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Origin and fluxes of atmospheric REE entering an ombrotrophic peat bog in Black Forest (SW Germany): Evidence from snow, lichens and mosses

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Abstract

The fate of the Rare Earth Elements (REE) were investigated in different types of archives of atmospheric deposition in the Black Forest, Southern Germany: (1) a 70 cm snow pack collected on the domed part of a raised bog and representing 2 months of snow accumulation, (2) a snow sample collected close to the road about 500 m from the peat bog, (3) two species of lichens and (4) a peat profile representing 400 years of peat accumulation as well as a "preanthropogenic" sample and the living moss layer from the top of the core. REE concentrations in peat are significantly correlated to Ti which is a lithogenic conservative element suggesting that REE are immobile in peat bog environments. Snow, lichens and peat samples show similar PAAS (Post Archean Australian Shale) normalized REE distributions suggesting that the complete atmospheric REE signal is preserved in the peat profile. However, the annual flux of REE accumulated by the peat is ca. 10 times greater than that of the bulk winter flux of REE. This difference probably indicates that the REE concentrations in the snowpack are not representative of the average REE flux over the whole year. Despite the pronounced geological differences between this site (granite host-rock) and a previously studied peat bog in Switzerland (limestone host-rock) similar REE distribution patterns and accumulation rates were found at both sites. Given that both sites confirm an Upper Continental Crust signature, the data suggests both sites are influenced by regional and not local, soil-derived lithogenic aerosols.
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1. Introduction

In the last decades, there has been an increasing interest in trace metals in natural environments (e.g., Nriagu and Pacyna, 1988; Vernet, 1992; de Vries and Bakker, 1995; Hernandez et al., 2003) and particularly in atmospheric precipitation (Struempler, 1976; Galloway et al., 1982; Barrie et al., 1987; Noll et al., 1990; Atteia, 1994; Barbaris and Betterton, 1996; Takeda et al., 2000; Roy and Négrel, 2001; Ferrari et al., 2002; Nieminen et al., 2002; Walker et al., 2003; Zhang and Liu, 2004). This is of importance because atmospheric deposition constitutes a major contribution of numerous heavy metals, which are of potential toxicity for ecosystems. In remote areas (at high latitudes for instance), records of elevated concentrations of these trace elements provide evidence of long range transport of anthropogenic pollutants from urbanized regions (e.g., Boutron and Patterson, 1987; Berg et al., 1994; Halstead et al., 2000).

Among these trace metals, data for Rare Earth Elements (REE) in atmospheric precipitation are still very scarce (Freydier et al., 1998; Ikegawa et al., 1999; Aubert et al., 2002; Zhang and Liu, 2004) since these elements are often

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below the ng L^{-1} level, even in areas affected by human activities and thus mostly require a pre-concentration before analysis. Nevertheless, the knowledge of the REE behaviour at the atmosphere–soil interface is of importance because REE have similar and conservative behaviour and a relatively lack of human sources. Consequently, REE have been recently used as tracers and reference elements in broad fields of environmental studies (Greaves et al., 1999; Chiarenzelli et al., 2001; Sahoo et al., 2001; Shotyk et al., 2001; Bayon et al., 2002; Krachler et al., 2003; Stille et al., 2003; Gaiero et al., 2004).

Peat bogs are fed exclusively by atmospheric deposition and are readily age dated (Givelet et al., 2004). Thus, they have been widely used as archives of past atmospheric deposition (Shotyk et al., 1996, 2001, 2002; Görres and Frenzel, 1997; Kempter et al., 1997; Weiss et al., 1997; Benoit et al., 1998; Martinez-Cortizas et al., 1999; Roos-Barraclough et al., 2002).

Nevertheless, to our knowledge, it is only the fourth time including the present study that complete REE patterns are investigated in peat profiles (Yliruokanen and Lehto, 1995; Akagi et al., 2002; Krachler et al., 2003). Yliruokanen and Lehto show that REE patterns in Finnish peat bogs are similar to those of the surrounding rocks and that REE concentrations follow the status of the bog (minerotrophic vs. ombrotrophic), that is to say, the mineral content of the peat. The study by Krachler et al. (2003) on a peat core in the Swiss Jura (Étang de la Gruère: EGR), confirms that REE concentrations more or less follow concentrations of other conservative elements like Sc, that is to say, the mineral content. The peat profile from EGR also shows an increase of REE concentrations that corresponds to the beginning of the industrial period and increasing deposition of dust. Unlike soil-grown plants (Fu et al., 2001), peat mosses (*Sphagnum*) and grass (*Carex*) do not show a Ce anomaly in their REE patterns (Akagi et al., 2002; Fu et al., 2004). This is in agreement with a simple thermodynamic model (Akagi and Masuda, 1998) showing no possible formation of Ce anomaly at the low pH and E$_H$ found in peat bogs. Therefore, the REE patterns of peat are not biologically fractionated and allow potentially the identification of an atmospheric signal.

Thus, the first objective of this study is to establish the fate of REE and particularly their potential mobility in a "chemically aggressive" environment because anoxic conditions and acidic pore waters should be mechanisms changing the atmospheric REE preservation in the peat column. This can be investigated by comparing REE behaviour to those of Zn and Ti. Both elements have contrasted and relatively well-known behaviours in peat. The second aim of this work is to compare the REE distributions in peat to those of the present deposition in order to evaluate the variations of the REE atmospheric signal over the years. For that purpose REE distribution patterns of snow (particles and wet deposition), as well as lichens, have been determined. Epiphytic lichens, which are very sensitive to environmental changes, are often used to monitor the present atmospheric inputs of elements and especially trace metals (e.g., Puckett, 1988; Loppi et al., 1994, 1995; Zhang et al., 2002). Lichens with a slow growth rate (few millimetres per year) depend on nutrients from air constituents (wet, dry and gases) (Nash and Egan, 1988; Nash, 1996; Rossbach et al., 1999) and can accumulate trace elements (in particulate form or bounded to cation exchange sites) in the intercellular spaces of the thallus (Rodrigo et al., 1999). Lichens are powerful biomonitors because they are evergreen allowing bioindication at any time and for many years. Finally, REE distribution patterns and accumulation rates in the Black Forest peat bog are compared with those previously measured by Krachler et al. (2003) in EGR 100 km away in Northern Switzerland in order to determine in how far the atmospheric REE characteristics in peat bogs are of regional or supra-regional significance.

