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Dominique Aubert, Peter Stille, Anne Probst, François Gauthier-Lafaye, Laurent Pourcelot, et al.. Characterization and migration of atmospheric REE in soils and surface waters. *Geochimica et Cosmochimica Acta*, 2002, 66, pp.3339-3350. 10.1016/S0016-7037(02)00913-4 . insu-03642961

**HAL Id: insu-03642961**

**<https://insu.hal.science/insu-03642961>**

Submitted on 19 Oct 2023

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# Characterization and migration of atmospheric REE in soils and surface waters

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**Abstract**—Rainwater and snow collected from three different sites in France (Vosges Mountains, French Alps and Strasbourg) show more or less similar shapes of their REE distribution patterns. Rainwater from Strasbourg is the most REE enriched sample, whereas precipitations from the two mountainous, less polluted catchments are less REE enriched and have concentrations close to seawater. They are all strongly LREE depleted.

Different water samples from an Alpine watershed comprising snow, interstitial, puddle and streamwater show similar REE distributions with LREE enrichment (rainwater normalized) but MREE and HREE depletion. In this environment, where water transfer from the soil to the river is very quick due to the low thickness of the soils, it appears that REE in streamwater mainly originate from atmospheric inputs. Different is the behaviour of the REE in the spring- and streamwaters from the Vosges Mountains. These waters of long residence time in the deep soil horizons react with soil and bedrock REE carrying minerals and show especially significant negative Eu anomalies compared to atmospheric inputs. Their Sr and Nd isotopic data suggest that most of the Sr and Nd originate from apatite leaching or dissolution. Soil solutions and soil leachates from the upper soil horizons due to alteration processes strongly depleted in REE carrying minerals, have REE distribution patterns close to those of lichens and throughfall. Throughfall is slightly more enriched especially in light REE than filtered rainwater probably due to leaching of atmospheric particles deposited on the foliage and also to leaf excretion.

Data suggest that Sr and Nd isotopes of the soil solutions in the upper soil horizons originate from two different sources: 1) An atmospheric source with fertilizer, dust and seawater components and 2) A source mainly determined by mineral dissolution in the soil. These two different sources are also recognizable in the Sr and Nd isotopic composition of the tree's throughfall solution. The atmospheric contributions of Sr and Nd to throughfall and soil solution are of 20 to 70 and 20%, respectively. In springwater, however, the atmospheric Sr and REE contribution is not detectable.

## 1. INTRODUCTION

The knowledge of the transport processes of rare earth elements (REE) at the atmosphere-soil interface is of importance since REE become more and more involved in industrial processes and, therefore, become enriched in the environment. They also gained importance as good analogues for the trivalent actinides and because some REE isotopes occur as fission-derived long-lived radionuclides in nuclear waste. However, fission-derived REE and actinides can also be released into the atmosphere after a serious nuclear plant accident like in Chernobyl (Ukraine) in 1986. During this accident large quantities of radioactive materials were dispersed throughout Ukraine and almost whole Europe. The input of large amounts of mother and daughter isotopes into the biosphere had the consequence that both soils and hydrosphere experienced serious contamination (von Gunten et al., 1988; Mundschenk, 1992; Barci-Funel et al., 1995; Nylén and Grip, 1996).

“Hot spot” soils were discovered throughout almost whole Europe soon after the Chernobyl accident. Special enrichments of radionuclides have been observed in mountainous regions

like south-eastern part of France (Alps) and the Vosges mountains among others. This phenomenon has already been observed after nuclear weapon tests in the 50 to 60's where the radioactive isotopes fallouts have been found to be more important in mountainous regions (Cigna et al., 1987; Bunzl and Kracke, 1988).

Reactor derived REE like Sm and Nd show strong isotopic anomalies due to fission and neutron capture reactions. These “anomalous” isotope ratios have been used to detect fissiogenic REE migration in groundwater (Stille et al., 1999).

In the Mercantour massif (Alps) a soil has been found heavily contaminated by atmospheric deposition. <sup>241</sup>Am enrichments have been detected and <sup>137</sup>Cs concentrations are hundred to thousand times higher than in common mountain soils (Pourcelot et al., 2001). The data further suggest that wind and morphology of the ecosystem strongly controlled the enrichment process of Cs fallout at the time of the Chernobyl accident. At this site, water and snow samples have been collected to determine the REE characteristics of the atmosphere. In addition lichens, interstitial and river water samples from the Vosges Mountains (Aubure, France) and rainwater from Strasbourg have been collected and analyzed for REE and Sr and Nd isotopes. The aim of this study was not only to characterize the recent atmospheric fallout and to distinguish

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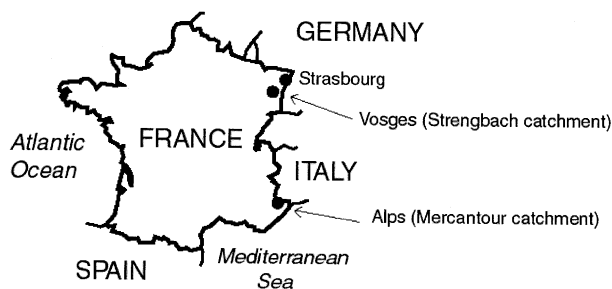


Fig. 1. Sampling sites.

between natural REE input (marine, biogenic, continental crust) and anthropogenic emissions but also to elucidate migration of these atmospheric REE in a soil profile.

## 2. GEOLOGICAL SETTING

The two studied sites are shown on the map (Fig. 1). The first one, the Strengbach forested catchment (80 ha area), is located 58 km SW from Strasbourg, on the eastern part of the Vosges Mountains (North East of France). The elevation ranges from 883 m at the outlet to 1146 m at the catchment divide. This catchment is submitted to a temperate oceanic mountainous climate with dominant western winds. The monthly averages of daily mean temperatures range from  $-2^{\circ}\text{C}$  to  $14^{\circ}\text{C}$  (Probst et al., 1990). Rainfall (1400 mm per year as an average; Probst et al., 1995; Probst and Viville 1997) is spread all over the year. Snowfall season usually lasts 4 months from December to April.

The bedrock consists on a coarse grained base-poor Hercynian leucogranite. The rather deep soils (80 cm average) that have developed on this granite are sandy and stony and lay on a saprolite that can reach 10 m depth. These soils belong to the brown acidic to ochreous podzolic soils serie. A forest covers 95% of the catchment area.

The second site is located in the Southern French Alps (Mercantour catchment). It covers a 135 ha area between 2800 m and 1950 m of altitude. In spite of its mountainous location, this catchment is strongly influenced by Mediterranean climate characteristics. 35% of the total precipitation occurs as snow. The monthly averages of daily mean temperatures range from  $-3^{\circ}\text{C}$  to  $12^{\circ}\text{C}$ .

The bedrock consists of migmatites and amphibolites. The soils, rich in organic matter (alpine ranker soil type), developed on moraine deposits and are not more than 10 cm thick. Above 2300 m of altitude, the steep slopes ( $>30^{\circ}$ ) are not covered with soil.

In this catchment, temporary streams are supplied by snow-melt water during summer. Moraine deposits constitute an important permeable zone, facilitating vertical water drainage. The resurgence of moraine waters in the lower part of the catchment forms several small permanent creeks that finally compose the Chastillon stream at the outlet. The vegetation is composed by a larch forest in the lower part of the catchment, whereas grassland and pastures occupy a large surface below 2400 m of altitude. In the upper part of the catchment the vegetation cover is very scarce.

It is important to note that the hydrological conditions are

rather different for the two sites. The soil profiles in the Alpine domain of the Mercantour catchment are very thin (less than 10 cm) and therefore, the residence time of the water percolating these soils is generally very short. In the Strengbach catchment of the Vosges Mountains, the soil profiles can be more than one meter thick and lay on a deep saprolite. Therefore, waters remain much longer in this soil system and may react much stronger with the rock and soil minerals.

