neutral shallow groundwater.

Very high EF values of Be, Mg and Sr in streamwater suggest rapid export of these elements with respect to their low concentrations in bulk precipitation. The relatively low EF of Ca for streamwater may result from its highest concentration (from II.A group) in the bulk precipitation or due to a significant sink of Ca in biomass uptake.

The EFs of Be, Mg, Ca and Sr leachable fractions in stream sediment were significantly higher than those in soils. These increased EFs of the mobile fraction of the II.A group

(except Ba) elements in stream sediment reflected the concentrations of these elements in surface water. Ba had the lowest EF of the leachable fraction in sediment, due to its low abundance in surface water and low export rate from the catchment.

6.1 Summary on studied ratios

(Sr:Ca)*1000

The (Sr:Ca)*1000 ratio demonstrated that beech and spruce preferentially take up Ca over Sr. The beech trees were more effective in preferential uptake of Ca similarly to other sites. (Sr:Ca)*1000 ratios from the leachable fractions of soils were elevated in beech stands to a greater extent than in spruce, particularly due to the higher Sr concentration in beech soils. The (Sr:Ca)*1000 ratios of soil solution were significantly lower than those in the soil exchange pool or those in the soil leachable fraction, perhaps as a result of significant Ca dry deposition.

The lowest (Sr:Ca)*1000 ratios in total soil concentrations were found in the topmost layers O and A are the result of preferential Ca uptake (as these layers contain significant amounts of organic material) and also a result of increased solubility of Sr oxalates over those of Ca.

Mg:Ca

High values of total soil Mg:Ca ratios contrast with low Mg:Ca ratios for exchangeable or acid leachable ratios in the upper horizons O and A, suggesting possible preferential removal of available Mg as has been implied by other authors. The low values of the Mg:Ca ratio of the acid leachable and exchangeable soil fractions suggest proportionally increased availability of Ca relative to Mg. The Mg:Ca ratios of soil solution are quite similar to the Mg:Ca ratios of the leachable and exchangeable soil fractions. High Mg:Ca ratios of the leachable fraction in the bottom layers of soil profiles suggest possible formation of secondary minerals containing Mg (e.g. chlorite). The low Mg:Ca ratios of the soil exchange complex support this idea.

Although Ca was preferentially depleted from soils during the high acid deposition period, Mg more rapidly re-adsorbed to stream sediment. The long-term increase of the Mg:Ca ratio in streamwater may indicate the position of the LP ecosystem on the Mg:Ca ratio curve obtained from the acidification experiment and may represent evidence of recovery from acid deposition induced soil acidification.

