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Impact of atmospheric deposition, biogeochemical cycling and water–mineral interaction on REE fractionation in acidic surface soils and soil water (the Strengbach case)

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ABSTRACT

Leaf litter contains not only important quantities of elements derived from decomposition of organic matter, but also atmospheric compounds. This is illustrated by Sr and Nd isotope data from soils of the Strengbach catchment, which show that soil litter contains more than 50% of atmospheric Sr and Nd. Downward migrating soil water becomes strongly acidic during flow through litter and humus layers (pH 3.8–4 at 5–10 cm depth), causing not only intense mobilization of elements in the underlying acid brown and podzolic soils at depths between 10 and 50 cm, but also the downward transfer of some litter derived compounds. The Sr and Nd isotope data allow to quantify that soil water from 10 to 70 cm depth contains 45 to 65% of litter derived Nd and Sr. Sequential leaching experiments have been performed on soil samples in order to recover adsorbed trace elements or those fixed in acid soluble mineral phases such as Fe–Mn oxyhydroxides and phosphate minerals. The isotope data of these leachates of the uppermost soil horizons point similarly to the presence of important quantities of litter derived Sr and Nd in the uppermost 30 cm of the soils. With the exception of the litter layer, the soil profiles are substantially depleted in Ca and P down to 50 cm depth, which can be related to low apatite and plagioclase contents. These minerals have probably been preferentially weathered and Ca and P have been removed by percolating soil water and plant uptake. Leaching of primary granite derived apatite controls rare earth element (REE) fractionation only below 50 cm depth. Rhabdophane (REE-PO_4) has been observed as secondary replacement mineral of apatite. This replacement is reflected by Ca/P ratios that are low at the surface and which increase regularly with depth, implying that some of the apatite derived P has been integrated into newly formed rhabdophane and some of the P and Ca have been exported, either by soil solutions or plant uptake. During downward transport, litter derived elements are adsorbed on soil particles and/or coprecipitate with authigenic minerals such as Fe–Mn oxyhydroxide or rhabdophane. Alternatively, litter derived elements may remain in solution or, like Ca, be absorbed by vegetation. The soil solutions from the uppermost 30 cm of the soil profiles and the corresponding soil leachates show very similar REE distribution patterns and are, compared to the waters of the Strengbach stream, which drains the forested catchment, strongly enriched in light rare earth elements (LREE). However, soil solutions from 60 to 70 cm depth are, compared to litter, strongly LREE depleted and show stream water-like REE distribution patterns. It is suggested that this evolution of the REE in the soil solutions is due to the following processes taking place above 50 cm depth: (1) precipitation of LREE-rich phosphate minerals like rhabdophane, (2) diminution of the formation of organic dissolved or colloidal phases in association with Fe–Mn and Al oxyhydroxides and (3) preferential LREE uptake by vegetation. Below 50 cm the REE distribution patterns are further modified by dissolution–precipitation reactions and adsorption. The combination of all these fractionation processes finally leads to the REE patterns of the Strengbach stream at the catchment outlet.

1. Introduction

The formation of soils is controlled by processes of mechanical and chemical weathering leading to the disaggregation of rocks and minerals, and organic matter. Acids provided by the plant–root-system, bacterial metabolism, and degradation of organic matter lead

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to the partial or total dissolution of primary and secondary minerals. These chemical weathering processes are accelerated by acid atmospheric deposits. As reported by Probst et al. (1990, 1992a,b), open field precipitation in the forested Strengbach catchment have a mean pH of 4.5 and are poorly mineralized with sulfate, nitrate and ammonium as major ions. This leads, together with litter derived organic acids and the low buffer capacity of the catchment soil and granitic bedrock, to the formation of strongly acid soil water with pH values of 3.8 to 4 in the uppermost 10 cm of the soil profiles (Table 5). For the Strengbach catchment and other catchments under humid temperate climate it has been shown that neutralization of acid soil water by weathering of the bedrock and soil minerals, as well as desorption of cations fixed on soil particles results in significant loss of base cations such as Ca, Mg, K and Na from the catchment (Pacès, 1985, 1986; Probst et al., 1992a,b; Probst et al., 2000). Some of the mobilized elements, however, are absorbed by vegetation and partly released by leaf excretion and/or decomposition of plant tissue in the litter layer. Therefore, elements such as Ca, Mg, K, P and Fe, which are important nutrients for plants, may leave the hydrological cycle and enter into a closed plant nutrient cycle (Berner and Berner, 1996; Likens et al., 1996; Poszwa et al., 2000; Perakis et al., 2006). Trace metals such as lanthanides and actinides may also follow this closed biochemical plant–nutrient cycle (Stille et al., 2006; Aouad et al., 2006).

