

Use of geochemical signatures, including rare earth elements, in mosses and lichens to assess spatial integration and the influence of forest environment



L. Gandois ^{a, b, *}, Y. Agnan ^{a, b}, S. Leblond ^c, N. Séjalon-Delmas ^{a, b}, G. Le Roux ^{a, b},
A. Probst ^{a, b}

^a Université de Toulouse, INP, UPS, EcoLab (Laboratoire Ecologie Fonctionnelle et Environnement), ENSAT, Avenue de l'Agrobiopole, 31326 Castanet-Tolosan, France

^b CNRS, EcoLab, 31326 Castanet-Tolosan, France

^c Muséum National d'Histoire Naturelle, 57 rue Cuvier, Case 39, 75005 Paris, France

H I G H L I G H T S

- Coupled analysis of TM signature and REE in forest ecosystem compartments.
- Regional integration of atmospheric deposition by biomonitors.
- Mosses reflect canopy influence on TM atmospheric deposition.

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In order to assess the influence of local environment and spatial integration of Trace Metals (TM) by biomonitors, Al, As, Cd, Cr, Cs, Cu, Fe, Mn, Ni, Pb, Sb, Sn, V and Zn and some rare earth element (REE) concentrations have been measured in lichens and mosses collected in three French forest sites located in three distinct mountainous areas, as well as in the local soil and bedrock, and in both bulk deposition (BD) and throughfall (TF). Similar enrichment factors (EF) were calculated using lichens and mosses and local bedrock for most elements, except for Cs, Mn, Ni, Pb, and Cu which were significantly (KW, $p < 0.05$) more enriched in mosses. Similar REE ratios were measured in soils, bedrock, lichens and mosses at each study sites, indicating a regional integration of atmospheric deposition by both biomonitors. Both TM signature and REE composition of mosses revealed that this biomonitor is highly influenced by throughfall composition, and reflect atmospheric deposition interaction with the forest canopy. This explained the higher enrichment measured in mosses for elements which concentration in deposition were influenced by the canopy, either due to leaching (Mn), direct uptake (Ni), or dry deposition dissolution (Pb, Cu, Cs).

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1. Introduction

Trace metals (TM: Al, As, Cd, Cr, Cs, Cu, Fe, Mn, Ni, Pb, Sb, Sn, V and Zn) are highly dispersed in the atmosphere, mostly by human emissions (Nriagu and Pacyna, 1988; Steinnes et al., 1997; Rauch and Pacyna, 2009), with potential harmful effects on ecosystems (Ulrich and Pankrath, 1983; Nriagu, 1990; Adriano, 2001). In order

to survey extensively TM dispersion in the environment and their potential impact on ecosystems, large scale studies often use biomonitors (Boileau et al., 1982; Harmens et al., 2008; Steinnes, 1995). Lichens and mosses are ubiquitous in forest ecosystems, and have been widely used as monitors of TM atmospheric pollution mainly because they lack of any root system and have no or limited cuticles (Garty, 2001; Szczepaniak and Biziuk, 2003). Different TM accumulation capabilities have been reported for lichens and mosses (Nieboer et al., 1978; Beckett and Brown, 1984; Bargagli et al., 2002), and even between different lichen and moss species in relation to their various ecologies and morphologies. Lichens,

* Corresponding author. CNRS, EcoLab, 31326 Castanet-Tolosan, France.

E-mail addresses: laure.gandois@gmail.com, laure.gandois@ensat.fr (L. Gandois).

which are slow growing association of fungi and algae, and mosses, can both grow on soils (terricolous) and tree barks (corticolous). These two groups of organisms have different life span: mosses live for a few years (During, 1979), when lichens have generally longer life span up to several decades (Manson and Hale, 1959; Armstrong and Bradwell, 2010). If regional correspondence could be established between estimation of Cd and Pb total deposition and their content in mosses (Harmens et al., 2012), an accurate estimation of TM atmospheric deposition cannot be established using TM content in mosses (Aboal et al., 2010). Trace metal accumulation in mosses and lichens is influenced by several processes, including uptake of elements from the soil and surrounding vegetation, and loss of elements (Boquete et al., 2011). In forested ecosystems, biomonitors receive atmospheric inputs that have been modified by the canopy. Concentrations of both major and trace elements are greatly influenced by the interaction with the forest cover, including assimilation or release of elements by the canopy and accumulation of dry deposition on leaves or needles (Heinrichs and Mayer, 1977; Godt et al., 1986; Probst et al., 1992; Gandois et al., 2010). These processes have to be taken into account when considering biomonitors collected in forested areas.

Rare earth elements (REE) are a group of trace chemical elements with similar physicochemical characteristics (Henderson, 1984). Different bedrocks show specific REE compositions. Therefore, the pattern of the REE series is widely used to trace sources and processes in petrology (Weill and Drake, 1973; Chauvel and Jahn, 1984; Vidal et al., 1984) and Earth's surface sciences (Tricca et al., 1999; Aubert et al., 2001; Laveuf and Cornu, 2009). Their lithogenic origin and conservative behaviour make them pertinent tracers of dust dispersion. Rare earth element are directly analysed in aerosols (Ferrat et al., 2011; Gueguen et al., 2012; Yang et al., 2007) or in precipitations (Zhang and Liu, 2004; Spickova et al., 2010), or indirectly in peat bogs (Aubert et al., 2006; Shoty et al., 2001) and lichens (Agnan et al., 2014) to investigate the origin of atmospheric deposition.