## 3. SITES EQUIPMENTS AND SAMPLING

The Strengbach catchment has been investigated since 1986 and was originally monitored to observe the effects of acid rain on a forested ecosystem (Probst et al., 1990). In this catchment, bulk precipitation is regularly collected in polypropylene funnel collectors (during snow season, buckets are used). Throughfall under conifers is sampled by using 2 m-long open gutters and soil solutions are collected at different depths using zero tension lysimeter plates. Four springs rising 4 m down in the granite flow into a general collector which is partly harnessed for drinking supplies. Streamwater is controlled by an H-flume notch weir and water level is monitored both by ultrasonic and mechanical limnigraphs.

A brown ochreous soil (PP; dystrochrept) has been sampled at different depths. Three samples from 5 cm, 90 cm and 180 cm depth have been studied in this work. The upper layers of this soil profile (upper 10 cm) are rich in organic matter (Fichter et al., 1998). Due to the low quantities of interstitial waters and their very low REE concentrations, we collected a composite soil solution which is a mix from 10 to 60 cm depth. Lichens, whose nutrients are known to derive largely from airborne particulate matter (e.g., Nieboer et al., 1978; Puckett, 1988), have been sampled at the surface of tree barks. Rainwater has also been sampled on the roof of the "Centre de Géochimie de la Surface" in Strasbourg.

In the Mercantour catchment, a workshop area has been opened on a pasture zone with anomalous high radioactivity ("hot spots") to study migration and mobility of radionuclides in soils and waters. On this site, surface water samples (stream, soil and puddle water and also snow) have been collected. The soil water has been collected at 3 to 5 cm depth using in situ porous cup samplers.

Continental crust dust is not the only source of rainwater REE. Most probably fertilizers entering the atmosphere contribute also to the rainwater REE budget (Martin and McCulloch, 1999). Therefore, two fertilizer samples have been integrated in the study and analyzed for their REE concentrations and Sr and Nd isotopic compositions.

## 4. ANALYTICAL METHODS

Water samples have been collected in acid-cleaned polypropylene bottles and filtered in the laboratory using  $0.45\ \mu\text{m}$  pore size Millipore HAWP membranes. The fraction that passed this filter is called the dissolved load and consists of colloids and the "true" dissolved fraction. The filtered water was stored in polypropylene flasks and acidified with suprapure HCl quality to reach a pH between 1 and 2.

The REE concentrations in our water samples are very low and, therefore, a specific enrichment method was required. A liquid-liquid extraction technique using HDEHP as organic solvent was applied to enrich the REE by a factor of at least 100 (Shabani and Masuda, 1991; Tricca et al., 1999). REE extraction blanks are presented in Table 1. Comparing the blank concentrations to the most diluted rainwater

Table 1. REE concentrations (ng/l) in the blank and in the most diluted sample (rainwater) and blank contribution (%) to this rainwater.

	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Blank average (n = 5)	0.074	0.083	0.005	0.031	0.005	0.003	0.007	0.003	0.009	0.004	0.010	0.004	0.013	0.006
Rainwater (ng/l)	1.68	1.38	0.17	0.76	0.63	0.19	0.86	0.22	1.48	0.30	0.83	0.15	0.96	0.15
Blank contribution (%)	4.4	6.0	2.9	4.0	0.8	1.6	0.8	1.4	0.6	1.3	1.2	2.7	1.4	4.0

sample from the Vosges Mountains, it appears that the blank contribution to rainwater is less than 5% except for Ce. The liquid-liquid extraction method allows to remove most of the major elements preventing a good ICP-MS analysis and to separate almost completely the REE from elements causing mass interferences on the inductively coupled plasma-mass spectrometry (ICP-MS). Usually, 0.5 to 2 L of solution were necessary to achieve concentrations that could be measured by ICP-MS (VG PlasmaQuad PQ2+). The detection limit is 0.01  $\mu\text{g/L}$  and the error of measurement  $<5\%$ . The same extraction technique has been applied to obtain sufficient Nd (at least 20 ng) for Nd isotopic measurements.

Minerals were separated from the 100 to 200  $\mu\text{m}$  fraction of the crushed fresh bedrock by using heavy liquid (sodium polytungstate, ©Sometu) and by hand-picking techniques under optical binocular (see also Aubert et al., 2001). Chemical analyses by scanning transmission electron microprobe (STEM) finally certified the quality of each mineral concentrate separation. REE concentrations of these minerals were determined by using ICP-MS after a triacid dissolution (hot mixture of  $\text{HNO}_3$ , HF and  $\text{HClO}_4$ ) in closed Teflon Savillex. The same digestion method was applied to the fertilizer samples. Lichens were digested during one week in hot (150°C) concentrated  $\text{HNO}_3$  acid before ICP-MS analysis.

To characterize the origin of the REE that can be desorbed by natural solutions in the soil (pH of soil solutions under conifers are in between 3 and 4 in the surface horizons of the Strengbach catchment, see Dambrine et al., 1995), we performed leaching experiments using very diluted HCl (0.001 N). Extractions were conducted during 21 days, at room temperature, using 10 g of soil and 50 mL of acid solution. At the end of the experiments, the pH of the solutions reached values comprised between 3.8 and 4.2. This range of pH would avoid precipitation of the leached REE. After centrifugation, the supernatant was analyzed for REE.

Standard techniques were applied for Sr and Nd isotopic analysis. All Sr and Nd isotope analyses were performed on a fully automatic VG Sector thermal ionization mass spectrometer (TIMS) with a 5-cup multicollector after Sr and Nd enrichment and separation from the bulk

sample using cation exchange resin. Typically, ammonium citrate and HCl as eluents were used for Sr whereas Nd was separated from the remaining REE fraction by using  $\alpha$ -hydroxisobutyric acid as eluent. Sr was loaded with nitric acid on a W single filament using  $\text{Ta}_2\text{O}_5$  as an activator. The ratio  $^{86}\text{Sr}/^{88}\text{Sr} = 0.1194$  was used for fractionation correction. During the measuring period the NBS 987 Sr standard yielded  $^{87}\text{Sr}/^{86}\text{Sr} = 0.710258 \pm 13$  ( $\pm$  sigma mean,  $n = 9$ ). Nd was measured by using Ta-Re double filament assemblies. The 0.7219 value for the  $^{146}\text{Nd}/^{144}\text{Nd}$  ratio was used for fractionation correction. During the period of measurement the  $^{143}\text{Nd}/^{144}\text{Nd}$  ratio of the La Jolla standard was  $0.511856 \pm 7$  ( $\pm$  sigma mean,  $n = 6$ ).

## 5. RESULTS AND DISCUSSION

### 5.1. The Rainwater and the Snow

The REE concentrations of filtered rainwater, snow and seawater are reported in Table 2. The rainwater collected in the Vosges (Strengbach catchment) has the lowest REE content ( $\Sigma\text{REE}$ : 10 ng/L), whereas the one sampled in Strasbourg is the most concentrated ( $\Sigma\text{REE}$ : 260 ng/L). Snow from the French Alps (Mercantour watershed) shows intermediate REE concentrations ( $\Sigma\text{REE}$ : 45 ng/L - 66 ng/L). The PAAS (Post Archean Australian Shale, (Taylor and McLennan, 1985)) normalized patterns of the different rainwaters and of one snow sample (snow 2) are compared to seawater strongly depleted in LREE (La to Nd) (Fig. 2). In fact, the LREE have been found to be preferentially enriched in the particulate load of the precipitations (Heaton et al., 1990; Sholkovitz et al., 1993; Freyrier et al., 1998). Therefore, the weaker LREE depletion for snow 1, which has been exposed for a long period of time to atmospheric precipitation, might be due to leaching or dissolution of

Table 2. REE concentrations (ng/l) in the different water samples (snow, rainwater, soil solutions, springwater and streamwater) collected at the different sampling sites and in seawater (Tachikawa et al., 1999). Eu anomalies ( $\text{Eu}/\text{Eu}^*$ ) are normalized to the Vosges rainwater.