2. Sampling site description

The Kohlhütten Moor peat bog is located in the southern part of the Black Forest (South West Germany) (N 47°,52′,697/E 008°,02′,544, Fig. 1) at an altitude of 1044 m asl. This peat bog is a *Sphagnum*-dominated raised bog with a maximum peat accumulation of 6 m. It is an ombrotrophic peatland characterized by a low pH (4) at the surface and low ash content in the peat (<2%). A
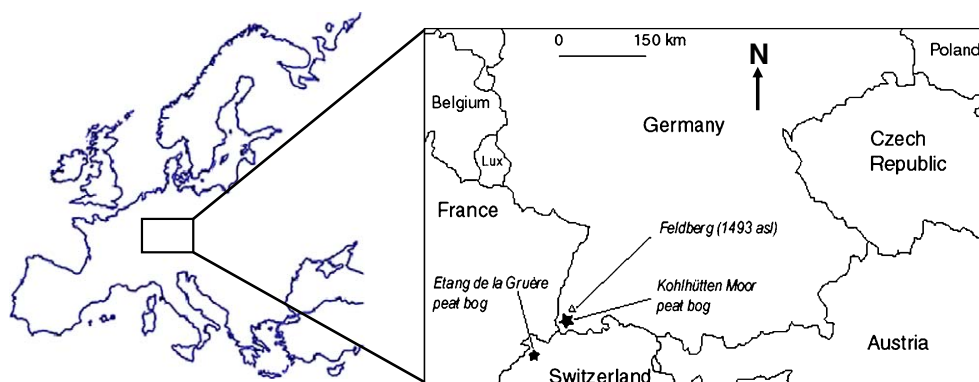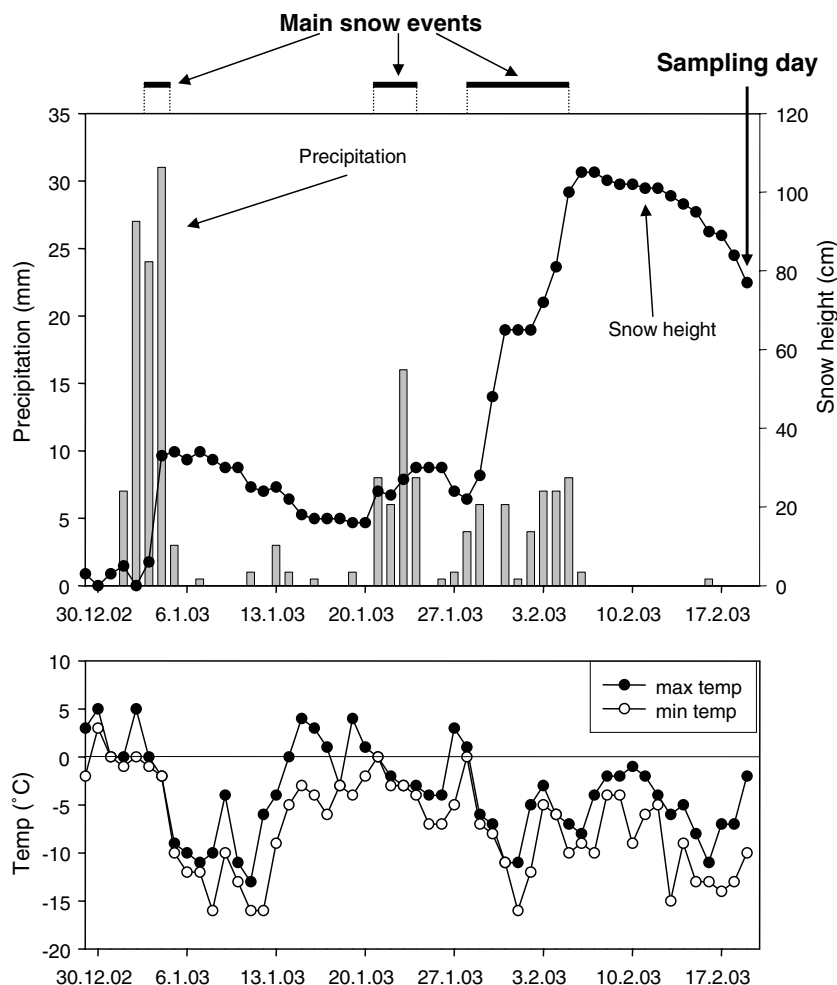

Fig. 1. Sampling sites.

Fig. 2. Climatic data record (precipitation, snow height and temperature) at the Feldberg weather station (1493 m asl) for the January 2002–March 2003 period.

complete description of the site is given in electronic annex EA-1.

No weather record for the site itself is available. However, meteorological data (precipitation height, snow height, maximum and minimum daily temperatures) recorded at the Feldberg weather station (1493 m asl), which is located 15 km away from the Kohlhütten Moor peat bog, are given in Fig. 2. These data demonstrate a snow cover and accumulation on the peat bog since early January until the sampling day. On site, the samples were taken when the snow height was approximately 70 cm.

3. Sampling procedure

3.1. The vertical snow profile

The 19th of February 2003, a snow profile was dug in the 70 cm snow pack located on the ombrogenic part of the peat bog. The upper 50 cm consisted of soft fresh snow. The lowermost 20 cm of the profile were characterized by two icy layers suggesting a melting of the snow during the second half of January. This is reflected by positive temperatures recorded at the Feldberg station (Fig. 2) and also by the major element chemistry (Le Roux et al., 2005). Each 10 cm layer was collected wearing PET gloves in sterile plastic bags previously "rinsed" with snow from the same level. Classical clean procedures for snow sampling were applied (Boutron, 1990; Nriagu et al., 1993). According to snow stratigraphy and major element chemistry, snow samples from 0 to 10 cm, 20 to 30 cm and 60 to 70 cm were selected in order to investigate REE concentrations. An additional snow sample was collected near the road (about 500 m far from the snow profile) outside the pine forest surrounding the bog in order to evaluate the influence of direct traffic and salting during the winter season. The snow-containing bags were kept frozen in an insulated box until their filtration in the Strasbourg laboratory. Snowmelt was done at room temperature overnight. Melted snow was filtered in a clean room using pre-cleaned 0.45 μm Millipore HAWP membranes. The filtered samples were conditioned in acid-cleaned polypropylene bottles and acidified with a sufficient amount of laboratory bi-distillated HNO_3 to reach a pH between 1 and 2. A non-acidified aliquot was preserved for pH determination and major

element analyses. The four filtered samples of melted snow were then stored at 4 °C.

