Science of the Total Environment 487 (2014) 1–12

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Origin and distribution of rare earth elements in various lichen and moss species over the last century in France

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HIGHLIGHTS

- Rare earth were explored in current and herbarium lichens and mosses in France.
- Rare earth patterns indicated a lithogenic origin from weathering of regional bedrock.
- Herbarium data showed a converging regional influence over one century (1870–2010).
- Bark substrate had no influence on REE content.
- For timescale comparison, normalization was recommended instead of concentrations.

ARTICLE INFO

Article history:
Received 29 October 2013
Received in revised form 27 March 2014
Accepted 27 March 2014
Available online xxxx

Editor: James P. Bennett

Keywords:
REE
Anomalies
Lichens
Mosses
Herbarium
Bark
Bedrock

ABSTRACT

Rare earth elements (REE) are known to be powerful environmental tracers in natural biogeochemical compartments. In this study, the atmospheric deposition of REE was investigated using various lichens and mosses as well as herbarium samples from 1870 to 1998 from six major forested areas in France. The comparison between the REE distribution patterns in organisms and bedrocks showed a regional uniformity influence from dust particles originating from the bedrock and/or soil weathering that were entrapped by lichens and mosses. These lithological signatures were consistent over the last century. The REE patterns of different organism species allowed minor influence of the species to be highlighted compared to the regional lithology. This was even true where the morphological features played a role in the bioaccumulation levels, which were related to the variable efficiency in trapping atmospheric dust particles. A comparison between REE profiles in the organisms and bark indicated a lack of influence of the substrate on lichen REE content. Lichens and mosses appear to be robust passive monitors of REE atmospheric deposition over decades because the mineral data was preserved in herbarium samples despite organic degradation being shown by carbon isotopes and SEM observations. To overcome the bias of REE concentration that resulted from organic degradation, the use of a normalized method is recommended to interpret the historical samples.

1. Introduction

Natural and anthropogenic emissions contribute to the enrichment of atmospheric trace element content (Rauch and Pacyna, 2009) and lead to local/regional or long-range atmospheric deposition (Rosman et al., 1994; Wolff et al., 1999). The atmospheric deposition of trace metals is known to affect ecosystem health (Ulrich and Pankrath, 1983). Therefore, to ensure the protection of ecosystems, the contribution of these atmospheric elements on land surfaces must be assessed (Nilsson and Grennfelt, 1988). Direct tentative evaluations of metal deposition by instrumental measurement have been performed (Azimi et al., 2003; Gandois et al., 2010a; Garnaud et al., 1999); however, the process is complex and expensive. Thus, biological monitoring has been developed over the past 30 years (Hawksworth and Rose, 1970; Swieboda and Kalemba, 1978) and has proven to be a good alternative tool (Loppi et al., 1997; Markert et al., 2003; Harmens et al., 2010), particularly in the spatial evaluation of atmospheric deposition. Lichens and mosses are known to be sensitive to atmospheric contaminants because of their biological features (Conti and Cecchetti, 2001; Wolterbeek, 2002) that make them susceptible to accumulating trace metals from the atmosphere (Rühling and Tyler, 1968; Loppi et al., 1997). A major challenge remains in assessing the contribution of natural versus anthropogenic inputs of metals to ecosystems. Among the trace metals, geochemical tracers such as rare earth elements (REE)

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http://dx.doi.org/10.1016/j.scitotenv.2014.03.132
0048-9697/

have been demonstrated to be powerful tools to characterize the origin of these accumulated elements (Carignan and Gariepy, 1995; Chiarenzelli et al., 2001).

The chemical family of REE (also called lanthanides) includes 14 natural trace metallic components from La to Lu, which excludes Pm (non-naturally occurring in a stable form); although some authors include Sc and Y as well (Ichihashi et al., 1992; Pang et al., 2002). These elements have robust chemical characteristics, such as the same electronic structure, oxidation state and electronegativity (Henderson, 1984). REE can be subdivided into three groups: light rare earth elements (LREE) from La to Nd, medium rare earth elements (MREE) from Sm to Dy and heavy rare earth elements (HREE) from Ho to Lu. Despite their physicochemical similarities, LREE are more soluble and less able to form complexes than HREE (Goldschmidt, 1937; Henderson, 1984; Cantrell and Byrne, 1987) and Ce and Eu are characterized by double oxidation states (Ce^{3+}/Ce^{4+} and Eu^{2+}/Eu^{3+}). The REE groups are used as tracers in various geochemical fields such as the surface geochemistry (Tricca et al., 1999; Aubert et al., 2001; Laveuf and Cornu, 2009), or the geology of the earth or moon (Weill and Drake, 1973; Taylor, 1982; Gromet and Silver, 1983).

Particularly, REE distribution patterns using lichen content analysis have been demonstrated as efficient in determining the origin of metals compared to bulk precipitation or local lithology (Chiarenzelli et al., 2001; Aubert et al., 2002, 2006; Rusu et al., 2006; Spickova et al., 2010). Recently, Agnan et al. (2013) emphasized the lithologic influence on lichen metal content in the southwest of France. Nevertheless, literature investigations are often focused on a single area or one specific region, although different compartments (lichens, mosses, bark, soil or deposition) are considered when accounting for REE behavior (Markert and de Li, 1991; Rusu et al., 2006; Spickova et al., 2010). REE investigations that consider various sites on a national scale remain scarce, particularly when considering the entire REE pattern. Indeed, few studies have considered the geochemical signatures, such as REE anomalies, to characterize the origin of these elements. The influences of various environmental parameters are poorly documented. Only Chiarenzelli et al. (2001) have sought to characterize the role of the substrate using the terricolous lichen species *Cladonia* when considering species influence. Furthermore, few historical data on REE are available (peat and soil archives). The REE registered in lichens and mosses on a century scale are rare; however, Agnan et al. (2013) have shown that they could bring interesting comparisons between past and present lichen samples.