	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Eu/ Eu*
<i>Mercantour catchment</i>															
Snow 1 (Alps) October	8.98	17.55	2.27	9.31	1.98	0.43	1.91	0.22	1.27	0.22	0.96	n.d.	n.d.	n.d.	0.84
Snow 2 (Alps) February	3.29	16.03	2.13	10.83	6.21	1.53	7.97	1.31	7.90	1.33	3.65	0.40	2.63	0.32	0.84
Puddle water	38.50	90.38	12	53.13	12.43	3.34	13.42	1.98	12.33	2.77	8.9	1.18	8.29	1.2	0.99
Soil water 1	278	615.6	85.1	306.3	98		48.3	6.05	0.79						
Soil water 2	204	560	73.85	319.6	79.6	25.6	55.55	9.9	75.8	16.3	42.6	7.6	23.85	4.7	1.41
Streamwater	120	30.48	25.25	100.65	14.16	2.85	12.55	1.23	6	1.38	4.47	0.56	3.93	0.65	0.81
<i>Vosges catchment</i>															
Rainwater	1.68	1.38	0.17	0.76	0.63	0.19	0.86	0.22	1.48	0.30	0.83	0.15	0.96	0.15	—
Throughfall	20.9	29.8	3.80	16.88	4.00	0.96	4.15	0.69	3.62	0.74	2.07	0.34	2.80	0.51	0.89
Soil solution	188.4	114.5	12.80	58.0	17.6	3.9	19.8	3.6	19.0	3.2	8.7	1.7	10.9	1.3	0.80
Streamwater	26.6	73.1	14.1	84.9	38.7	7.0	50.0	8.4	46.8	8.1	22.5	3.4	25.5	3.8	0.61
Springwater	50.5	174.2	33.2	195.2	95.3	16.6	151.5	26.5	145.3	23.4	57.2	7.3	49.5	7.1	0.53
<i>Strasbourg</i>															
Rainwater	22.18	56.71	9.38	46.26	26.18	7.25	31.88	4.98	29.20	5.30	15.30	2.24	n.d.	2.94	0.97
<i>Seawater (*)</i>															
	3.33	3.94	0.88	4.00	0.77	0.22	0.93	0.16	1.16	0.26	0.78	0.11	0.65	0.11	1

\* From Tachikawa et al. (1999).

n.d. : not determined.

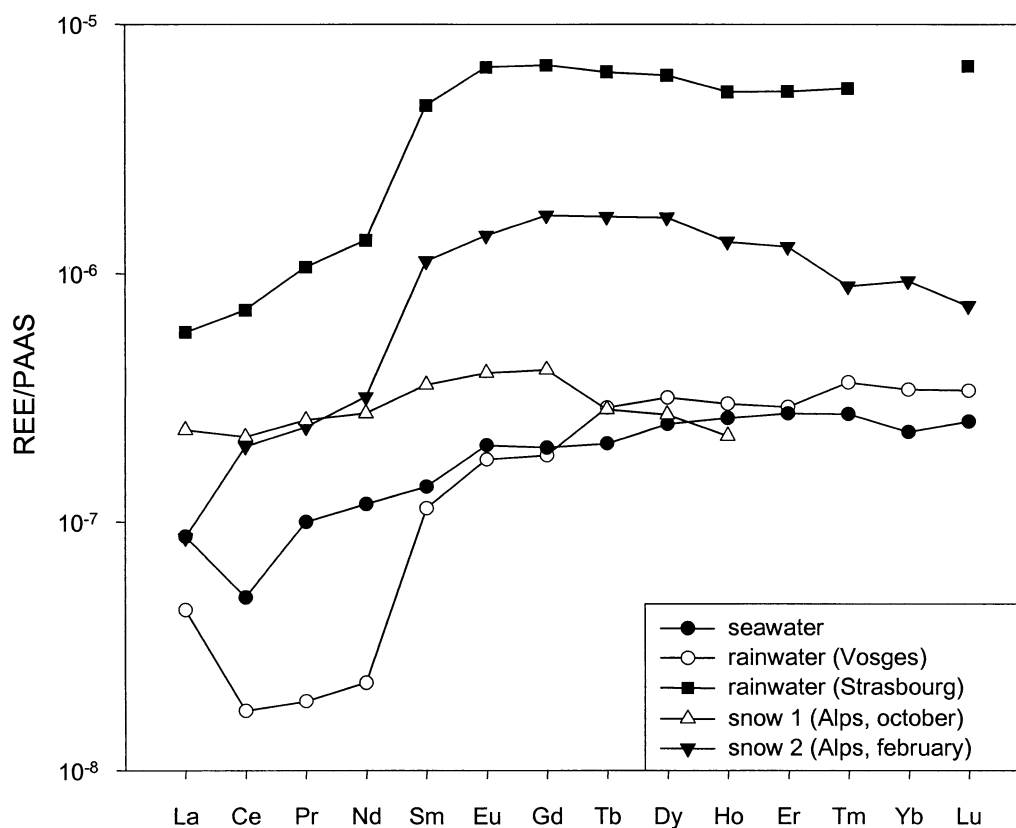


Fig. 2. REE distribution patterns in different rainwater and snow samples.

LREE enriched particles. Apart from the snow 2 sample, that shows a slight depletion from Dy to Lu, precipitation's MREE to HREE distribution patterns are relatively flat. The rainwater from the Vosges Mountains (Strengbach catchment) shows a negative Ce anomaly but also a distribution pattern very close to that of seawater for the MREE and HREE (Sm to Lu). The REE distribution patterns of the here studied atmospheric precipitates differ from those discussed by Sholkovitz et al. (1993) which show a strong HREE depletion and a negative Eu anomaly for most of the samples.

To recognize REE migration of atmospheric origin in soils we decided to use rainwater for REE normalization. We had only the possibility to determine the REE concentrations and distributions of rainwater from the Vosges Mountains and the city of Strasbourg. From a lead isotope study, we know that the atmospheric precipitates in the Strengbach catchment (Vosges Mountains) are much less affected by anthropogenic pollution than those around the city of Strasbourg (Stille, unpublished data). It is also important to note that the fresh snow sample (snow 2) collected quickly after precipitation shows a REE distribution which is very similar to that of the rainwater sample from the Vosges Mountains chosen for REE normalization.

## 5.2. The surface Waters from the French Alps (Mercantour Catchment)

The REE concentrations of the waters sampled in the Mercantour catchment are compiled in Table 2. Soil waters are the

most REE-enriched solutions ( $\Sigma\text{REE}$ : 1500 to 1750 ng/L) whereas streamwater and puddle water (saturated soil water) show REE concentrations intermediate between those of snow 1 and those of soil solutions ( $\Sigma\text{REE}$ : 260 to 324 ng/L). All the REE distribution patterns of the Mercantour surface waters normalized to the Vosges rainwater are rather the same (Fig. 3). They are characterized by a LREE enrichment (La to Nd) and a progressive MREE and HREE depletion that can be quantified by the rainwater normalized (Er/Nd)<sub>N</sub> ratio. The streamwater is the most HREE depleted with a (Er/Nd)<sub>N</sub>=0.04 whereas interstitial waters are the least HREE-depleted solutions with a (Er/Nd)<sub>N</sub> of 0.12 to 0.17. Only streamwater shows a strong negative Ce anomaly. This negative Ce anomaly can be explained by the removal of Ce (IV) as CeO<sub>2</sub>, which is the stable form of Ce in water at high pH conditions (Brookins, 1989). In the Mercantour catchment, streamwater shows pH around 7.5 whereas interstitial waters (particularly saturated soil waters) and snow are characterized by less basic pH (5.5 and 6.7, respectively). This Ce anomaly in streamwater can also be explained by a Ce removal from the soil solution on the colloidal matter. Ingri et al. (2000) report a correlation between Ce enriched organic colloids and negative Ce anomalies in the Kalix river in Sweden. This mechanism can be invoked in the Mercantour catchment since the soils in this area are very rich in organic matter (>30%). Nevertheless, the streamwater REE distribution pattern strongly resembles those of snow (snow 1; snow exposed for several months) and the soil waters collected at the same time in this small catchment. This suggests that