3.2. Lichens

Two species of lichens were also sampled on trees located in the sampling site. These two species are *Usnea fillipendula* commonly called "fishbone beard lichen" and *Evernia prunastri*. These lichens were collected during the snow campaign except one *Usnea* sample (collected in spring 2002). The lichen samples were placed in clean plastic bags until fully air dried. No washing procedure of the lichens was done in order to avoid the leaching of soluble particles adsorbed on the thallus (e.g., Nimis et al., 1993). The *Evernia* species were divided into two groups: two bulk samples (*Evernia* 1 and *Evernia* 2) and the lichen extremities (*Evernia* ext.) (2–3 mm) taken from other *Evernia* specimens than *Evernia* 1 and 2. The lichen extremities are supposed to have grown recently and should have incorporated the most recent atmospheric material. Then lichens were crushed in a clean agate mortar before being digested 75 min at 240 °C in a microwave autoclave with HNO_3 and HBF_4 as reagents, following the procedure described in Krachler et al. (2002).

3.3. Recent peat profile

In a previous sampling campaign (electronic annex EA-1), samples of peat from the ombrogenic part of the peat bog were collected using a Wardnaar corer and sub-sampled in 1 cm slices following the procedure described by Givelet et al. (2004). In this study, we considered only the uppermost part of the peat bog which represents ∼400 years of peat accumulation, based on ^{210}Pb age dating (Appleby and Oldfield, 1978) and ^{14}C age dating.

Therefore, we only measured samples from the first 25 cm of the peat profile plus a deep sample (346 cm depth) taken as a reference material characterizing the "preanthropic" period (3000 cal. B.C). The uppermost peat sample (PS) consists of living *Sphagnum* mosses. Peat samples were digested with the same procedure as for lichens.

4. Analytical methods

Chemical analyses were undertaken at the Centre de Géochimie de la Surface in Strasbourg and at the Institute of Environmental Geochemistry in Heidelberg.

4.1. Snow samples

The concentrations of most REE in snow are under the ng L^{-1} level. Therefore, a specific enrichment method was required. A liquid–liquid extraction technique using an organic phosphate solvent (HDEHP) was applied to enrich the REE by a factor of at least 100 (Shabani and Masuda, 1991; Shabani et al., 1992; Tricca et al., 1999). Generally

1.5–3 L of solution were necessary to achieve concentrations that could be measured by Inductively Coupled Plasma-Quadrupole Mass Spectrometer (ICP-QMS). The extraction yield of REE was checked twice (before the first sample extraction and after the last sample extraction) with a composite 0.01 ppb standard REE solution created using individual 1000 ppm REE standard solutions from Specpure. The extraction yields for each Rare Earth were consistent with the average obtained by Tricca (1997). No contamination by the different reagents is noticeable since REE concentrations in procedure blanks are always below the detection limit of the ICP-MS (10 ng L^{-1}).

REE and other elements have been also determined in the particulate load of two snow samples (from 0 to 10 cm depth and the road snow sample), after dissolution of the particles, previously removed from the filter in ultrasonic bath, in concentrated bi-distillated concentrated HNO_3.

4.2. Peat and lichen samples

Peat and lichen compositions were analyzed using ICP-AES and ICP-QMS in Strasbourg. In contrast to lichens, no peat reference material with certified elemental concentrations is presently available. Therefore, in addition to a lichen reference material (IAEA-336 lichen, International Atomic Energy Agency, Vienna, Austria), several plant materials (GBW 07602, Bush Branches and Leaves, Institute of Geophysical and Geochemical Exploration, Langfang, China; SRM 1547, Peach Leaves, NIST; SRM 1573a, Tomato Leaves, NIST) with certified and information concentrations for REE and other trace elements were analyzed in order to control the quality of digestion and analytical procedures. These standard materials were digested in the same runs together with the Black Forest peat and lichen samples. Procedural blanks were conducted and revealed no contamination from the reagents except for Tb in all runs and for Eu and Gd in only one run. Thus, these elements are not represented in the diagrams for several samples when the blank contribution accounted for more than 10%. Measurements of the Reference Standards for all the elements fell in the range of the certified values (Table 1). Moreover, peat samples were also measured for Ti by XRF (Cheburkin and Shotyk, 2005).

4.3. Chronology of peat accumulation

^{210}Pb was measured using low background γ spectrometry (GCW4028, HPGE, Canberra) in Heidelberg. The maximum depth of unsupported ^{210}Pb detection is −18 cm. An age-depth model was calculated by the CRS Age model (Appleby and Oldfield, 1978). For deeper samples, a linear age-depth model was based on 23 ^{14}C AMS dates for the entire peat column (6 m, not shown) (Le Roux et al., 2005). Age-depth models based on ^{14}C and ^{210}Pb are in good agreement when they overlap.