The objectives of this study are to assess the spatial integration and the influence of local forested environment on TM record by biomonitors in forest ecosystems. Two types of biomonitors have been selected for their contrasted ecology: terricolous mosses and corticolous lichens. In order to investigate elemental transfer in the forested ecosystems, tracers of elemental origin and mobility in ecosystems, including REE and TM signatures have been analysed in various compartments of the ecosystem: soil and bedrock, precipitation (open field and throughfall) and biomonitors. This study has been carried out in three contrasted forested sites, covering a wide range of environmental conditions, and located in three distinct mountainous areas in order to assess the spatial integration of biomonitors.

2. Material and method

2.1. Study sites

The study sites belong to the French RENECOFOR network (Réseau National de suivi à long terme des Ecosystèmes Forestiers, i.e. National Network for the long term Monitoring of Forest Ecosystems), managed by the ONF (Office National des Forêts, i.e. National Forest Board). This network is part of the ICP Forest network (International Co-operative Programme on Assessment and Monitoring of Air Pollution Effects on Forests, <http://icp-forests.net>). Three sites (EPC 08, EPC 63 and SP 11) were chosen because they are located, in three different mountainous areas (Ardenne, Massif Central, and Pyrenees) of France (Fig. 1, Table 1), and were previously investigated by Gandois et al. (2010) for trace metal deposition.

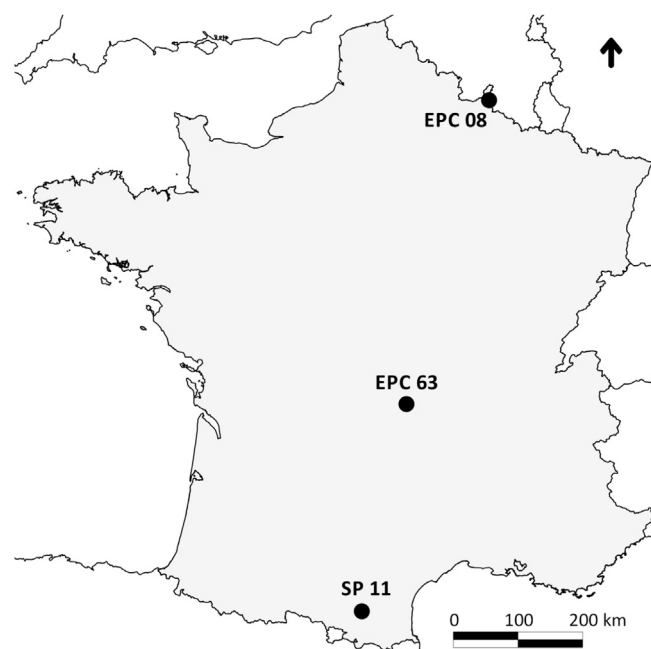


Fig. 1. Location of the three studied sites.

2.2. Sample collection and preparation

2.2.1. Soils and bedrocks

With regards to trace metal and REE, the soil and bedrock total composition was analysed within the ICP Forest network framework. Five soil samples were collected for each site (0–10 cm, 10–20 cm, 20–40 cm, 40–80 cm, 80–100 cm) in 2007–2012 for the first four layers (using a hand auger) and in 1998–1999 for the deepest layer (in soil pit). The samples were sieved (<2 mm) and powdered before analyses.

2.2.2. Atmospheric depositions

In the studied sites, both BD and TF were sampled weekly for one year from September 2007 to October 2008 following a protocol described in Gandois et al. (2010). This publication focused on selected element (Al Cu Pb Fe Ni Mn Cd Zn, Sb). We included here the analysis of other elements (As, REE, see Table 2) that had been analysed in the samples (Gandois, 2009).

2.2.3. Biomonitors

2.2.3.1. Mosses. Mosses were collected in the vicinity of the RENECOFOR plots in 2007 and 2008, following an adaptation of the 2006 ICP Vegetation network protocol: (Harmens et al., 2008). Two terricolous species were sampled under the canopy and more than 3 m away from the tree trunks: *Hypnum cupressiforme* Hedw., (Hc) in EPC 08 and EPC 63, and *Thuidium tamariscinum* (Hedw.) B., S. & G. (Tt) in EPC 63 and SP 11. Three replicates were sampled for each species. One replicate was made by pooling ten small plots of mosses collected on the soil. Mosses samples were brought back to the laboratory, dried at 40 °C, and grinded in a Ti-mill. They were then digested (H₂O₂/HNO₃) in a clean room using a microwave oven at 220 °C and 20 bar pressure, following the ICP vegetation procedure (ICP Vegetation, 2005). The blanks showed no contamination during the digestion process: the measured concentrations were always below the detection limits. The repeatability of the method was checked by mineralisation and analytical determination of triplicates of samples. Coefficients of variation were less than 5%.

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