

The characteristics of rare earth elements in bulk precipitation, throughfall, foliage and lichens in the Lesní potok catchment and its vicinity, Czech Republic

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ABSTRACT: A comparison of rare earth elements' (REE) atmospheric signatures in various ecosystem compartments was carried out in the vicinity of the Lesní potok catchment (LP), Czech Republic. REE signatures were investigated from 2004 to 2006 in rainwater, throughfall, tree foliage (*Picea abies*, *Fagus sylvatica*) and lichens (*Hypogymnia physodes*) for selected elements (Al, Ca, Fe, K, Mg, Mn, Na, P, S, Si). REE concentrations increased in the following sequences: bulk precipitation < beech throughfall < spruce throughfall and spruce needles < beech leaves ≪ lichens.

The crustal origin of REEs in bulk precipitation was confirmed by its high correlation with lithogenic elements, by the seasonal variation in REE concentrations and by comparison of REE distribution patterns of the upper continental crust, local granites and soil. Enrichment factors calculated in relation to bulk precipitation and normalized to Na enabled elimination of the influence of dry deposition and wash-out. Higher REE concentrations in throughfall were then identified to be the result of the wash-out of dry deposition, while REEs were found to bioaccumulate in vegetation, although at a much smaller rate than the essential elements K, Mn, P, Mg and Ca.

KEYWORDS: rare earth elements, bulk precipitation, throughfall, vegetation

SUPPLEMENTARY MATERIAL: various REE and major ions concentrations are available at <http://www.geolsoc.org.uk/SUP18437>.

INTRODUCTION

Rare earth elements (REE) have very similar physical and chemical properties, forming a chemically coherent group of elements. In the present study we use the abbreviation REE for elements from lanthanum to lutetium, and also yttrium, which is sometimes included amongst the REEs due to its comparable chemistry. Because of their coherent behaviour, REEs are often used as geochemical tracers in various types of natural processes. Particularly, Gd was used as an environmental tracer in hydrological studies (Bau & Dulski 1996; Moller *et al.* 2000, 2003; Knappe *et al.* 2005) because REE distribution patterns of surface and ground water from urban areas often show anthropogenic Gd anomalies resulting from the application of organic Gd compounds as a contrast medium in magnetic resonance imaging.

The growing use of REEs in agriculture and industry has caused significant increase in interest in REE geochemistry (Hedrick 1995). The sources of REE emission to the atmosphere are mainly petroleum-cracking catalysts in oil refineries

and oil-fired power plants (Olmez & Gordon 1985; Kulkarni *et al.* 2006), the production and use of phosphate fertilizers (Volokh *et al.* 1990), fossil fuel combustion (Vassilev 1994) and waste incineration (Zhang *et al.* 2001).

With the increasing use of REEs, their accumulation in biomass has been studied in farm crops as well as in natural ecosystems, for example, in rice (Yuan *et al.* 2001), wheat (Zhang & Shan 2001), Norway spruce (Wytenbach *et al.* 1994), fern (Fu *et al.* 1998), moss (Akagi *et al.* 2002), and seaweeds (Fu *et al.* 2000). Subsequently, the REEs have been used as tracers of the original plant species during the formation of coal (Fu *et al.* 2004). Amongst the vegetation studied for REE distribution, of special importance are those types which can successfully be used for biomonitoring, such as lichens.

There has been growing interest in atmospheric REE behaviour that focused on lichens (Rossbach *et al.* 1999; Chiarenzelli *et al.* 2001; Aubert *et al.* 2002), tree bark (Lahd Geagea *et al.* 2007) and atmospheric precipitation (Freydier *et al.* 1998; Ikegawa *et al.* 1999; Aubert *et al.* 2002, 2006; Zhang & Liu 2004; Ryu *et al.* 2007). However, the understanding of REE