Table 1
Chemical analyses of the different certified materials used to validate the digestion procedure of the peat and lichen samples

Elements ICP-MS	Tomato leaves SRM 1573a		Bush Branches GBW 07602		Peach leaves SRM 1547		Lichen IAEA-336		
	Measured	(inform. val.)	Measured	Certif. val. (inform. val.)	Measured	(inform. val.)	Measured 1	Measured 2	Rec. val. 95% C.I. (inform. val.)
La	2.12	(2.3)	1.20	1.23 ± 0.07	9.33	(9)	0.61	0.57	0.66 ± 0.1
Ce	1.69	(2)	2.40	2.4 ± 0.19	10.53	(10)	1.27	1.21	1.28 ± 0.17
Pr	0.34		0.27		1.88		0.15	0.15	
Nd	1.28		1.04	(1.1)	7.41	(7)	0.59	0.59	(0.60 ± 0.18)
Sm	0.19	(0.19)	0.20	0.19 ± 0.01	1.15	(1)	0.113	0.113	0.106 ± 0.014
Eu	0.045		0.039	0.037 ± 0.002	0.21	(0.17)	0.024	0.025	(0.023 ± 0.004)
Gd	0.25	(0.17)	0.20		1.31	(1)	0.099	0.094	
Tb	0.018		0.020	(0.026)	0.13	(0.1)	0.011	0.012	(0.014 ± 0.002)
Dy	0.11		0.14		0.57		0.084	0.090	
Ho	0.023		0.027		0.10		0.016	0.016	
Er	0.064		0.080		0.27		0.047	0.049	
Tm	0.007		0.011		0.028		0.007	0.007	
Yb	0.045		0.072	0.063 ± 0.011	0.16	(0.2)	0.042	0.044	(0.037 ± 0.012)
Lu	0.006		0.011		0.021		0.0063	0.0066	(0.0066 ± 0.0024)

Concentrations are in $\mu g\, g^{-1}$; Certif. val.: certified value; inform. val.: information value; Rec. val.: recommended value 95% confidence interval.

5. Results and discussion

5.1. REE in peat

The REE concentrations data are presented in Table 2. The shapes of all REE concentration profiles with depth in the peat core are similar, with the profiles of La, Eu and Yb concentrations shown for example (Fig. 3). The depth profile of Zn, which is known to be mobile, taken up by the plants living at the surface of the bog (Rausch et al., 2005) and to have significant anthropogenic sources, is also shown. Those are compared with Ti which is a conservative lithogenic element both during weathering and upon burial in peat, and that has no significant anthropogenic source (e.g., Shotyk et al., 2001). Hereafter, only the La profile is discussed because it can be taken to represent the other Rare Earth Elements. La concentrations range between 0.26 and 3.37 $\mu g\, g^{-1}$ for the 25 uppermost centimeters of peat. The La concentrations increase regularly from depth to the top of the bog until 5.7 cm (the greatest La concentration) and then quickly decrease in the surface samples to ca. 0.36 $\mu g\, g^{-1}$. The lowest La concentrations were found close to the surface and are similar to that of a preanthropic sample (P.A.) (0.22 $\mu g\, g^{-1}$, Fig. 3 and Table 2) from a depth of 346 cm depth.

For a comparison, Zn concentrations in the modern and recent samples are about 10 times higher than the Zn concentration in the preanthropic sample. Ti profile concentrations with depth are similar to that of La. Moreover, the correlation between La and Ti confirms that La and REE in general are conservative elements in peat bogs and mostly originate from natural sources. To emphasize the natural origin of REE, enrichment factors for Zn and La relative to Ti in the continental crust have been calculated as:

$$\mathrm{EF(X)} = ([X]_{sample}/[Ti]_{sample})/([X]_{UCC}/[Ti]_{UCC})$$

with $[X]_{sample}$, the considered element concentration (Zn or La) in peat; $[Ti]_{sample}$, the Ti concentration in peat sample; $[X]_{UCC}$, the considered element concentration (Zn or La) in the Upper Continental Crust; $[Ti]_{UCC}$, the Ti concentration in the Upper Continental Crust.

Concentrations of REE, Ti, La and Zn in the upper continental crust were taken from McLennan (2001). Whereas Zn shows very large enrichment in all samples (up to 80) due to anthropogenic deposition and plant retention, La is not enriched and has a similar behavior than Ti as depicted by the absence of any significant EF variation with depth (Fig. 4). As Ti, La has a predominant natural origin, is not significantly taken up by plants and is immobile in peat. Moreover, the La EF for local rocks (surrounding granite) is slightly higher (in the range 1.4–1.8) than that found in peat samples which suggests that the bog receives atmospheric dust from well beyond the local rocks or that the local soils which supply the dust are depleted in REE relative to the rocks from which they are derived. In order to evaluate the variation in REE abundance, the REE distribution patterns of peat samples have been normalized to the Post Archean Australian Shale (PAAS), a reference composition that represents an average of the continental crust (McLennan, 1989). The spectra of the most representative samples are plotted in Fig. 5: the two uppermost samples corresponding, respectively, to the living plants (PS), the first peat sample (P1), the most enriched samples at 5.7 cm depth (P6), P20 at approximately 20 cm and the preanthropic sample (P338). The distribution pattern of the adjacent granite (Abtal Granite, Emmermann et al., 1975) is also given. The REE patterns in peat are quite similar for all samples and exhibit rather flat spectra with a slight MREE enrichment (Sm, Eu and Gd). These REE distribution patterns thus show that there has been no drastic modification of the REE composition of atmospheric deposition over the

Table 2
Ti, Zn and REE concentrations ($\mu g\,g^{-1}$) in peat samples from the Black Forest peat bog

Sample	Depth (cm)	Age dating	Ti ($\mu g\,g^{-1}$)	Zn ($\mu g\,g^{-1}$)	La ($\mu g\,g^{-1}$)	Ce ($\mu g\,g^{-1}$)	Pr ($\mu g\,g^{-1}$)	Nd ($\mu g\,g^{-1}$)	Sm ($\mu g\,g^{-1}$)	Eu ($\mu g\,g^{-1}$)	Gd ($\mu g\,g^{-1}$)	Tb ($\mu g\,g^{-1}$)	Dy ($\mu g\,g^{-1}$)	Ho ($\mu g\,g^{-1}$)	Er ($\mu g\,g^{-1}$)	Tm ($\mu g\,g^{-1}$)	Yb ($\mu g\,g^{-1}$)	Lu ($\mu g\,g^{-1}$)
PS	Surface	2004	90.09	58.21	0.386	0.794	0.092	0.345	0.063	0.014	0.058	0.007	0.044	0.009	0.026	0.004	0.026	0.004
PS1	0.4	1992	66.87	65.00	0.330	0.266	0.077	0.283	0.053	0.012	0.046	0.006	0.035	0.007	0.022	0.003	0.023	0.003
PS6	5.7	1951	428.11	57.77	3.369	6.784	0.777	2.961	0.534	0.115	0.486	0.062	0.339	0.066	0.191	0.027	0.184	0.027
PS20	20.1	1710	97.38	33.87	0.600	1.243	0.148	0.569	0.108	0.025	0.124	0.015	0.078	0.015	0.047	0.007	0.043	0.006
PS338	346	3220 BC	36.25	1.81	0.220	0.442	0.051	0.200	0.036	0.010	0.045	—	0.024	0.004	0.017	0.002	0.014	0.002
Granite					55	82		45	6	1.2		0.72	3.9				1.8	0.33