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7 **Annexes**

Table 22 Annual input and output fluxes of elements at the LP catchment

year	DI mm	pH	H meq.m ⁻²	Be µeq.m ⁻²	Mg meq.m ⁻²	Ca meq.m ⁻²	Sr µeq.m ⁻²	Ba µeq.m ⁻²	Na meq.m ⁻²	K meq.m ⁻²	Mn meq.m ⁻²	Fe meq.m ⁻²	Al meq.m ⁻²	F meq.m ⁻²	Cl meq.m ⁻²	SO ₄ ²⁻ meq.m ⁻²	NO ₃ ⁻ meq.m ⁻²
BULK	1994	666	4.17	45.9	7.4	3.6	16.7		5.1	2.9	0.4	1.7	4.0	1.9	6	58	24
	1995	806	4.21	42.3	8.9	3.5	11.3		7.7	5.1	0.7	1.5	4.8	1.8	10	59	27
	1996	694	4.22	39.2	4.4	3.9	15.3	22	6.8	2.4	0.7	1.4	5.0	2.1	7	60	29
	1997	726	4.29	34.7	3.5	3.8	14.2	20	9.0	3.8	0.8	1.4	6.5	1.4	9	56	32
	1998	671	4.47	21.6	3.1	3.1	14.0	18	7.1	4.2	1.0	1.4	6.2	0.9	7	38	24
	1999	529	4.48	16.4	0.9	2.6	9.1	9	6.7	2.3	0.5	1.6	1.9	0.3	10	12	20
	2000	612	4.46	21.1	3.1	2.7	9.2	12	4.5	2.0	0.6	1.5	2.6	0.4	7	23	21
	2001	741	4.55	19.7	1.5	3.0	12.0	5	3.0	2.4	0.4	1.5	1.3	0.4	5	29	26
	1997	366	3.91	39.6	2.6	23	36	41	8.9	49.2	10.5	1.2	7.9	4.4	18	147	47
	1998	344	4.08	19.8	2.6	24	33	35	8.3	60.7	9.4	0.9	5.2	2.7	22	127	48
SPRUCE THR.	1999	288	4.29	12.2	1.8	24	28		7.5	33.6	5.3	0.5	3.3	1.5	13	75	47
	2000	300	4.36	14.6	1.8	29	35	31	9.4	44.1	6.5	1.5	3.1	1.6	19	82	57
	2001	420	4.61	9.1	1.3	18	26	24	5.8	49.3	6.3	0.7	1.9	1.5	13	75	42
	1997	427	4.62	10.9	1.8	14	26	24	6.3	25.0	2.6	0.8	4.4	1.9	10	47	27
BEECH THR.	1998	398	4.86	3.3	3.4	30	40		9.4	43.7	7.1	0.6	3.9	1.5	20	47	19
	1999	373	4.75	5.8	0.9	9	22	17	5.5	20.3	1.7	0.2	1.8	0.8	8	31	28
	2000	412	4.84	8.6	1.5	16	27	24	5.7	38.2	2.3	0.3	1.3	0.9	13	39	28
	2001	484	4.75	8.2	1.7	16	28	25	4.6	36.0	2.6	0.6	3.0	1.0	9	38	27
INPUT	1997	400		23.8	2.1	18	30	32	7.4	35.9	6.2	1.0	6.0	2.7	14	92	36
	1998	374		10.7	3.1	27	37	31	8.9	51.3	8.1	0.7	4.5	2.0	20	83	32
	1999	335		8.6	1.3	12	23	22	6.4	26.3	3.3	0.3	2.5	1.1	10	51	36
	2000	362		11.3	1.6	17	28	29	7.4	40.9	4.2	0.8	2.1	1.2	15	59	41
	2001	456		8.6	1.5	17	27	29	5.1	42.0	4.3	0.6	2.5	1.2	11	55	34
EXPORT	1994	113	4.83	1.7	123.0	73	113		38.2	4.7	0.4	0.1	13.2	4.6	13	200	11
	1995	122	4.86	1.7	259.2	87	143		45.2	4.4	1.2	0.4	14.1	5.3	15	231	9
	1996	151	4.80	2.4	315.5	102	168	681	53.3	5.7	1.4	0.5	18.7	6.6	16	288	6
	1997	98	5.05	0.9	127.6	59	81	312	34.2	2.8	0.7	0.5	9.9	3.9	12	160	4
	1998	35	5.15	0.2	30.7	19	28	102	13.5	1.1	0.2	0.4	2.2	1.2	5	50	2
	1999	73	4.99	0.7	75.8	42	57	227	25.4	2.0	0.4	0.4	7.4	3.1	8	111	5
	2000	67	4.91	0.8	70.9	36	51	192	23.1	1.7	0.3	0.3	6.1	2.5	8	90	9
2001	63	4.92	0.8	73.0	35	48	169	22.9	1.4	0.3	0.5	6.1	2.3	7	91	4	