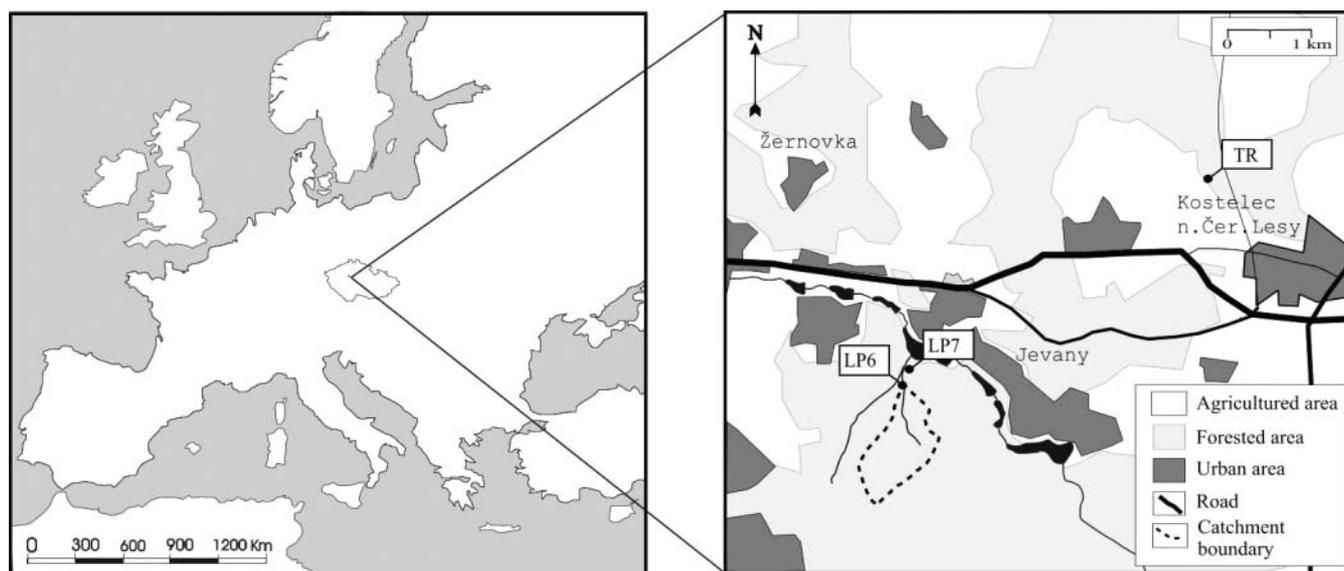


Fig. 1. Location of LP catchment in Europe and surrounding of LP catchment and TR site.

behaviour in atmospheric processes is still very limited, despite the growing importance of the knowledge of REE behaviour and its application potential.

The aim of the present work is to compare the input signals of atmospheric REEs in different media sampled at one site. The indicators of atmospheric deposition investigated comprise rainwater, throughfall, tree foliage and lichens. This work also focuses on the relationships between REEs and selected major and minor elements (i.e. Al, Ca, Fe, K, Mg, Mn, Na, P, S, Si).

MATERIAL AND METHODS

Study site and sampling

The behaviour of REEs and Y in precipitation was studied from 2004–2006 in the Lesní potok (LP) catchment and its vicinity. The LP catchment is located in the Nature State Reserve, Voděradské bučiny, 30 km SE of Prague, capital of the Czech Republic. The broader surroundings are a rural landscape lacking significant local sources of pollution. This allowed the use of the LP catchment as a typical model landscape for the biogeochemical monitoring of the selected major and trace elements, and for the evaluation of their natural and anthropogenic sources in the environment (Skřivan *et al.* 1995; Minařík *et al.* 1998).

The catchment is situated at an altitude of 406–500 m a. s. l. and covers an area of 0.765 km². Mean annual precipitation is 635 mm, and the mean annual temperature is 9°C. Beech throughfall was sampled at the site LP6 located in the immediate vicinity of the closing weir of the catchment. Spruce throughfall was sampled at site LP7 located 50 m north of the weir. Bulk precipitation was sampled at the site Truba (TR) located 4 km NE of the catchment (Fig. 1).

Bulk precipitation and throughfall were sampled monthly. Due to extremely low concentrations of elements in these media, three subsequent monthly bulk and throughfall samples were combined and preconcentrated using a rotary vacuum evaporator (Büchi, Rotavapor B-200). Bulk precipitation samples were collected in polyethylene (PE) samplers with a glass funnel. The throughfall collector was equipped with a glass conical bulb placed onto a funnel, so that the throughfall flowed into the collecting bottle without contamination by needles or other organic debris. The details of the sampling techniques have been described by Skřivan *et al.* (1995).

Precipitation samples were acidified with dilute nitric acid to prevent losses by adsorption, and filtered using a 0.45- μ m membrane filter. Preconcentration was performed in a quartz bulb, which was previously checked and where no contamination by trace elements was proven.

Foliage samples were collected at the throughfall sampling sites at the end of the growing seasons in 2005 and 2006. Samples of the lichen species *Hypogymnia physodes* were collected during August and September 2004 from tree trunks throughout the entire catchment area.

Tree foliage samples were collected from Norway spruce (*Picea abies*) and European beech (*Fagus sylvatica*) of different ages. Approximately 5 g of leaves or 1 year-old needles were collected from different parts of the tree canopy. Approximately 10 g or more of lichen thalli were collected from different host trees at heights from 0.5 to 1.5 m. Bark fragments were removed manually with plastic tweezers and samples were examined by binocular microscope to ensure purity.