In addition, the REE concentrations from the local granite are given (from Emmermann et al., 1975).
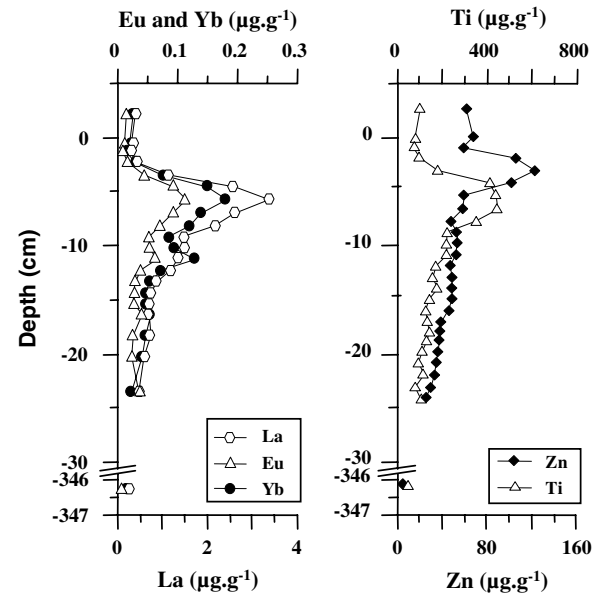

Fig. 3. La, Eu, Yb, Zn and Ti depth profiles in the Black Forest peat samples. The sample located at 346 cm depth corresponds to the preanthropic sample PS338.
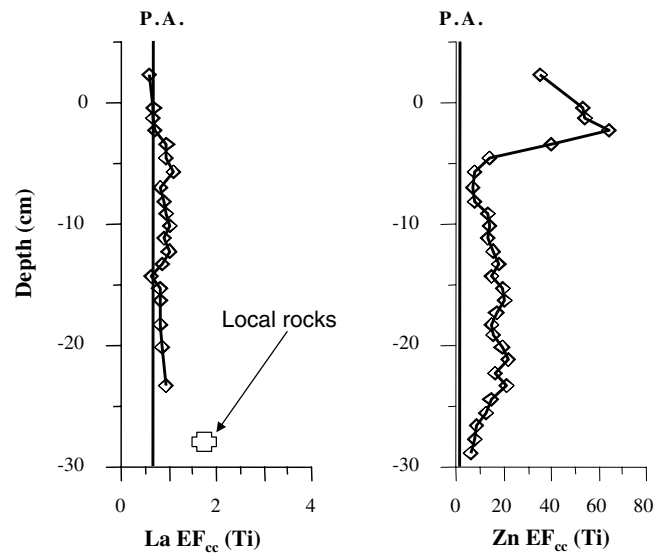

Fig. 4. La and Zn enrichment factors in peat samples calculated using Ti as the reference lithogenic immobile element in peat. P.A. refers to the preanthropic sample PS338.

years. No specific anthropogenic contamination has been recorded in these peat samples. The local granite REE pattern is also flat and consequently has a REE composition rather close to the average of the continental crust.

5.2. REE in snow

5.2.1. Rare Earth Elements in the dissolved fraction

REE concentrations in the four selected snow samples are reported in the Table 3. Samples SBF 20–30 and SBF 60–70 show similar REE concentrations and have
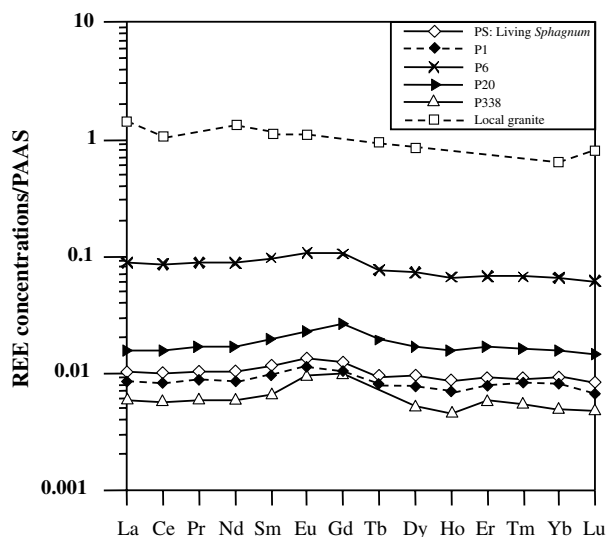
Fig. 5. PAAS normalized REE distribution patterns in several Black Forest peat samples and in the corresponding local granite.