In this study, we attempted to determine the concentration levels, distribution patterns and geochemical anomalies of REE accumulated in several species of corticolous lichens and mosses from various regions of France (and neighboring countries) using present-day and historical samples. There were a number of objectives: (i) evaluate the levels of accumulated REE in organisms collected in the two periods in different areas of the country, (ii) assess the temporal evolution of bioaccumulated REE by comparing standardized patterns in current and herbarium samples, (iii) determine the respective influence of lithological erosion sources and tree bark substrates on bioaccumulated REE by comparing the REE distribution patterns in regional bedrock and tree bark, and (iv) evaluate the organism species influence on REE bioaccumulation using six lichen and three moss species.

2. Materials and methods

2.1. Study area and collected species

This study used 218 samples, including 6 lichen species with 3 foliose lichens (*Hypogymnia physodes* (L.) Nyl., *Parmelia sulcata* Taylor (and in some stations *Flavoparmelia caperata* (L.) Hale, *Parmelina tiliacea* (Hoffm.) Hale, *Punctelia borreri* (Sm.) Krog and *Hypotrachyna revoluta* (Flörke) Hale when *P. sulcata* was absent) and *Xanthoria parietina* (L.) Th. Fr.) and 3 fruticose lichens (*Evernia prunastri* (L.) Ach., *Pseudevernia*

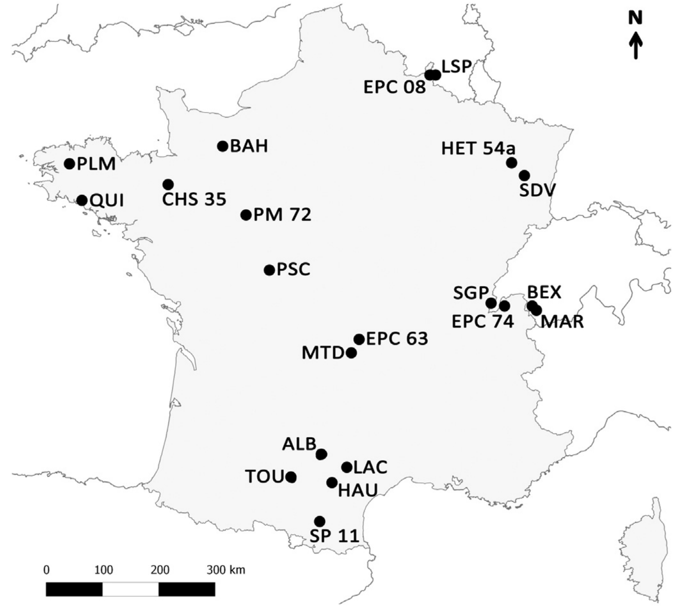

Fig. 1. Studied area with the 21 sampling sites in various regions of France and neighboring countries.

furfuracea (L.) Zopf., *Usnea* sp.) and 3 moss species (*Hypnum cupressiforme* Hedw., *Pleurozium schreberi* (Brid.) Mitt., *Scleropodium purum* (Hedw.) Limpr.). The samples were obtained from 21 sites located in various regions of France and neighboring countries (Belgium and Switzerland) in forested conditions (pine, fir, spruce, oak and beech) far from any source of contamination (Fig. 1). The site selection was conditioned by the presence of herbarium samples and different environmental contexts from various regions of France: the western region has an oceanic climate; Massif Central, Vosges and Ardennes areas have a semi-continental climate, and Alps and Pyrenean Mountains have a mixed mountain and semi-continental climate. This study included seven sites from the French monitoring network of forest ecosystems RENECOFOR (Réseau National de suivi des Écosystèmes Forestiers: SP 11, EPC 63, EPC 74, HET 54a, EPC 08, PM 72 and CHS 35) that belong to the International Co-operative Programme (ICP) forest network; these sites have previously been investigated for atmospheric metal contamination (Gandois et al., 2010b; Hernandez et al., 2003). The sites (Table 1a) exhibited a wide regional diversity of lithology from sedimentary (alluvium, limestone, sandstone) to magmatic rocks (e.g., granite, basalt or schist). The samples included 25 herbarium specimens collected between 1870 and 1998 with 14 different species from 6 herbaria belonging to the University of Toulouse (Index Herbariorum: TL) and a 1998 sample from Geneva (a gift from the French lichenologist Mr. Sussey). All of the details regarding the herbarium specimens are presented in Table 1b. The locations mentioned in the herbarium specimen labels were used to facilitate the current sampling at the same sites.

2.2. Sampling procedure

As described in Agnan et al. (2013), the present-day sampling considered an area of approximately 25,000 m^2 and included 3–5 homogeneous sub-areas that were represented by a single data value from several tens of thalli with a diameter greater than 2 cm, which indicated an age and integration period of atmospheric deposition of several years or decades. With the exception of the Saint-Dié-des-Vosges stations (terricolous mosses), the sampling was performed on all sides of the tree trunks to reduce the influence of micrometeorological parameters