All vegetation samples were dried to constant weight in a flow box. No washing procedure was done, to avoid the leaching of soluble matter from tissues (e.g. Cohen *et al.* 1999; Čeburnis & Steinnes 2000; Lorenzini *et al.* 2006). A digestion of 0.5 g of sample was performed in a mixture of 4 ml of HF and 10 ml of HNO₃ (both Suprapur grade, Merck) using a microwave digestion unit (Milestone, MLS 1200 mega). All laboratory vessels were leached in HNO₃ (1:3) for at least 24 hours and rinsed with deionized water (Elga, <18 M Ω ⁻¹ cm⁻¹).

Analytical methods

All samples were used for Al, Ca, Fe, K, Mg, Mn, Na, P, S, and REE analyses. Silicon was analysed only in bulk precipitation and throughfall samples because its analysis in vegetation samples was not compatible with the digestion procedure used (i.e. SiF₄ vaporizes).

The concentrations of Al, Ca, Fe, K, Mg, Mn, Na, P, S, and Si were determined with an IRIS Intrepid II XPS inductively coupled plasma atomic emission spectrometer (ICP-AES) using axial plasma view and a cyclone-type nebulizer. The following wavelengths and detection limits were used (in nm; μ g l⁻¹): Al (328.1; 0.4); Ca (393.4; 0.05); Fe (259.9; 0.6); K (766.5; 10.0); Mg (280.3; 0.1); Mn (259.3; 0.6); Na (589.0; 1.0);

P (213.6; 10.0); S (182.0; 2.0); Si (251.5; 1.0). Each sample was analysed twice. Quality control of the analysis was ensured by inserting a quality control sample into the analytical run after 10 samples.

The REE concentrations were determined by quadrupole-based inductively coupled plasma-mass spectrometry (ICP-MS) using the PlasmaQuad (VG Elemental). In the case of precipitation samples, no dilution was required. Digested vegetation samples were diluted at least twofold with ultra-pure water. Calibration was performed using a REE standard mixed solution (Astasol, Analytica Praha). The REE isotopes chosen as the most abundant for each element or to minimize matrix or polyatomic interferences were: 89Y, 139La, 140Ce, 141Pr, 146Nd, 147Sm, 157Gd, 159Tb, 163Dy, 165Ho, 167Er, 169Tm, 172Yb and 175Lu. Formation of oxides (MeO^+/Me^+) was monitored using Ce solution ($10 \mu\text{g l}^{-1}$ in 2% HNO_3) (Strnad *et al.* 2005). The measured ratio ($^{156}\text{CeO}^+ / ^{140}\text{Ce}^+$) varied around 0.006 and was minimized by suitable gas flow rate settings. The data were processed online using VG PlasmaLab software and corrections were applied for instrumental drift and matrix effects. In this study In and Re at a concentration of $10 \mu\text{g l}^{-1}$ in 2% HNO_3 were used as internal standards. The count rates for the measured REE isotopes were corrected on the basis of interpolation of the ^{115}In and ^{187}Re correction factors. The detection limits (DL), calculated as the 3σ level of the procedural blank, were as follows, in $\mu\text{g l}^{-1}$: 0.0039 for Y, 0.0070 for La, 0.0030 for Ce, 0.0020 for Pr, 0.0025 for Nd, 0.0094 for Sm, 0.0087 for Gd, 0.0020 for Tb, 0.0079 for Dy, 0.0021 for Ho, 0.0050 for Er, 0.0020 for Tm, 0.0041 for Yb and 0.0010 for Lu. The data for Eu were not processed in the study due to its bias caused by the spectral interference of $^{135}\text{Ba}^{16}\text{O}$ on ^{151}Eu .

RESULTS AND DISCUSSION

The concentrations of REEs and major ions in bulk precipitation, beech throughfall, spruce throughfall, tree foliage and lichens are presented in Supplementary Publication Tables 1 to 5. During geochemical processes, the trivalent REEs show coherent behaviour leading to predictable fractionation trends due to their identical valences and the systematic decrease of ionic radii with increasing atomic number. Certain geochemical processes cause the redistribution of REEs, changing the ratio of lighter REEs (LREE) to heavier REEs (HREE) or selective concentration of particular REE, which manifests itself as anomalies in the REE patterns. In order to evaluate the variation in REE abundance, the REE distribution patterns of the studied samples were normalized to the upper continental crust (UCC) (Kamber *et al.* 2005). The relations between LREEs and HREEs, quantified by the UCC normalized ratio of $(\text{La}/\text{Yb})_{\text{UCC}}$, the Y/Ho ratio and the UCC normalized Ce and Gd anomalies are also given in the supplement. To avoid the calculation of anomalies using other anomalous elements, the following equations were applied: $\text{Ce}/\text{Ce}^* = \text{Ce}_{\text{UCC}} / (2\text{Pr}_{\text{UCC}} - \text{Nd}_{\text{UCC}})$ and $\text{Gd}/\text{Gd}^* = \text{Gd}_{\text{UCC}} / (2/3\text{Tb}_{\text{UCC}} + 1/3\text{Sm}_{\text{UCC}})$, which were presented previously by Lawrence *et al.* (2006).