On the other hand, because no snowfall occurred during the 7–19 February period, dust and aerosols could have accumulated in the superficial layer and could have been leached during the melting of the snow before analysis. This could explain the higher dissolved REE concentrations recorded in the upper snow sample. As an average, REE concentrations in SBF road are 1.5 times and 10 times higher than those in SBF 0–10 and SBF 60–70, respectively. PAAS normalized REE distribution patterns of snow samples are quite similar (Fig. 6) and display an overall flat shape with a slight middle REE enrichment, Gd being the most enriched element in each sample. Only the snow collected close to the road exhibits a negative Eu anomaly.
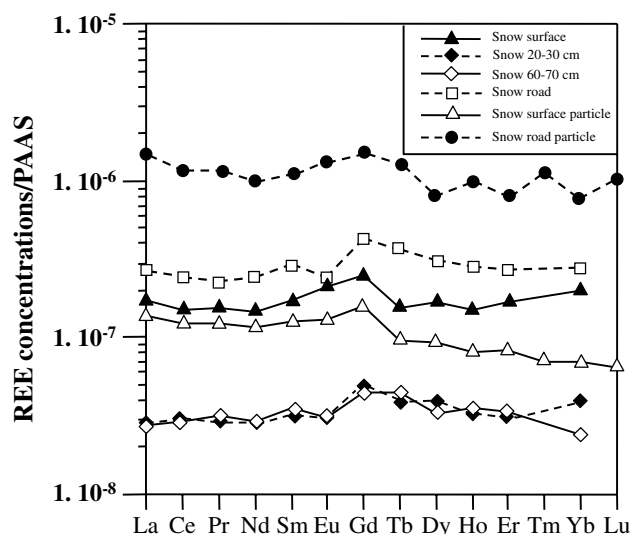
lower concentrations compared to the surface snow samples and especially SBF road, which is affected by traffic and salting.

Computed back trajectories (3 days) (Draxler and Rolph, 2003) show that air mass directions varied considerably between snow events (SW for the early January snow event, N for the beginning of the second half January snow event and NW for the February snow event (for more details see Le Roux et al., 2005). SBF 60–70 was not part of the same snow event as SBF 0–10 and SBF 20–30 but shows quite similar dissolved REE concentrations to those of SBF 20–30 suggesting that REE concentrations in the dissolved fraction of precipitation are independent of air mass origin.

Fig. 6. PAAS normalized REE distribution patterns of snow samples.

Table 3
REE concentrations in the four selected snow meltwater samples (ng L^{-1}) and in the particles from the snow collected close to the road (SBF road P.M.) and from the surface snow (SBF 0–10 P.M.) (μg g^{-1} in particles and ng L^{-1} in bulk snow with particle weights of 1.563 mg/l and 2.133 mg/l in SBF 0–10 and SBF road, respectively)

Sample	SBF road (ng L^{-1})	SBF 0–10 (ng L^{-1})	SBF 20–30 (ng L^{-1})	SBF 60–70 (ng L^{-1})	SBF Road P.M.		SBF 0–10 P.M.	
					μg g^{-1}	ng L^{-1}	μg g^{-1}	ng L^{-1}
Depth (cm)	0–10	0–10	20–30	60–70	0–10		0–10	
La	10.31	6.53	1.63	1.05	26.25	56.00	3.34	5.22
Ce	18.93	11.97	2.43	2.34	42.79	91.28	6.34	9.92
Pr	1.97	1.35	0.25	0.28	4.79	10.21	0.69	1.07
Nd	8.26	5.00	1.01	1.00	15.82	33.75	2.51	3.92
Sm	1.60	0.95	0.18	0.19	2.79	5.94	0.45	0.70
Eu	0.25	0.22	0.03	0.03	0.67	1.42	0.09	0.14
Gd	1.99	1.16	0.24	0.21	3.29	7.01	0.47	0.74
Tb	0.29	0.12	0.03	0.03	0.46	0.98	0.05	0.07
Dy	1.41	0.79	0.19	0.15	1.75	3.73	0.28	0.43
Ho	0.28	0.15	0.03	0.03	0.46	0.99	0.05	0.08
Er	0.75	0.48	0.09	0.09	1.06	2.27	0.15	0.24
Tm	nd	nd	nd	nd	0.22	0.46	0.02	0.03
Yb	0.78	0.57	0.11	0.07	0.99	2.10	0.13	0.20
Lu	nd	nd	nd	nd	0.21	0.45	0.02	0.03

nd, below the detection limit.

Compared to PAAS normalized REE distribution patterns of some rainwater and snow samples from the Vosges Mountains (about 80 km northwest) and Mercantour (South of France) given by Aubert et al. (2002, data not shown), the Black Forest snow samples do not show any HREE enrichment. However, these samples are punctual and not necessarily representative of the global REE composition on the whole year. Thus, this does not allow concluding to different REE sources in the three sites.

5.2.2. Particulate matter trapped in snow

Particles in melted snow correspond to 1.563 and 2.133 mg L^{-1} in SBF 0–10 and SBF road, respectively. In Table 3 are given the REE concentrations in the particles (μg g^{-1}) and also the particle contribution to the melted snow calculated from the weight of particles in (ng L^{-1}). REE concentrations are very much higher (between 6 and 12 times) in the dust sample from SBF road (SBF road P.M.) than in SBF 0–10 P.M. Both samples show comparable flat PAAS normalized REE distribution patterns with only a slight HREE depletion (Fig. 6). Similar to the dissolved fraction of snow, Gd appears to be the most enriched element in the particles found in snow.

The particulate/dissolved ratio in SBF 0–10 is on the order of 1/1, whereas in the SBF road the particulate/dissolved ratio is more or less 5/1. This is not due to higher REE concentrations in PM SBF road but simply due to a higher particle load in the snow sample collected near the road. In addition, compared to their respective dissolved REE concentrations, particulate matter in both samples are HREE depleted as shown in Fig. 7. One may hypothesize a preferential leaching of the HREE from the particles during the snowmelt.
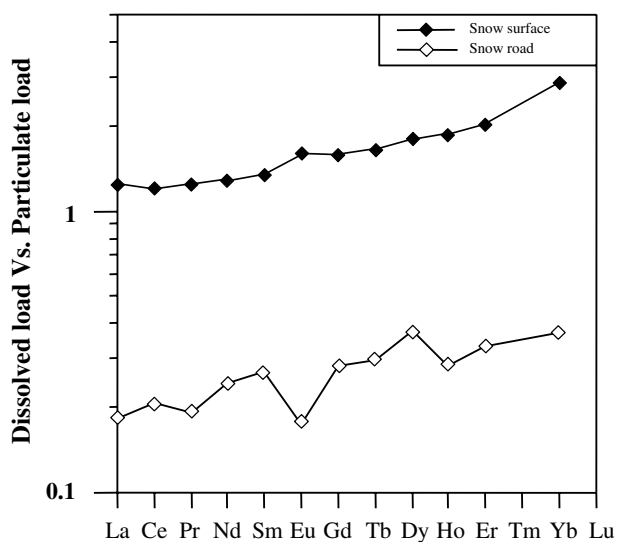
5.3. Atmospheric REE incorporated in lichens