Table 23 Correlation matrix of the bulk fluxes at site TR

	DI	pH	H	Be	Mg	Ca	Sr	Ba	Na	K	Fe	Mn	Al	F	Cl	NO ₃ ⁻	SO ₄ ²⁻
DI	1.00																
pH		1.00															
H			1.00														
Be				1.00													
Mg					1.00												
Ca						1.00											
Sr							1.00										
Ba				0.82	0.88	0.79	0.59	1.00									
Na								0.57	1.00								
K					0.61	0.65		0.89		1.00							
Fe		0.57						0.61			1.00						
Mn								0.66				1.00					
Al								0.79					1.00				
F				0.57				0.88						1.00			
Cl															1.00		
NO ₃ ⁻	0.69		0.76	0.71	0.61	0.66		0.82		0.51				0.73		1.00	
SO ₄ ²⁻	0.69		0.67	0.53	0.76	0.74		0.88							0.81	1.00	

n=46; p < 0.001

Table 24 Correlation matrix of the spruce throughfall fluxes at site LP7

	DI	pH	H	Be	Mg	Ca	Sr	Ba	Na	K	Mn	Fe	Al	F	Cl	SO ₄ ²⁻	NO ₃ ⁻	NH ₄ ⁺	
DI	1.00																		
pH		1.00																	
H			1.00																
Be				1.00															
Mg	0.67				1.00														
Ca	0.68					1.00													
Sr			0.61	0.69	0.56	0.59	1.00												
Ba								1.00											
Na	0.58								1.00										
K	0.86									1.00									
Mn	0.55		0.69		0.93	0.90	0.62		0.77	0.63	1.00								
Fe												1.00							
Al			-0.52	0.78	0.56	0.63	0.69		0.62		0.66		1.00						
F					0.56	0.57				0.64		0.81		1.00					
Cl	0.69		0.63		0.91	0.91			0.91	0.79	0.76			0.62	1.00				
SO ₄ ²⁻	0.69		0.80		0.91	0.92	0.69		0.80	0.73	0.86		0.65	0.63	0.85	1.00			
NO ₃ ⁻	0.80		0.56		0.82	0.86			0.84	0.84	0.64			0.66	0.91	0.81	1.00		
NH ₄ ⁺	0.80				0.68	0.71			0.63	0.85	0.52	0.51		0.66	0.77	0.75	0.91	1.00	

Table 25 Correlation matrix of the beech throughfall fluxes at site LP6

	DI	pH	H	Be	Mg	Ca	Sr	Ba	Na	K	Mn	Fe	Al	F	Cl	SO ₄ ²⁻	NO ₃ ⁻	NH ₄ ⁺	
DI	1.00																		
pH		1.00																	
H			1.00																
Be				1.00															
Mg					1.00														
Ca						1.00													
Sr							1.00												
Ba								1.00											
Na									1.00										
K										1.00									
Mn											1.00								
Fe												1.00							
Al													1.00						
F														1.00					
Cl															1.00				
SO ₄ ²⁻																1.00			
NO ₃ ⁻																	1.00		
NH ₄ ⁺																		1.00	
																			1.00

n=42; p < 0.001

Table 26 Correlation matrix of the LP soil solution parameters

	pH	H	Be	Mg	Ca	Sr	Ba	Na	K	Mn	Fe	Al	F	Cl	NO ₃ ⁻	SO ₄ ²⁻	
pH	1.00																
H	-0.83	1.00															
Be			1.00														
Mg			0.80	1.00													
Ca	0.69		0.50	0.87	1.00												
Sr			0.73	0.94	0.88	1.00											
Ba			0.57				1.00										
Na			0.61	0.93	0.88	0.88		1.00									
K									1.00								
Mn										1.00							
Fe											1.00						
Al											0.65	1.00					
F													1.00				
Cl													0.64	1.00			
NO ₃ ⁻															1.00		
SO ₄ ²⁻															0.94	0.57	1.00

n=48; p < 0.001

Table 27 Correlation matrix for 89 samples of the solutes and parameters from the LP stream water in period 1994 - 2001