Concentrations of the elements determined were found to be lower in bulk precipitation compared to throughfall. This is caused by the processes occurring when precipitation penetrates and interacts with the tree canopy. The composition of throughfall is determined by: (1) the ions in incident precipitation that pass through the canopy without absorption; (2) ions previously dry-deposited to the canopy, which are then removed during rainfall; and (3) ions that originate from internal plant sources (foliar leaching). Additionally,

interception loss due to in-canopy evaporation increases the ion concentrations (Lindberg *et al.* 1990). The concentrations of the studied elements in spruce throughfall were higher than those in beech throughfall due to the larger surface of assimilatory organs in spruce and its perennial foliage and/or by the fact that deciduous trees do not have foliage during the winter.

The elements in tree foliage have two main sources: supply of elements taken up by the root system, and deposition which occurs principally through dry deposition and the impact of windborne particles (Bargagli 1998; Lövestam *et al.* 1990). Concentrations of REEs are significantly higher in beech leaves compared to spruce needles, similar to Al, Ca, Fe, Mg and Na. Spruce needles have markedly higher concentrations of P and moderately higher concentrations of K and Mn compared to beech leaves.

Concentrations of REEs and some other trace elements (Al, Fe) found in lichens significantly exceeds those in samples of foliage, while typical nutrients prevail in foliage. Since lichens absorb essential nutrients as well as many non-essential or harmful substances, they are commonly used for biomonitoring of air pollution. Epiphytic lichens obtain nutrients only from bulk precipitation and deposited dust. Unlike vascular plants, they lack an epidermis, stomata and a waxy cuticle and can accumulate trace elements in particulate form or bound to cation exchange sites in the intercellular spaces of the thallus.

Correlation analysis and the origin of REEs

The concentrations of REE groups are strongly mutually correlated in all cases. The mutual correlation is stronger for throughfall compared to bulk precipitation ($R > 0.86$, $p < 0.01$ for throughfall, $R > 0.76$, $p < 0.01$ for bulk precipitation).

Total REE concentrations in bulk precipitation strongly correlate with Ca, Mg, Si, Al, Fe and P (Spearman correlation coefficient $R = 0.86$; 0.90; 0.88; 0.63; 0.75; 0.79, respectively; $p < 0.01$; in the case of Al and P, $p < 0.05$). A common feature of Ca, Mg, Si, Al, and Fe is their lithogenic character. Silicon, Al and Fe are major constituents of common rock-forming minerals; Ca and Mg are also commonly found in minerals and rocks. Therefore the source of atmospheric REEs is most probably the leaching or dissolution of mineral dust particles. The weaker REE correlation with Al might reflect the lower concentration of REE in clay minerals; the correlation with P being weaker than with Ca and Mg suggests that sources of REEs may also be minerals such as monazite and apatite, which are accessories in the mineral dust.

The REEs in both types of throughfall are correlated only with Fe ($R = 0.75$, $p < 0.01$ for beech throughfall, $R = 0.61$, $p < 0.05$ for spruce throughfall) and, in the case of beech throughfall, also with Ca ($R = 0.86$, $p < 0.01$). The different structure of the correlation matrices for throughfall compared to that for bulk precipitation as well as the stronger mutual correlation of REEs in throughfall can be explained by the previously mentioned interaction processes between solutes and foliage that change concentrations of the elements in throughfall.

The dataset of tree assimilatory organs was much smaller compared to the time series of bulk precipitation and throughfall. For this reason, the correlation coefficients of element concentrations in foliage and bark are not discussed here. REEs in lichens were well correlated with Al, Fe ($R > 0.75$, $p < 0.01$), S and Mn ($R > 0.65$, $p < 0.01$). These elements are thought to be essential but also toxic (Fe, Mn, S) or non-essential (Al) for lichens (Bennett & Wetmore 1997) and their origin is mainly lithogenic (except S).