REE concentrations in the *Usnea* specie are roughly 5 times less REE enriched than the *Evernia* specie (Table 4). The PAAS normalized REE distribution patterns in both kinds of lichens are rather horizontal with only a small MREE enrichment (mainly Sm, Eu and Gd) (Fig. 8). This reflects a major crustal origin for the dissolved and particulate material incorporated by these organisms. Upon more careful examination, the two bulk *Evernia* samples show similar distribution diagrams with the maximum enrichment for Gd whereas *Usnea* species resembles the separated *Evernia* extremities with Eu as the most enriched RE. This indicates that *Usnea* and *Evernia* extremities have incorporated the same atmospheric material and further suggests that, as for *Evernia* extremities, the selected *Usnea* samples are rather young and would reflect the composition of the recent atmospheric REE fallouts in the Black Forest. However, the "instantaneous" REE atmospheric signal given by the snow is more comparable to the *Evernia* composition than that of the *Usnea* because Gd appears to be the most enriched REE in both surface snow and

Table 4
REE concentrations in the lichen samples (μg g^{-1})

| Sample	*Usnea* (Winter 2003)	*Usnea* (Spring 2002)	*Evernia* 1	*Evernia* 2	*Evernia* extremities
La	0.433	0.506	2.583	1.810	1.969
Ce	0.994	1.030	5.397	3.931	4.458
Pr	0.115	0.124	0.637	0.453	0.521
Nd	0.470	0.481	2.522	1.807	2.137
Sm	0.090	0.092	0.478	0.343	0.432
Eu	0.022	0.020	0.100	0.074	0.099
Gd	0.078	0.078	0.471	0.365	0.355
Tb	0.010	0.013	0.060	0.044	0.052
Dy	0.071	0.065	0.348	0.260	0.335
Ho	0.014	0.012	0.068	0.051	0.070
Er	0.041	0.038	0.201	0.154	0.201
Tm	0.006	0.005	0.028	0.021	0.029
Yb	0.037	0.033	0.177	0.137	0.186
Lu	0.005	0.005	0.026	0.020	0.028

Fig. 7. Dissolved load vs. particulate load ratios in snow sample collected at the surface of the bog and in the snow sample collected close to the road.
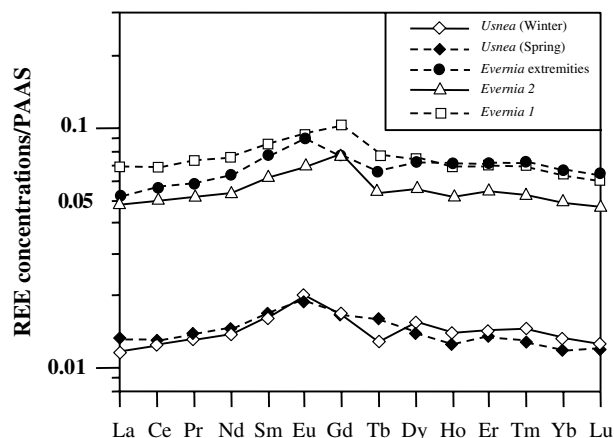

Fig. 8. PAAS normalized REE distribution patterns of the lichen samples.

Evernia lichen. This result further suggests that the material incorporated recently in the lichens (from the separated extremities of the lichens) does not exactly reflect the average composition of the matter assimilated during its whole growth. A non-uniform redistribution of the incorporated matter in the lichen tissues can also be invoked to explain the REE spectra differences as already reported for mosses (Brown and Brumelis, 1996). If one assumes that HREE from particles are more rapidly leached than LREE (as discussed in the previous section) and thus easily incorporated by the lichen this would explain the relative HREE enrichment in lichens compared to snow dust. However, this assumption contradicts the findings from Chiarenzelli et al. (2001) who have reported a greater assimilation (bio-fractionation) of LREE compared to HREE in lichens.

5.4. Origin of the REE trapped in the different archives

One of the basic interests of this paper was to compare REE patterns of peat samples with other indicators of atmospheric deposition. On the whole, lichens REE distribution patterns, as well as, those of snow are very similar to those of peat samples from the same area. A different way to distinguish between the potential sources of REE incorporated in the different samples is to express the REE data as a diagram showing La/Sm vs. La/Yb (Fig. 9). In this diagram are also plotted the values for the local granite and the mean upper continental crust (UCC). This diagram suggests that snow particles (surface snow and road snow samples) would largely originate from the local bedrock whereas the dissolved part is more consistent with an UCC composition. Only the SBF 20–30 plots far off this end-member toward an hypothetic B end-member. REE in peat and lichen samples are a mixing between an UCC component and another end-member A (with low La/Sm and La/Yb ratios) which remains to determine. Whereas REE patterns suggest common sources for the
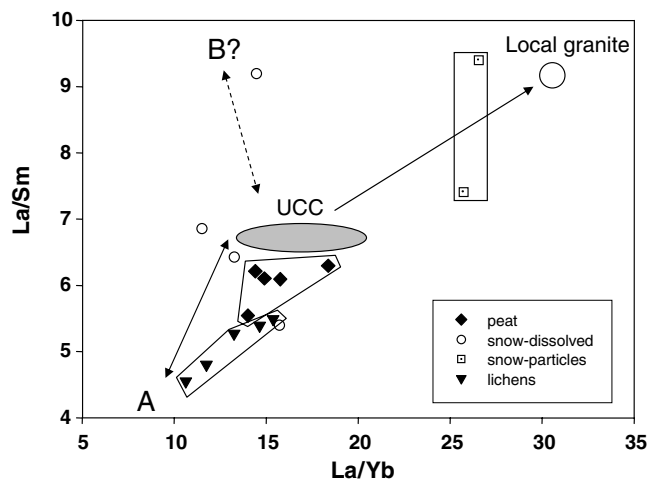
different atmospheric archives, Fig. 9 shows that REE imprints of peat and dissolved snow samples differ from that of the local bulk rock samples.