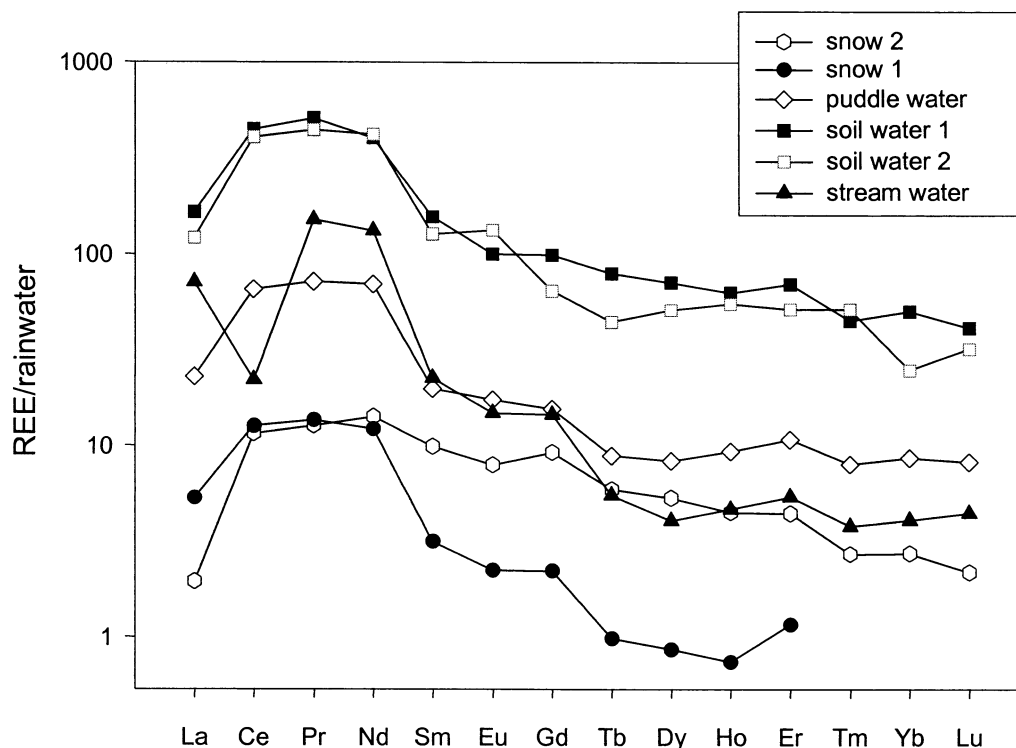


Fig. 3. REE distribution patterns of surface waters and snow samples collected in the French Alps (Mercantour).

atmospheric input, especially old snow could have been an important provider of REE to the surface and soil waters in the Mercantour catchment. This is not astonishing since the soil horizons are very thin compared to those of the Vosges catchment and that the residence time of these surface waters in the soil are very short. Thus, these waters are not for long time in contact with the soil minerals and, therefore, carry a rather atmospheric than soil REE signature.

### 5.3. The Strengbach Catchment in the Vosges Mountains

#### 5.3.1. REE distributions in waters and lichens

REE concentrations in the surface waters collected in the Strengbach catchment are reported in Table 2 and Figure 4. REE are more enriched in throughfall than in rainwater probably due to the leaching of particles (dry deposits) deposited on tree foliage and to leaf excretion. Compared to throughfall, spring and streamwaters display different REE distribution patterns. Soil solution (collected from 10–60 cm depth) shows an intermediate pattern between throughfall and springwater. The different solutions can be characterized by their rainwater normalized Eu anomalies ( $\text{Eu}/\text{Eu}_N: 2\text{Eu}_N/(\text{Sm}_N + \text{Gd}_N)$ ). There is a decreasing negative Eu anomaly from spring and streamwater (0.53 and 0.61, respectively) to soil solution and throughfall (0.8 and 0.89, respectively). The smaller MREE and HREE depletion observed for spring- and streamwater compared to soil solution and throughfall can be expressed by the rainwater normalized (Er/Nd)<sub>N</sub> ratio. Soil solution and throughfall give a similar low ratio ( $\sim 0.14$ ) whereas streamwater (0.24) and springwater (0.27) exhibit higher ratios. These data might sug-

gest that the soil solution collected in the upper soil horizons contains a larger portion of atmospheric REE than the springwater whose chemical and isotopic signatures are strongly influenced by apatite alteration (Probst et al., 2000; Aubert et al., 2001).

REE concentrations of lichens are compiled in Table 3. Lichens are epiphytic plants that possess no roots. They totally rely on nutrients uptake from air constituents (wet, dry or gases; Rossbach et al., 1999). Thus, they usually constitute good tracers for atmospheric deposition to the ecosystems, particularly for the trace elements (e.g., Folkson, 1979; Sloof and Wolterbeek, 1991; Nash and Gries, 1995; Carignan and Gariépy, 1995; Getty et al., 1999; Chiarenzelli et al., 2001; Doucet and Carignan, 2001). The concentrations in the lichens are highly variable depending on the exposition and the age of the sample. The REE distribution patterns of the lichens normalized to Aubure rainwater are close to that of throughfall (Fig. 4). This is not surprising since throughfall consists mainly of wet and dry deposits (in contrast to filtered rainwater that represents only the wet deposits) but it also contains a small contribution deriving from leaf excretion. Thus, lichens that are able to incorporate wet and dry material show REE distribution patterns similar to that of throughfall.

#### 5.3.2. REE distributions in soil leachates and soil solutions

Leaching experiments have been performed on 3 soil samples with very dilute acid solutions (0.001 N HCl) to study the adsorbed REE. Previous studies have shown that such experiments are particularly well suited to extract REE of anthropo-

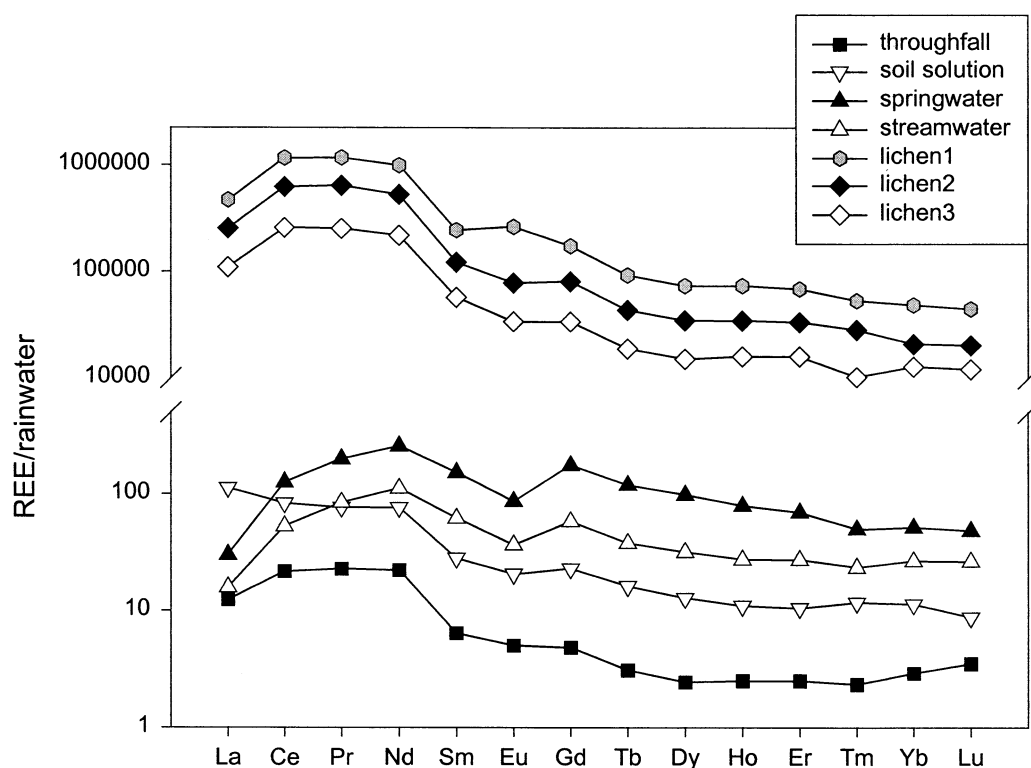


Fig. 4. REE distribution patterns of surface waters and lichens from the Vosges mountains (Strengbach catchment).

genic origin from a contaminated soil (Steinmann and Stille, 1997). Leaching experiments at such a pH are commonly used to desorb material from the exchangeable fraction. The soil profile has already previously been studied for REE (Aubert et al., 2001). It has been shown that in the upper part of the profile especially REE carrying minerals like apatite and monazite have been leached out due to reactions with acid soil solutions. Thus, especially the upper part of the soil profile is very much depleted in soil REE and should be appropriate to find out the atmospheric REE. The soil solution originates from this part of the soil.