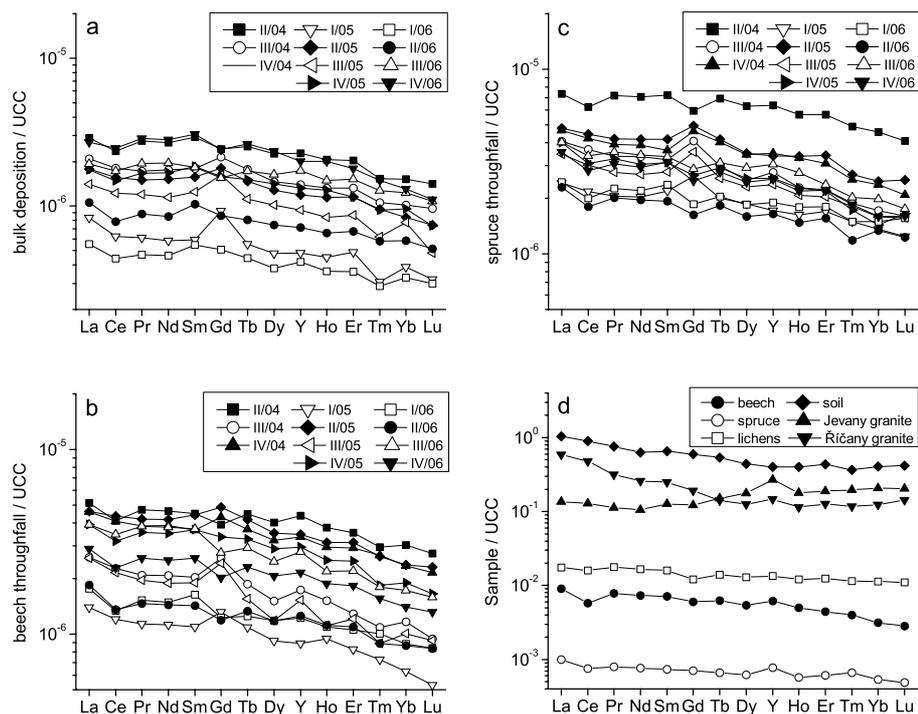


Fig. 2. UCC-normalized REE distribution patterns of (a) bulk precipitation, (b) beech throughfall, (c) spruce throughfall and (d) foliage, lichens, soil and partially weathered underlying granites. The Roman numerals indicate numbers of the quarter (I–IV), the Arabic numerals indicate the year. Average REE distribution patterns in beech and spruce foliage and lichens are presented in (d). REE distribution patterns of soil and rocks were based on the data published by Minařík *et al.* (1998).

REE distribution patterns

The REE distribution patterns in bulk precipitation, throughfall, tree foliage and lichens, normalized to the UCC, are rather similar and their main features correspond to those of local granites and soil (Fig. 2).

The REE distribution patterns of all the studied materials are characteristic in having a LREE enrichment and slight HREE depletion that can be quantified by the $(La/Yb)_{UCC}$ ratio approaching 2. Normalized ratios $(La/Yb)_{UCC}$ are $c. 1.9 \pm 0.2$ in bulk precipitation, $c. 2.1 \pm 0.2$ in beech throughfall and 2.0 ± 0.3 in spruce throughfall. All values of $(La/Yb)_{UCC}$ of bulk precipitation and throughfall fall within the $(La/Yb)_{UCC}$ ratio of local granites and soil. The UCC-normalized values, calculated from data published by Minařík *et al.* (1998), are 0.7 for Jevany granite, 4.8 for Říčany granite and 2.5 for soil (the horizons' thickness weighted average). LREE enrichment is also characteristic for anthropogenic REE emissions from refineries and power plants. Nevertheless, these emissions are characterized by much higher ratios of LREE to HREE: their normalized ratios $(La/Yb)_{UCC}$ are between tens and hundreds (Olmez & Gordon 1985; Kulkarni *et al.* 2006). Thus, strong contribution by anthropogenic REE emissions can be excluded on the basis of the REE distribution patterns.

The REE distribution patterns of tree foliage displays similar HREE depletion to the precipitation samples. More pronounced HREE depletion is typical for beech leaves with $(La/Yb)_{UCC}$ ratios of $c. 2.6 \pm 0.6$ compared to spruce needles (cf. the $(La/Yb)_{UCC}$ ratio of $c. 2.0 \pm 0.4$). Similar to this study, Stille *et al.* (2006) reported the preferential accumulation of LREE by vegetation. In the latter study, foliage exhibited relatively low HREE depletion and corresponded more to the REE ratios of the UCC, as well as to the REE distribution patterns of lichens and precipitation from this catchment.