Stille et al. (2006) observed in their combined Sr and Nd isotope study that Sr and REE of stream water and trees of the small Strengbach catchment mainly originate from preferential dissolution of apatite during weathering and that the preferential uptake of LREE by vegetation amplifies the depletion of LREE in the catchments surface runoff. Apatite is an important source of Ca and P and, therefore, dissolution of this mineral is an important nutrient source for vegetation. Trees fractionate not only the REE but also the Ca isotopes (Schmitt et al., 2003; Cenki Tok et al., 2009). The lighter ^{40}Ca isotopes are preferentially enriched in the plants tissue; therefore, the remaining soil solution is ^{40}Ca depleted and enriched in the heavier ^{44}Ca isotope. The Ca isotope data show that besides apatite and plagioclase, the atmosphere also contributes substantially to the Ca budget of vegetation. Ca isotope data of throughfall samples from the same forested Strengbach catchment further indicate that their Ca composition contains a ^{40}Ca enriched plant-derived Ca, a ^{40}Ca depleted soil water-derived Ca, and an atmosphere-derived Ca component. Mixing calculations between these end-members suggest that at least 70% of the Ca present in the throughfall has an atmospheric origin (Schmitt and Stille, 2005). Similarly, Aubert et al. (2002a) point out, based on Sr and Nd isotopes, that the atmospheric contribution to throughfall is about 20% to 70%. Thus, the atmosphere contributes substantially to the Ca, Sr, and Nd budget of vegetation and, therefore, also to that of surface soil.

A combined isotope and REE study of the soils in this catchment indicates that apatite and zircon are the most important phases controlling the Th and REE concentrations in the soil and that selective weathering of apatite causes strong REE fractionation within a 2 m thick soil profile (Aubert et al., 2001). However, this

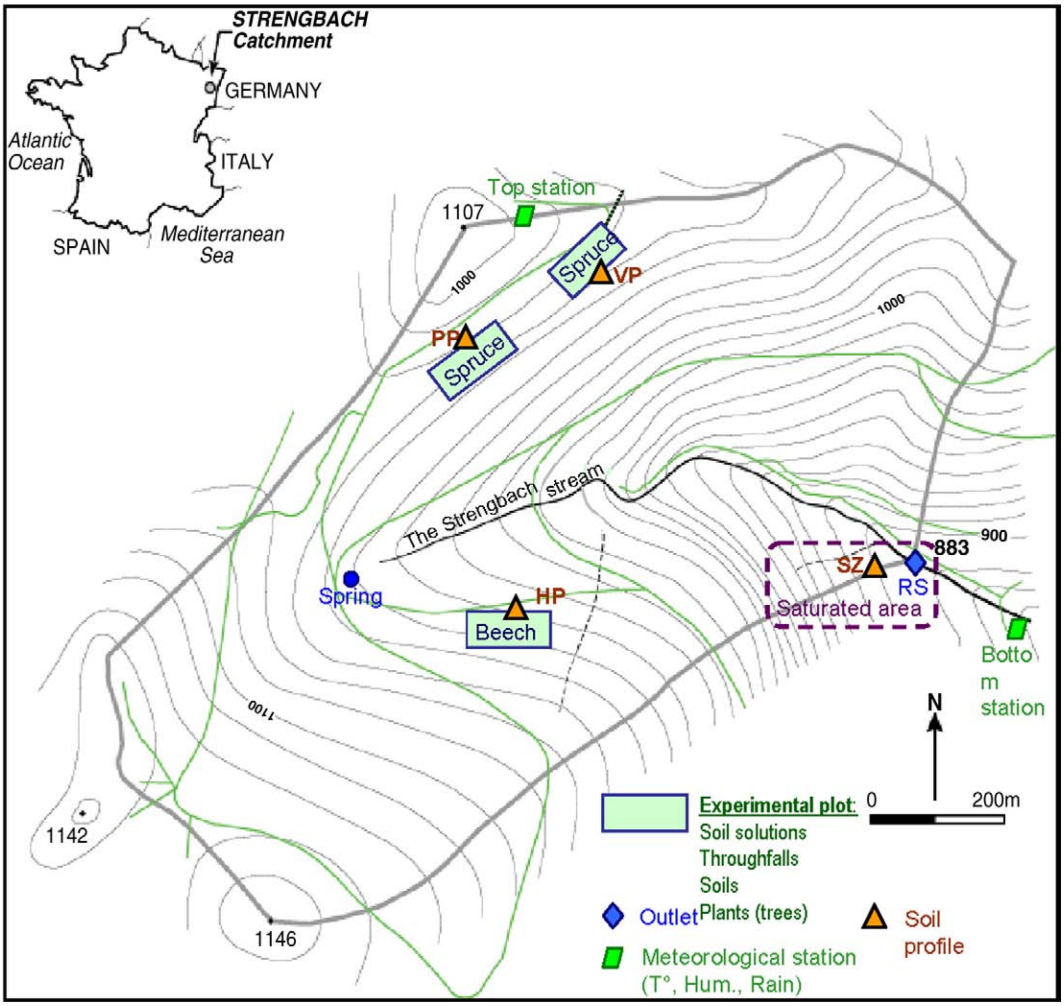

Fig. 1. Uppermost Strengbach catchment with sampling sites HP, PP and ZS. HP soil profile below beech and PP soil profile below spruce trees. ZS: soil profile in the water saturated zone close to the catchment outlet.