The REE contents of the leachates are reported in Table 4. Deep soil horizon leachates show higher REE concentrations than the shallower horizons indicating that with increasing

depth, more REE are adsorbed on the solid phase of the soil. The leachates of the horizon from close to the surface and from 90 cm depth show, like do the soil solution, an atmospheric REE distribution pattern as observed for lichens and throughfall (Fig. 5). Normalized to rainwater the leachates show an increasing negative Eu anomaly from the top soil horizon to the deepest one. The leachate from the deepest soil horizon strongly resembles that of springwater or that of apatite. Thus, with increasing depth the amount of adsorbed REE originating from mineral dissolution increases also (Aubert et al., 2001). Apatite and monazite dissolution seem to be the most important mechanisms controlling the REE signatures of stream- and springwater. It is interesting to note that the soil solution

Table 3. REE concentrations ( $\mu\text{g/g}$ ) in lichens, fertilizers and loess.

	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Lichen 1	0.785	1.595	0.194	0.754	0.152	0.05	0.15	0.021	0.109	0.022	0.057	0.008	0.047	0.007
Lichen 2	0.428	0.858	0.107	0.401	0.076	0.015	0.07	0.01	0.052	0.01	0.028	0.004	0.02	0.003
Lichen 3	0.184	0.354	0.042	0.166	0.036	0.007	0.029	0.004	0.022	0.005	0.013	0.002	0.012	0.002
Fertilizer 1 <sup>a</sup>	44.0	63.9	8.26	31.8	5.71	1.67	6.49	0.84	5.21	1.25	4.26	0.75	5.92	1.11
Fertilizer 2 <sup>a</sup>	8.93	14.34	1.84	7.02	1.26	0.41	1.36	0.2	1.12	0.25	0.69	0.11	0.75	0.14
Fertilizer 3	6.11	4.21	1.17	4.98	0.99	0.29	1.17	0.19	1.28	0.32	0.94	0.15	0.93	0.16
Fertilizer 4	8.93	14.34	1.84	7.02	1.26	0.41	1.36	0.2	1.12	0.25	0.69	0.11	0.75	0.14
Loess 1 <sup>b</sup>	25.0	52.0	4.67	25.2	5.07	0.82	3.24	0.57	3.44	0.73	2.21	n.d.	2.05	n.d.
Loess 2 <sup>b</sup>	25.0	51.0	5.87	23.2	4.86	0.82	3.39	0.62	3.89	0.83	2.34	n.d.	2.36	n.d.

n.d. : not determined.

<sup>a</sup> : from Hu et al. (1998).

<sup>b</sup> : from Taylor et al. (1983).

Table 4. REE concentrations (ng/l) in HCl leachates from the different horizons of the brown ochreous soil (PP) and Eu anomalies (Eu/Eu\*) normalized to the Vosges rainwater.

	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Eu/ Eu*
PP 5 cm	0.6	1.25	0.15	0.65	0.1	d.l	0.1	d.l	0.15	d.l	0.05	d.l	d.l	d.l	—
PP 90 cm	1.75	3.2	0.35	1.3	0.25	0.05	0.4	0.1	0.4	0.05	0.1	d.l	d.l	d.l	0.61
PP 180 cm	5.85	14.75	1.258	5.05	1.35	0.2	1.95	0.35	1.9	0.3	0.6	0.05	0.25	d.l	0.48

d.l : below detection limit.

originating from the upper part of the soil profile shows, with the exception of La, a REE distribution similar to that of the corresponding soil leachates (Fig. 5) and similar to that of the throughfall solution (Fig. 4). This soil solution is especially characterized by a much smaller Eu anomaly (Eu/Eu\*:0.8) than that found for the deep soil leachate (180 cm; Eu/Eu\*:0.48) or for the spring- and streamwater (0.53 and 1.61, respectively). Thus, especially in the surface horizon, where REE carrying minerals disappeared due to weathering (5 cm to 90 cm), REE originating from atmospheric deposition and adsorbed onto soil particles can be identified after the leaching experiment. Deeper in the soil profile the atmospheric REE cannot anymore be identified due to the increasing presence of REE derived from weathering of especially phosphate minerals.

#### 5.4. The Origin of the REE in Lichen, Throughfall, Snow and Soil Solution

Except for LREE (La to Nd), the filtered rainwater from the Vosges has REE distribution patterns similar to that of seawater

(Fig. 2). However, snow, throughfall and lichen show very similar REE patterns but different from that of rainwater (Fig. 3 and 4). Compared to rainwater they are much more enriched in REE and are especially characterized by a strong LREE enrichment (Ce, Pr and Nd). Most probably these REE reflect the presence of atmospheric dust. Heaton et al. (1990) demonstrated that 50 to 90% of La and Sm in precipitation are in particles. Freydier et al. (1998) made the same observation on African tropical rainwater. They observed that more than 75% of La and Ce were included in the particulate phase. Dissolution of such particles would lead to LREE enrichments in rainwater and snow like in the October snow 1 from the French Alps (Fig. 2). Dissolution of such particles produces the REE distribution pattern of throughfall or lichens. Thus, the contribution of the particulate components to the atmospheric REE distribution is important. This has already earlier been shown for major elements (Probst et al., 1992). These particles are commonly considered to derive from the alteration of the continental crust (Sholkovitz et al., 1993; Grousset et al., 1998;

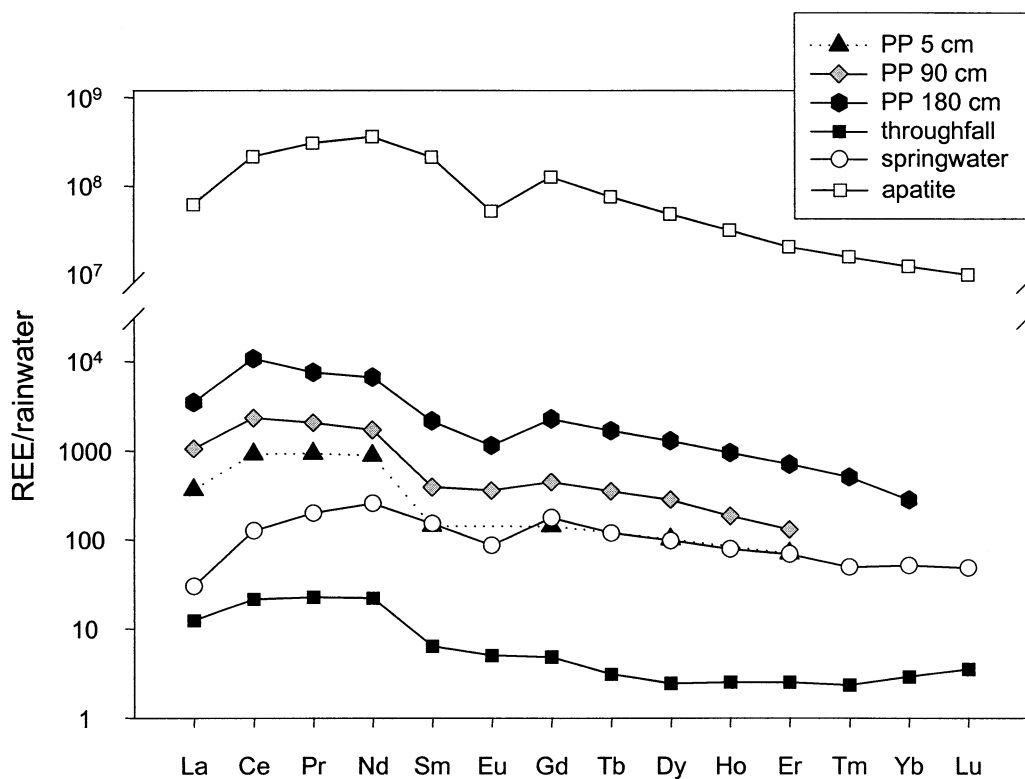


Fig. 5. REE distribution patterns of leachates from a soil profile using 0.001N HCl acid.