The lichens have an average $(La/Yb)_{UCC}$ ratio of 1.7 ± 0.1 , being thus the least HREE depleted and most resembling the upper continental crust. Higher HREE depletion of precipitation samples compared to lichens might seem surprising with regard to the commonly accepted findings that dust particles are generally LREE-enriched and HREE are preferentially

leached from those particles (Sholkovitz *et al.* 1993; Freydl *et al.* 1998; Aubert *et al.* 2006). Thus, the precipitation solution should be relatively HREE-enriched due to preferential leaching of HREEs. The reverse situation is probably the result of low REE concentrations in precipitation samples in combination with their hydrolysis, which may occur at a low rate during sample accumulation in the sampling device. Due to its smaller ion ratio, HREEs are subject to hydrolysis to a higher degree than larger LREEs and they can be adsorbed in the hydrolyzed form onto the surface of a sampling device or on the deposited particles.

The ratio, Ce/Ce^* , reaches an average value of 1.0 ± 0.1 in samples of bulk precipitation, throughfall and also spruce needles. Lower values are observed in beech leaves, with an average Ce anomaly 0.8 ± 0.1 and in lichens with average values 0.90 ± 0.01 . Plants usually show various magnitudes of Ce anomalies (Fu *et al.* 1998, 2000, 2001). The exceptions are only the peat vegetation with no Ce anomaly (Akagi *et al.* 2002) and mangroves with a positive Ce anomaly (Yu *et al.* 2007), in both cases owing to the different pH and redox conditions.

The values of the average Gd/Gd^* ratio are close to 1 in samples of precipitation (1.1 ± 0.2 for bulk deposition and throughfall) and tree foliage samples (1.0 ± 0.3 for spruce needles, 0.9 ± 0.1 for beech leaves). Lichens display a slightly lower average value of 0.83 ± 0.03 , nevertheless not markedly different from the value of the Gd anomaly of the underlying Jevany granite, which is 0.86 (the UCC-normalized value calculated from data published by Minařík *et al.* 1998).

The Y/Ho ratios (unnormalized) of all types of samples are close to the average upper continental crust value of 26 (Kamber *et al.* 2005). The bulk precipitation and throughfall values are closer to crustal values (with values 28.3 ± 1.2 for bulk deposition, 30 ± 3 for beech throughfall and 28.9 ± 1.4 for spruce throughfall), while values for tree foliage are slightly higher (31.8 ± 1.8 for beech leaves, 36 ± 5 for spruce needles). Lichens, with an Y/Ho ratio of 28.5 ± 1.1 , apparently reflect the values of precipitation. Yttrium is the geochemical twin of Ho with a near identical ionic radius resulting in the constant mass ratio in igneous rocks. An increase in the Y/Ho ratio is

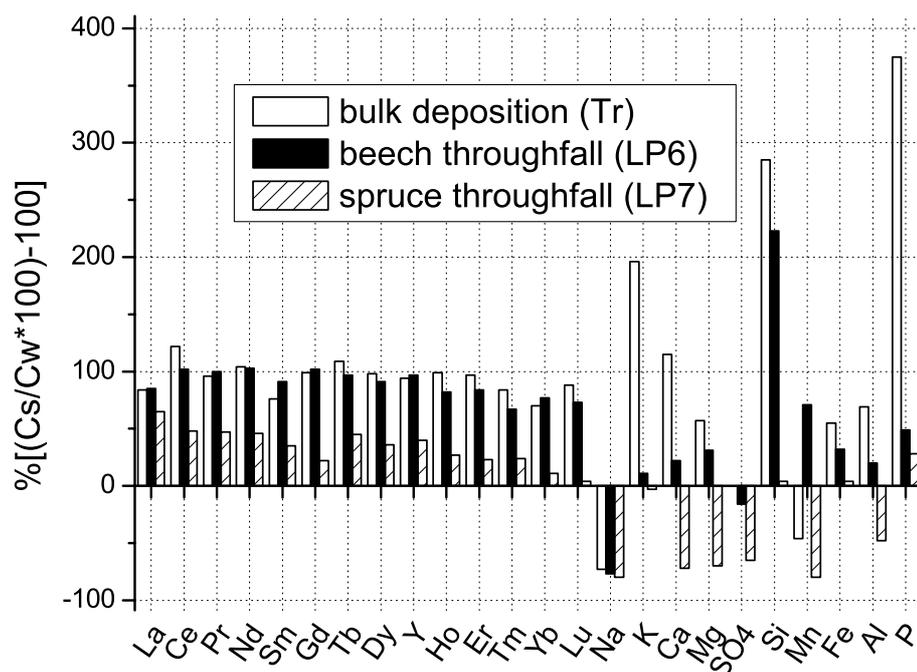


Fig. 3. Seasonal variations in element concentrations in bulk precipitation sampled at site TR, beech throughfall sampled at site LP6 and spruce throughfall sampled at site LP7 (expressed as the difference between summer and winter median concentration $[(C_s/C_w*100)-100]$, Y inserted between Dy and Ho).