	Q	pH	H	Be	Mg	Ca	Sr	Ba	Na	K	F	Cl	NO ₃ ⁻	SO ₄ ²⁻	SiO ₂	Alk.	Cond.	Mn	Al	Fe	BC		
Q	1.00																						
pH	-0.39	1.00																					
H	-0.78	1.00																					
Be	-0.67	0.57	1.00																				
Mg		0.43	1.00																				
Ca		0.43	0.93	1.00																			
Sr		-0.38	0.59	0.71	0.78	1.00																	
Ba			0.58	1.00			1.00																
Na		0.47		0.57	0.56		1.00																
K				0.44			1.00																
F			0.48	0.54	0.46	0.37			1.00														
Cl				0.41	0.37		0.64		0.43	1.00													
NO ₃ ⁻											1.00												
SO ₄ ²⁻											0.68	0.49	1.00										
SiO ₂	-0.55	0.43									0.67	0.50	-0.60	1.00									
Alk.	0.75	-0.41	-0.42							0.50	0.53			0.53	1.00								
Cond.			0.35	0.88	0.88	0.61			0.55	0.35	0.67	0.52		0.92		1.00							
Mn		0.45			0.50		0.77	0.61	0.70		0.41	0.34	0.58	0.67	0.42	1.00							
Al	0.44	-0.77	0.63	0.75	0.52	0.37	0.47		0.57			0.34	0.51	-0.43	-0.53	0.41	1.00						
Fe		0.49						0.71	0.39	0.62		0.34		0.53	0.69		0.75	1.00					
BC					0.96	0.98	0.71		0.68	0.46	0.46	0.46	0.86				0.89	0.54					1.00

Table 29 Correlation matrix for parameters of shallow groundwater

	Q (stream)	Q (groundwtr level)	pH	H	Be	Mg	Ca	Sr	Ba	Na	K	F	Cl	NO ₃ ⁻	SO ₄ ²⁻	SiO ₂	Mn	Fe	Al	
Q (stream)	1.00																			
gwt level	-0.88	1.00																		
pH			1.00																	
H			-0.94	1.00																
Be			0.74	1.00																
Mg			-0.84	0.92	-0.82	1.00														
Ca			-0.97	0.98	-0.77	-0.97	0.87	1.00												
Sr						0.87	1.00													
Ba								1.00												
Na								0.85	1.00											
K								0.98	0.89	0.96	1.00									
F											1.00									
Cl										0.79		1.00								
NO ₃ ⁻													1.00							
SO ₄ ²⁻										-0.74	-0.81			1.00						
SiO ₂										0.98	0.96	0.74			1.00					
Mn										0.97	0.95		0.70			0.96	1.00			
Fe										0.87	0.89					0.81	0.84	1.00		
Al										-0.91	-0.82		-0.72			-0.87				1.00

n=22; p < 0.001

Table 30 Correlation matrix for data on soil properties at LP catchment n=40; p < 0.001

	depth	pH _(H2O)	pH _(KCl)	H _(H2O)	H _(KCl)	C _(ox.)	N _(t)	TEA	CEC	Be	Mg	Ca	Sr	Ba	Na	Al	K	Mn	Fe	
depth	1.00																			
pH _(H2O)		1.00																		
pH _(KCl)		0.75	1.00																	
H _(H2O)		-0.73	-0.74	1.00																
H _(KCl)		-0.68	-0.80	0.98	1.00															
C _(ox.)		-0.63	-0.66			1.00														
N _(t)		-0.66	-0.65			0.99	1.00													
TEA		-0.67	-0.79	-0.90	0.85	0.87		1.00												
CEC		-0.50	-0.61	0.66	0.73	0.64	0.58		1.00											
Be		0.55								1.00										
Mg										0.86	1.00									
Ca										0.60	0.60	1.00								
Sr											0.88	0.88	1.00							
Ba			-0.64		0.75	0.83	0.81		0.62		0.70	0.60	0.60	1.00						
Na						0.56	0.56			0.71	0.70	0.60			0.72	1.00				
Al						0.55	0.57			0.78	0.77					1.00				
K						0.85	0.85					0.83	0.85				1.00			
Mn						0.55	0.55					0.69	0.56	1.00						
Fe										0.52										1.00

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