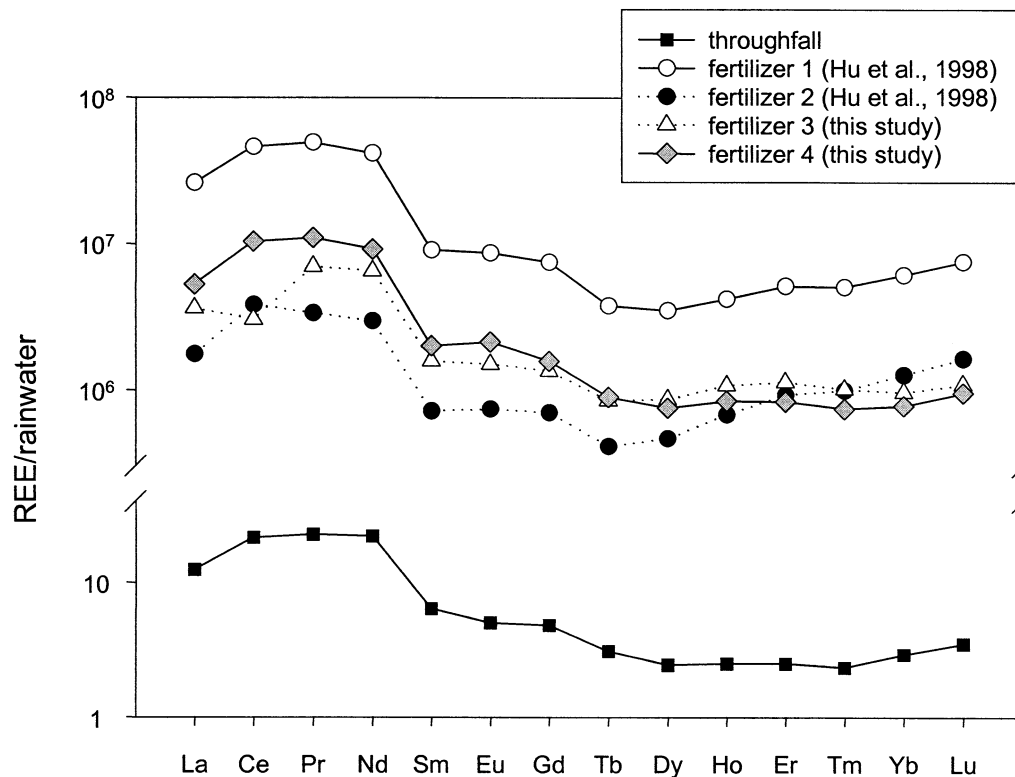


Fig. 6. REE distribution patterns of one throughfall and 4 fertilizer samples.

Greaves et al., 1999). Nevertheless, other anthropogenic sources of REE rich particles can contribute to a REE enrichment in the atmosphere. Olmez and Gordon (1985) or Kitto et al. (1992) have shown that fossil fuel combustion would release a great part of especially LREE (La, Ce and Nd) enriched particles. Another anthropogenic source for REE in the atmosphere are the fertilizers (Volokh et al., 1990). Fertilizers are produced from REE-rich phosphates (Hu et al., 1998; Martin and McCulloch, 1999). Therefore, the REE contents of two different fertilizers (used for flowers and for grass) have also been analyzed (Table 3). The REE distribution patterns of the different fertilizer samples including those of Hu et al. (1998) are very similar and show normalized to the Aubure rainwater a strong LREE enrichment (La to Nd; Fig. 6). But it is also interesting to note that the throughfall pattern is very similar to those of the fertilizers (Fig. 6) and therefore also to PAAS (Fig. 7). Therefore, the REE distribution patterns do not allow to decide to what extent the atmospheric particles derive from crustal weathering, fuel combustion or fertilizers.

Sr and Nd isotopic ratios of fertilizers and throughfall, soil solution and spring water have been determined (Table 5) to characterize the potential influence of fertilizers on the Sr and REE contribution of surface waters and to identify the different sources of Sr and REE.

The  $^{143}\text{Nd}/^{144}\text{Nd}$  isotope ratios of the two fertilizers are rather high, very different from those of loess or continental crust but similar to those of marine, Miocene phosphates from the world's largest Neogene phosphate deposits in North Carolina exploited for fertilizer production (Stille et al., 1994; Stille et al., 1996). However, their  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios are very low (0.7067 to

0.7078) and less radiogenic than Miocene seawater and fertilizers measured before (0.70807 to 0.70902; Négrel and Deschamps, 1996; Borg and Banner, 1996; Martin and McCulloch, 1999).

The  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of rainwater from the Vosges mountains (Strengbach catchment) vary between 0.70913 and 0.71318 (Table 5). The lower values are close to the present-day seawater  $^{87}\text{Sr}/^{86}\text{Sr}$  value of  $0.70916 \pm 2$  (McArthur et al., 1990). Because of its very low Nd concentration it was not possible to determine its  $^{143}\text{Nd}/^{144}\text{Nd}$  isotopic ratio.

The throughfall and the soil solution have similar  $^{143}\text{Nd}/^{144}\text{Nd}$  isotopic ratios (0.51212) but are significantly different from that of the more radiogenic spring water (0.51224). As shown earlier, the springwater has a Nd isotopic composition similar to that of apatite in the fresh, unaltered host-rock (Aubert et al., 2001). In this latter study, it has further been shown that the Sr and Nd isotope ratios of the different suspended load (suspension and residue of suspension after leaching) and dissolved load samples (leachate of suspension, spring- and streamwater) define a mixing curve of alteration products with apatite and plagioclase as mixing end-members (Fig. 8). The mixing model is build up using both Sr and Nd concentrations and isotopic ratios determined on plagioclase and apatite minerals extracted from the host rock (For more details, see Fig. 8 and Aubert et al., 2001). The mixing calculations suggest that 10 to 30% of Sr and Nd in stream- and springwater originates from apatite dissolution in the deeper part of the soil (Aubert et al., 2001). This also explains why the springwater has a REE distribution pattern similar to that of apatite. The mixing curve between the rainwater and springwater components indicates that huge amounts of rainwater are