observed as a consequence of particular geochemical processes, such as preferential sorption of Ho relative to Y on the scavenging Fe(–Mn) particles in the marine environment (e.g. Bau 1999; Bau *et al.* 1996). Yu *et al.* (2007) suggested that the elevated Y/Ho ratio in plant samples is caused by different transport of Y through the complex tree metabolism pathways compared to the REEs, but they also pointed out the lack of reliable Y/Ho data for plants. In our study, the slight increase in the Y/Ho ratio is nevertheless on the level of the analytical uncertainties and therefore does not enable the identification of any real Y/Ho fractionation.

The REE concentrations and distribution patterns in tree foliage and lichens corresponds to those in previous studies (Chiarenzelli *et al.* 2001; Aubert *et al.* 2002, 2006; Stille *et al.* 2006). Some differences were observed comparing REE distribution patterns of bulk precipitation and throughfall with previous studies showing greater LREE depletion (Aubert *et al.* 2002) or LREE enrichment (Ryu *et al.* 2007) of bulk precipitation and /or throughfall. The bulk precipitation and throughfall distribution patterns from this study more closely resemble those of the upper continental crust, while the cited works assume possible anthropogenic influence on the precipitation element concentrations.

Generally it was observed in our studies that the REE ratios of all studied materials are very consistent, comparable with previous results and do not differ significantly from the upper continental crust.

Seasonal variability

Concentrations of REEs and most of the major elements in precipitation were susceptible to seasonal variations (Fig. 3).

The increase of concentrations of most elements observed in the summer season (March–September) is attributed to increased dustiness in the summer. The systematic decrease of REE concentration from Tb to Lu ascribed to HREE depletion of dust particles (Sholkovitz *et al.* 1993; Freydier *et al.* 1998) was apparent at all sites of the precipitation sampling. The exceptions were: Na and Mn with increased concentrations in winter and SO_4^{2-} with comparable concentrations in both seasons at site TR; Na and SO_4^{2-} with increased concentration in winter

at site LP6; and Na, K, Ca, Mg, SO_4^{2-} , Mn, Al Mn with increased concentrations in winter at site LP7. Marked increases of Na concentrations in winter samples might originate from salt applications for de-icing purposes in winter (Lehndorff & Schwark 2008).

Elevated SO_4^{2-} concentration is an apparent result of house heating in the winter season. Desulphurisation of Czech power plants (combusting the Czech lignite with high S content) during the period 1990–2000 had led to the remarkable decrease of atmospheric deposition of S and other atmospheric contaminants (Vach *et al.* 2004). However, change happened after 2001, when rising prices of electric energy and fuel gas induced the return to lignite combustion occurring mainly in country households and causing gradual air quality deterioration (Kotlík *et al.* 2006; Machart & Machálek 2006).

A distinctive rise in winter concentration of essential elements, K, Ca, Mg, Mn in spruce throughfall at site LP7 was caused by particular characteristics of this site compared to the sites TR and LP6 because spruce retains foliage throughout the winter while beech defoliates. Therefore in the winter, beech throughfall more closely resembles the bulk precipitation than the spruce throughfall. During the decrease of vegetation activity in the winter season spruce needles are subject to leaching of essential elements (K, Ca, Mg, Mn), intensified by increased acid deposition of S.

The presence of higher winter concentrations of Mn in bulk precipitation at site TR may also have a similar explanation, i.e., tiny droplets of throughfall that are occasionally windblown from spruce forest in surroundings (Skřivan *et al.* 1995). In contrast to the macro-elements K, Ca and Mg, Mn concentrations in the rock dust are lower. This might cause a more marked influence of throughfall to Mn concentrations in winter at TR.

The interpretation of the winter increase of Al concentration at site LP7 is less clear. First, it may be due to the foliar leaching analogous to leaching of essential elements Na, K, Ca, Mg and Mn because Al, although being toxic, is present in spruce tissues (see Hodson & Sangster 1998; Prohaska *et al.* 1999). Secondly, it can be caused by the anthropogenic emission

source. Despite the fact that Al is considered to be a typical lithogenic element, Hashimoto & Sekine (1992) showed that Al emissions due to human activities may change the ratio of Al with respect to other typical lithogenic elements, such as Sc. Seasonal variability of fuel oil combustion can be an example of such emissions.