5.5. REE atmospheric fluxes

One main advantage of peat material is the possibility to construct a robust age-depth model based on ^{210}Pb and ^{14}C measurements and therefore to estimate REE accumulation rates. For the uppermost three samples, this accumulation rate for La is between 0.12 and 0.14 mg m^{-2} y^{-1} (Fig. 10a). Considering the mean precipitation of 1800 mm y^{-1} for this region of the Black Forest (Dierssen and Dierssen, 1984) and assuming that the REE concentrations in the surface sample (particulate + dissolved, [La]$_{bulk\_snow}$ = 12 ng L^{-1}) is representative of annual deposition, the REE flux is around 22 µg m^{-2} y^{-1}. There is therefore a large difference between the two estimates. The most probable reason for the discrepancy is that REE concentrations in precipitation at this period of the year are in fact not representative of the annual average. The particulate load in particular could have been underestimated simply because most of the local source was frozen and snow covered, thereby keeping soil-derived dust particles to a minimum. Also during our study, air masses mainly originate from the ocean (western winds) which probably supply less dust than northern or eastern air masses that carry material from the heavy industrialized regions (North Germany and Eastern Europe). Therefore, longer periods of precipitation and accurate precipitation survey would be necessary to compare directly REE atmospheric concentrations and REE accumulation rates in peat samples.
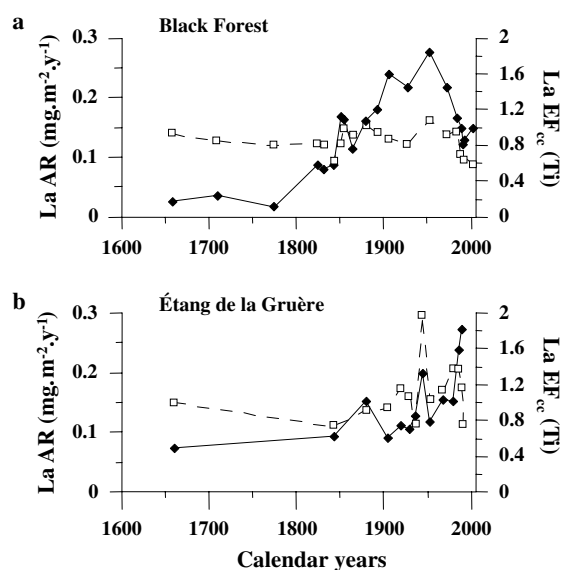

Fig. 10. La accumulation rate (AR) (black diamonds) and La enrichment factor calculated using Ti as the reference lithogenic immobile element in peat (white squares) (a) in the Black Forest peat bog and (b) in the Etang de la Gruère peat bog since 1650.

Fig. 9. Black Forest atmospheric archives plotted in a La/Sm vs. La/Yb diagram showing a mixing between several REE sources.

5.6. Comparison between REE records in the Black Forest peat bog and those of the Etang de la Gruère peat bog

As previously mentioned only one study gives temporal variations of REE in a peat profile (Krachler et al., 2003). This peat profile (EGR) is not far away (100 km South) from the peat bog investigated in this study. The surrounding areas and the substrata are significantly different in both cases: the Black Forest mountains are crystalline (granite) mountains whereas the Swiss Jura is dominated by calcareous rocks. Both peat profiles have similar REE concentrations and recent accumulation rates (A.R.) (expressed here by the La A.R.) (Figs. 10a and b). The A.R. range between 0.08 and about 0.3 mg m^{-2} y^{-1} for the early 1800s and the more recent time (1950 for the BF and 1990 for the EGR), respectively. Despite some differences, there is a marked increased in the A.R. of La at the beginning of the industrial period. The Black Forest peat bog also shows a decrease since the 1990s. This is not recorded in the Swiss peat bog because the Swiss peat profile ends in 1991. This increase and then recent decrease in REE flux is also reported in a study of mosses completed in Sweden (Rühling and Tyler, 2004).

La EF (Ti) in the EGR peat samples show the same range (0.8–1.2) as in the Black Forest (Figs. 10a and b). Only a peak dated from about 1950 shows an outlier value of 2 in the EGR which is not visible in Black Forest. At EGR, this distinct peak was explained by REE use in weapons during the second World War (Krachler et al., 2003).

REE distribution patterns in the recent Swiss bog samples (not shown) are rather flat like those of the Black Forest bog. La/Sm vs. La/Yb diagram for EGR (not shown) suggests also that REE in both bogs originate from similar sources with an upper crustal signature. Regional common atmospheric deposition for post-industrial anthropogenic Pb for NW Switzerland and SW Germany was also recently demonstrated by Le Roux et al. (2005).

6. Conclusions

A record of about 350 years of REE accumulation has been studied in a peat bog in Southern Germany. The close correlation between REE and Ti which is a conservative lithogenic element in peat as well as no significant La EF (Ti) are evidence for the conservative behaviour and natural origin of REE in peat.

Other atmospheric-derived REE in this peat bog environment have been investigated. REE in recent ombrotrophic peat samples, lichens and snowpack show similar flat PAAS normalized patterns with a very small middle REE enrichment confirming that the peat records REE atmospheric deposition over time. This result also suggests that atmospheric REE on this site have a primarily Upper Continental Crust signature. Even the enriched REE snow sample (particulate and dissolved load) collected close to the road does not show any anthropic signature. Atmospheric REE flux based on snow deposition is not

in agreement with REE accumulation rates in recent peat samples dated by ^{210}Pb. This is probably due to using a too short time-scale record of the atmospheric deposition (2 months) to calculate the REE fluxes. Particulate deposition is likely to have been especially underestimated during the winter period due to frozen and/or snow covered areas of dust production.

REE imprints of the local granite is different of the REE imprints of peat suggesting that the bog receive a major part of the dust from outside material. The comparison between the Black Forest and the Etang de la Gruère peat bogs about 100 km away and with different surrounding geological characteristics shows that REE behaviour is similar at both sites. This result confirms that dust particles are well mixed in the atmosphere and thus the REE atmospheric signature is consistent at a large regional scale.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.gca.2006.02.020.

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