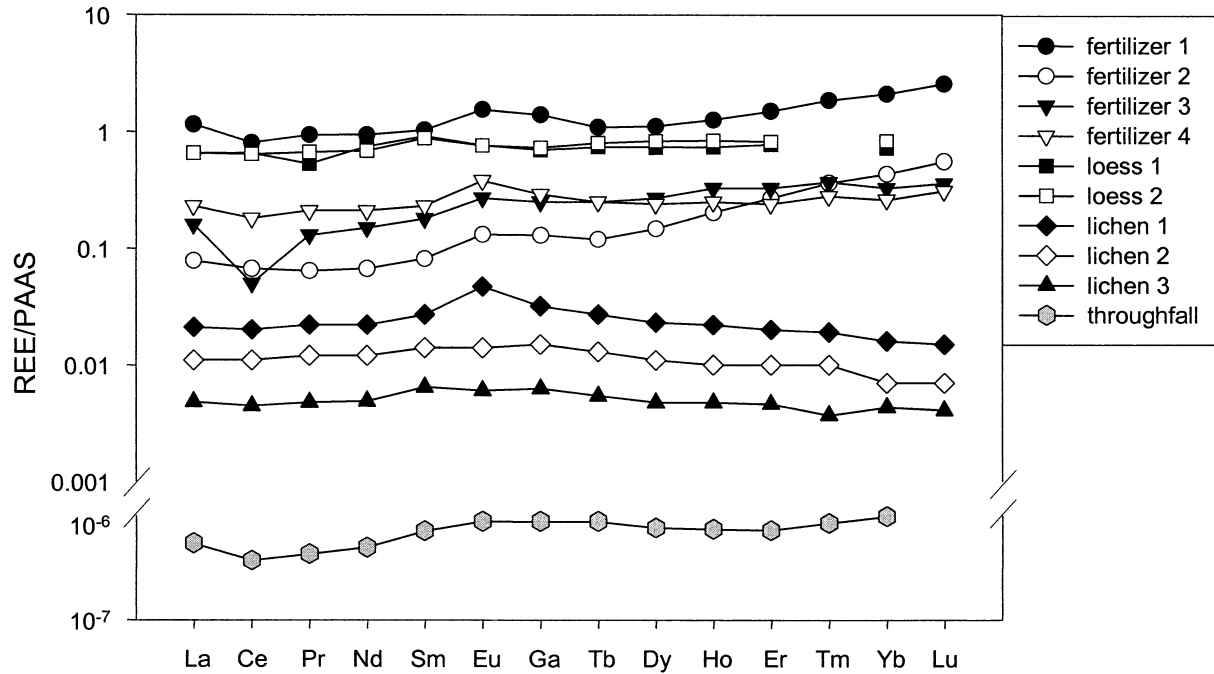


Fig. 7. PAAS normalized REE distribution patterns of fertilizers, loess, lichens and throughfall. Loess data are from Taylor et al., 1983.

necessary to change the springwaters Sr and Nd isotopic compositions. This result is in agreement with previous investigations in this catchment, where weathering processes have been found to be very efficient in controlling the acid neutralization

in this environment (Probst et al., 1992, Probst et al., 1995). Even during significant storm events, the atmospheric contribution to streamwater output would not exceed 10% of the total discharge at the outlet, which is mainly supplied by waters that

Table 5. Nd and Sr isotope data of water samples, separated minerals and fertilizers.

	Sr concentration	$^{87}\text{Sr}/^{86}\text{Sr}$	Nd concentration	$^{143}\text{Nd}/^{144}\text{Nd}$
	$\mu\text{g/l}$		$\text{ng/l}$	
Seawater	7000	0.70916 <sup>a</sup>	4 <sup>b</sup>	$0.51203 \pm 5$ <sup>c</sup>
Rainwater <sup>d</sup>	0.21	$0.71033 \pm 2$	—	—
	0.55	$0.71051 \pm 2$	—	—
	0.93	$0.71318 \pm 2$	—	—
	0.35	$0.71203 \pm 1$	—	—
	0.94	$0.70913 \pm 31$	—	—
Rainwater (mean value)	0.6	0.71096	0.8	—
Throughfall	2.6	$0.71284 \pm 1$	—	—
	3.0	$0.71558 \pm 1$	—	—
	1.0	$0.72727 \pm 3$	—	—
Throughfall (mean value)	2.2	0.71857	17	$0.51212 \pm 5$
Soil solution	7	$0.72289 \pm 5$	58	$0.51218 \pm 5$
Springwater	13	$0.72606 \pm 2$	195	$0.51224 \pm 4$
	$\mu\text{g/g}$		$\mu\text{g/g}$	
Apatite	790	$0.71612 \pm 1$	277	$0.51228 \pm 1$
Plagioclase	45	$0.74203 \pm 5$ <sup>e</sup>	7.4	$0.51205$ <sup>f</sup>
Fertilizer 3	245	$0.70781 \pm 4$	5	$0.51234 \pm 2$
Fertilizer 4	354	$0.70671 \pm 3$	7	$0.51231 \pm 2$

<sup>a</sup>: from McArthur et al. (1990).

<sup>b</sup>: from Tachikawa et al. (1999).

<sup>c</sup>: data from the North East Atlantic Ocean from Spivack and Wasserburg (1988).

<sup>d</sup>: from Aubert et al. (2002) excepted the last value (this study).

<sup>e</sup>: from Probst et al. (2000).

<sup>f</sup>: estimated by Aubert et al. (2002).