Enrichment factors

Enrichment factors were calculated to enable the comparison of particular studied samples. Bulk precipitation was taken as a reference sample representing the atmospheric inputs of studied elements, and their concentrations were normalized to the Na concentration. The nutritional need for Na by trees is small (Kramer & Kozłowski 1979) and foliage concentrations are very low. Therefore, Na can be considered to be a 'conservative' element showing little or no interaction with the tree canopy (Draaijers *et al.* 1997). Changes in its concentration in different samples are just the result of the different amount of wash-out of solid atmospheric aerosols captured on the surface of the foliage. This type of normalization enables elimination of the influence of different rates of atmospheric deposition on the vegetation surface.

Enrichment factors (EF) were calculated as:

$$EF = (X/Na)_{\text{sample}} / (X/Na)_{\text{bulk precipitation}}$$

The concentrations of relevant elements in bulk precipitation throughout the corresponding period were used for normalization in the case of throughfall, while the average concentration of bulk precipitation was used in the case of vegetation.

The EFs of REEs in throughfall are very close to 1, indicating that higher REE concentrations in throughfall compared to bulk precipitation were just the result of dry deposition wash-out and no foliar leaching was documented.

The values of EF of REEs in tree foliage reach several tens indicating the additional uptake of REEs via soil. Their range is significantly wider than those of lichens and throughfall. This is caused by the high variability in trace element concentrations, discussed for example by Wyttenbach *et al.* (1994), even for the individual trees of the same age class and site. The EFs of lichens range between 10–20, showing also significant bioaccumulation of REEs.

The major elements in foliage could be sorted on the basis of their EF into three groups: (1) less enriched (Al, Fe, S); (2) medium enriched (Mg, Ca); and (3) the most enriched (K, Mn, P). The respective EF of those three groups are, respectively, 5–20, 50–100 and 150–200 for beech foliage and 40–50, 150–400 and 2000–3000 for spruce foliage.

The EFs of Al and Fe (group 1) are close to 1 in throughfall, showing no foliar leaching similar to REEs. However, their higher EFs in vegetation compared to REEs suggest the higher bioaccumulation of Al and Fe.

The groups with the highest EF (groups 2 and 3) correspond to major nutrients. Higher EFs of those elements (2–50) in both types of throughfall also demonstrate their intense foliar leaching.

The trends in EF of major elements as are observed in tree foliage and also in throughfall can be seen as well in the EF of lichens: (1) S is less enriched with EF of *c.* 5; (2) Mg, Ca, Al and Fe are medium-enriched elements with EFs of *c.* 10–50; and (3) K, Mn and P are the most enriched elements with EFs of 50–110. The only difference in this grouping is higher bioaccumulation of Al and Fe relatively to other major elements in lichens compared to tree foliage.

CONCLUSIONS

A mutual comparison of REE signatures in bulk precipitation, throughfall, beech and spruce foliage and lichens was carried out from 2004 to 2006 in the Lesní potok catchment and its vicinity.

The concentrations of REEs and other analysed elements in precipitation increased in the following sequence: bulk precipitation < beech throughfall < spruce throughfall. The vegetation concentrations of REEs and of selected elements (Al, Fe) in beech leaves were found to be higher than in spruce needles, but they were both significantly exceeded by those found in lichens. However, typical nutrients prevailed in tree foliage. The relatively high REE concentrations with a small range of values showed the advantage of the use of lichens for biomonitoring. The REE concentrations can be attributed to lithogenic and biogenic sources. Anthropogenic origin of REE concentrations was excluded on the basis of REE distribution patterns.

The results suggest that atmospheric REEs on this site have a primarily Upper Continental Crust signature confirmed by the combination of correlation analyses, REE distribution patterns evaluation and seasonal variability investigations.

REE concentrations in bulk precipitation strongly correlated with lithogenic elements such as Ca, Mg, Si, Al, Fe and P. Upper Continental Crust-normalized REE distribution patterns were slightly HREE-depleted. This HREE depletion, expressed as (La/Yb)UCC, corresponded to the (La/Yb)UCC of local granites and soil. The seasonal variations in REEs and most of the other element concentrations in precipitation reflected the increased dustiness in the summer season and confirmed that the source of atmospheric REEs is most likely the leaching or dissolution of mineral dust particles originating from the local bedrock.

The enrichment factors calculated in relation to bulk precipitation and normalized to Na enabled the elimination of the influence of dry deposition and particle wash-out. The bioaccumulation of REEs via root uptake by the vegetation occurred at a much smaller rate than the bioaccumulation of essential elements K, Mn, P, Mg and Ca. REEs, unlike those elements, were not susceptible to foliar leaching in the throughfall. Enrichment factors of REEs in throughfall indicated that higher REE concentrations compared to bulk deposition were simply the result of the dry deposition wash-out.

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