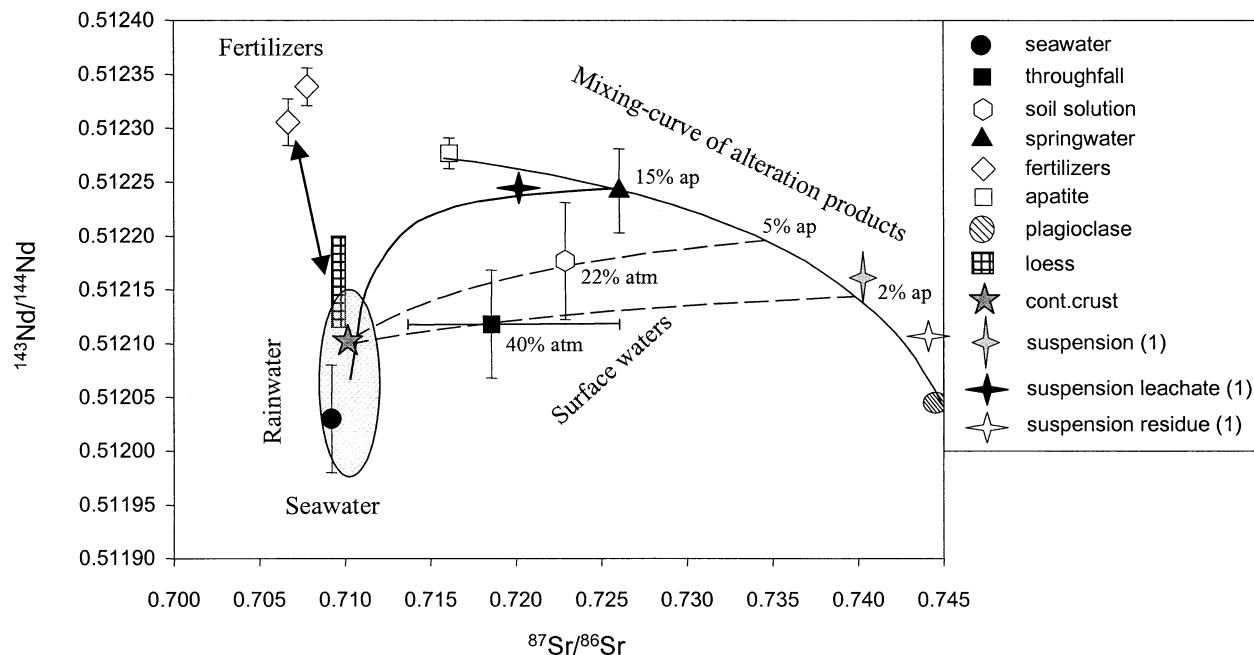


Fig. 8. Sr and Nd isotopic data of atmospheric components and surface waters. Apatite and plagioclase define a mixing curve of alteration products on which spring- and streamwaters as well as corresponding suspended loads plot. The curve has been calculated using the following parameters: apatite with  $^{143}\text{Nd}/^{144}\text{Nd}=0.51227$ ,  $^{87}\text{Sr}/^{86}\text{Sr}=0.716$ ,  $\text{Nd}=277\text{ppm}$  and  $\text{Sr}=790\text{ppm}$ ; plagioclase with  $^{143}\text{Nd}/^{144}\text{Nd}=0.51205$ ,  $^{87}\text{Sr}/^{86}\text{Sr}=0.745$ ,  $\text{Nd}=7.4\text{ppm}$  and  $\text{Sr}=73.7\text{ppm}$ . The percentages of apatite admixture to a plagioclase end-member are also given. Mineral of soil and bedrock plot to the right of this curve. Therefore, an atmospheric source with especially low Sr isotopic ratio is necessary to explain the isotope characteristics of throughfall and soil solution. Three different mixing curves between an atmospheric component and alteration end-members with different apatite-plagioclase ratios are given. The following parameters have been used for calculation of the mixing curves: atmospheric end-member (atmospheric dust close to loess) with  $^{143}\text{Nd}/^{144}\text{Nd}=0.51210$ ,  $^{87}\text{Sr}/^{86}\text{Sr}$ ,  $\text{Nd}=25\text{ppm}$  and  $\text{Sr}=360\text{ppm}$ ; alteration end-members with 2% of apatite and 98% of plagioclase for throughfall, 5% of apatite and 95% of plagioclase for soil solution and 15% of apatite and 85% of plagioclase for spring- and streamwater. Thus, soil solution and throughfall contain considerable amounts of an atmospheric component (22 and 40% respectively as an average). The Sr and Nd isotopic compositions of spring- and streamwater plot very close to the alteration curve and do not allow to calculate any atmospheric contribution. (1) data from Aubert et al. (2001).

flow in the deep layers of the soils (Idir et al., 1999; Ladouche et al., 2001; Aubert et al., 2002).

Aubert et al. (2001) further demonstrate that in the upper part of the soil profile apatite disappeared and REE have been leached out. Therefore, especially in the upper part of the soil profile atmospheric REE should be recognizable. The soil solution plots off the mixing curve of alteration products toward lower  $^{87}\text{Sr}/^{86}\text{Sr}$  and  $^{143}\text{Nd}/^{144}\text{Nd}$  ratios and therefore outside the field of rock-forming minerals. Thus, the Sr and Nd isotopic signatures found in this soil solution cannot simply be the result of leaching of rock and soil forming minerals. An additional component with an especially low Sr isotopic ratio is necessary to explain the isotopic characteristics of the soil solution. Thus, the isotope data strongly support the suggestion that the REE distribution patterns of soil solution and upper soil leachates (Fig. 4 and 5) reflect a REE contribution from the atmosphere. The Sr and Nd isotopic compositions of throughfall are even lower than those of the soil solution. This suggests that throughfall and soil solution carry in contrast to springwater a visible atmospheric Sr and Nd isotopic signature.

Three different mixing curves between an atmospheric component and 3 alteration end-members with different apatite-plagioclase ratios are shown in Fig. 8. The atmospheric mixing

end-member is considered to be solid, atmospheric dust with a Sr isotopic composition of 0.710. This value is close to loess from the Rhine valley (Taylor et al., 1983), rain- and seawater. The Nd isotopic composition of the atmospheric component might be highly variable during the year and is the result of variable contributions from marine, crustal and anthropogenic sources with rather similar Sr isotopic composition but very different  $^{143}\text{Nd}/^{144}\text{Nd}$  ratios. The  $^{143}\text{Nd}/^{144}\text{Nd}$  ratio of the atmospheric component might significantly increase especially during periods of intensive fertilizer manuring. This has been shown in a previous study on major inputs of nitrogen, pointing to the importance of fertilizer contribution in precipitation during the spring period (Probst et al., 1995). For the model it is assumed that the atmospheric component has a Nd isotopic composition intermediate between that of Atlantic seawater and that of loess and close to average continental crust (0.51210;  $\epsilon\text{Nd}=-10.5$ ; Tricca et al., 1999).

Including the rather large variation of the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios for throughfall in the mixing calculations it can be deduced that 17 to 70% of atmospheric component and 83 to 30% of an alteration component from the soil with 98% plagioclase and 2% apatite control the Sr and Nd budget of the throughfall. Thus, it suggests that leaf excretion could contribute to an increase of

the Sr and Nd isotopic compositions in throughfall. The soil solution probably contains a smaller amount of the atmospheric component (22%). In the springwater the atmospheric contribution is no more detectable. Its Sr and Nd isotopic composition is mainly controlled by an alteration component with a comparatively high apatite contribution of 15% and, therefore, a high apatite/plagioclase ratio.

## 6. SUMMARY AND CONCLUSIONS

PAAS normalized REE distribution patterns of filtered rainwater and snow from different areas in France show rather similar REE distribution patterns and have REE concentrations similar to those of seawater. Snow being for longer time exposed to additional atmospheric precipitation is similar to rainwater collected in the city of Strasbourg stronger REE enriched. The particle load of precipitation is preferentially LREE enriched.

Snow, puddle-, soil- and streamwater collected at the same time in the Mercantour catchment (French Alps) show similar REE distribution patterns. In this environment, where water transfer from the soil to the river is very quick due to the little thickness of the soils, it appears that REE in streamwater mainly originate from direct atmospheric inputs or from desorption of atmospheric REE at the soil level.

In contrast, REE distribution patterns of spring and streamwater from the Strengbach catchment (Vosges) are different from those of the atmospheric inputs. They carry compared to atmospheric inputs especially a significant negative Eu anomaly. These waters resided for longer time in the deeper soil horizons and reacted with REE carrying minerals from the soil and bedrock. The soil solution from the upper soil horizons however shows a REE distribution pattern which is different from spring- and streamwater but similar to that of lichen or throughfall. Thus, the soil solution percolating in soil horizons, which are strongly depleted in REE carrying minerals, allow to recognize an atmospheric signature. The exchangeable fraction of the soil behaves in a similar way. Leachates from horizons which were in contact with the analyzed soil solution show also the same REE distributions. However, the leachate of the deepest horizon has a REE distribution pattern very similar to that of apatite. This suggests that the exchangeable fraction of the deep soil horizons contains mainly REE released due to REE carrying phosphate minerals alteration. The Sr and Nd isotope data support these observations. The springwater originating from the deeper part of the soil system has Sr and Nd isotopic compositions plotting on the mixing curve of alteration products. Its isotopic signatures suggest that important quantities of Nd and Sr originate from apatite leaching or dissolution. However, the soil solution from the upper part of the soil system plots to the left of this mixing curve. Since minerals of the soil and bedrock plot either on the mixing curve or to the right side of the curve, the isotopic compositions of the soil solution cannot be explained by leaching of rock and soil forming minerals. An additional source with an especially low Sr isotopic ratio is necessary to explain the isotopic characteristics of the soil solution. The only possible source is the atmosphere. The atmospheric mixing end-member might be highly variable during the year and is the result of variable contributions from marine, crustal and anthropogenic (fertiliz-

ers) sources. Using atmospheric components and the curve of alteration products as mixing end-members one calculates that throughfall incorporates from 17 to 70% of atmospheric Sr and Nd, and the soil solution more than 20% of atmospheric and 80% of weathering components. The results further suggest that leaf excretion could confer a non negligible "soil component" to throughfall.

The here presented isotopic model is a new approach to trace and understand the cycling of atmospheric Sr and REE in soils, soil waters and plants from highly vulnerable ecosystems which suffer important soil acidification.

*Acknowledgments*—The authors are particularly grateful to Jean Jacques Frey, Bernard Kiefel, Robert Rouault and Jean Samuel from the CGS for their help in the laboratory. The constructive reviews by P. Möller and two anonymous reviewers are gratefully acknowledged.

Financial support was provided by the Région Alsace within the framework of the IFARE (Institut Franco-Allemand de Recherche pour l'Environnement) and the IPSN (Institut de protection et de sûreté nucléaire). D. Aubert benefits from a MRT (Ministère de la Recherche et de la Technologie) grant.

*Associate editor:* T. Paces

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