Atmospheric Environment 95 (2014) 96–104

Contents lists available at ScienceDirect

Atmospheric Environment

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

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

HIGHLIGHTS

- 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.

ARTICLE INFO

Article history:
Received 4 December 2013
Received in revised form
11 June 2014
Accepted 12 June 2014
Available online 13 June 2014

Keywords:
Mosses
Lichens
Trace metal
Rare earth element
Bulk deposition
Throughfall

ABSTRACT

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).

http://dx.doi.org/10.1016/j.atmosenv.2014.06.029
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which are slow growing association of fungi and algae, and mosses, can both grow on soils (terricolous) and tree barks (corticulous). 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; Shotyk 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 (Ardennes, Massif Central, and Pyrenees) of France (Fig. 1, Table 1), and were previously investigated by Gandois et al. (2010) for trace metal deposition.

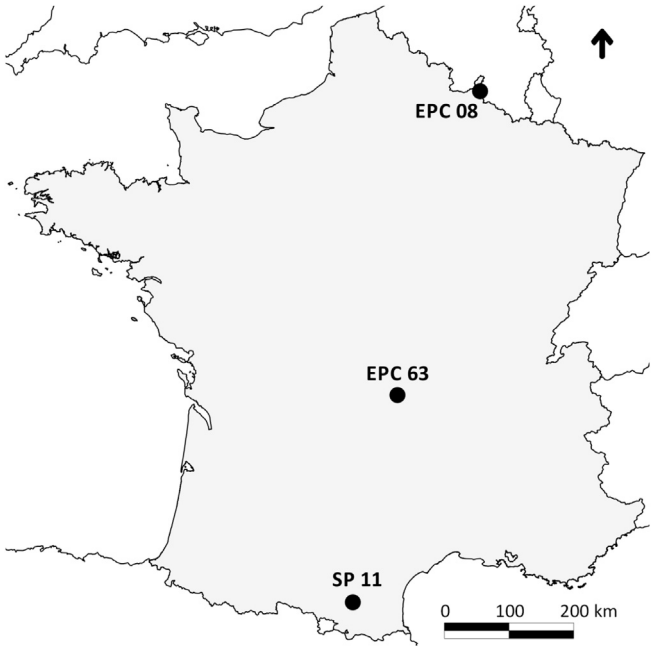

Fig. 1. Location of the three studied sites.

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 ECP 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 (H_2O_2/HNO_3) 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%.

Table 1
Study sites description.

Site	Location	Altitude (m a.s.l.)	Average annual precipitation[a] (mm)	Vegetation cover	Bedrock type	Soil type[b]
EPC 08	Ardennes	475	1300	*Picea abies* (L.) Karst.	Schist	Cambic podzol
EPC 63	Massif Central	950	990	*Picea abies* (L.) Karst.	Basalt	Andosol
SP 11	Pyrenees	950	1100	*Albies alba* Mill.	Carbonated marl	Stagnic luvisol

[a] Average for the period 1999–2005.
[b] WRB for soils (FAO).

2.2.3.2. Lichens. For lichen samples, sampling and mineralisation followed the protocol described by Agnan et al. (2013). Grown up lichens (several-year-old) were collected in 2011 on tree trunk using non-metallic material. Three corticolous lichen species were sampled among the most commonly found: *Xanthroria parietina* (L.) Th. Fr. (Xp) in the three sites, *Parmelia sulcata* Taylor (Ps) in EPC 63 and EPC 08, and *Evernia prunastri* (L.) Ach. (Ep) in EPC 08. Dried samples were powdered using nitrogen liquid and mineralised by an $HNO_3/HF/H_2O_2$ mixture in a cleanroom (EcoLab, Toulouse, France). The blank samples allowed checking no contamination during the procedure.

2.3. Sample analysis

Atmospheric deposition, moss and lichen samples were analysed for TM and REE with ICP-MS (7500 ce, Agilent Technologies, OMP-GET, Toulouse, France). The detection limit depended on the considered element: between 5 and 100 pg g^{-1}. Indium (^{115}In)/Rhenium (^{187}Re) were used as internal standards. The accuracy of digestion and analysis protocol was checked using certified standards. SLR-4 for water samples, pine needle SRM-1575a, Moss II and Moss III (Steinnes et al., 1997) for moss samples, and lichen IAEA-336, pine needle SRM-1575a and peach leaves SRM-1547 for lichen samples. Measured values were within the certified ranges. Similar recoveries (from −20% to 0%) were observed for the two protocols used for lichen and moss series, although using different acid mixtures.

The soil and bedrock samples were fused in Pt crucibles by $LiBO_2$ at 980 °C in an automatic tunnel oven. Samples were mineralised by a HNO_3/H_2O_2/glycerol mixture and analysed by ICP-MS (CRPG, Nancy, France). A blank and 5 international geostandards (Govindaraju, 1994) were prepared and analysed with each sample batch. Recovery efficiency on geostandard was >85% for all elements.

2.4. Statistical analysis

Statistical analyses were performed using the R software and the ade4 and ggplot2 packages. Significant differences were tested using the Kruskal–Wallis (KW) test ($\alpha = 0.05$). The principal component analysis (PCA) was performed on standard score TM data.

3. Results

3.1. Trace metal content in mosses and lichens

Trace metal contents in biomonitors are presented in Table 2. The measured TM concentrations in mosses were consistent with lower bound of the values reported for France and the rest of Europe in 2005 and 2010 (Harmens et al., 2010), except for Cr in SP 11, Pb in EPC 08 and Zn for all the sites. The data did not shown exceeding values like in Belgium and countries of Eastern Europe (e.g. Bulgaria, Serbia or Slovakia), in relation to the site location far from direct TM sources, reflecting background levels. For lichens, the TM concentrations fell between "very high naturality" class to "low naturality/alteration" class following the scale defined by Bargagli and Nimis (2002), except for Al and Fe in SP 11 with "middle alteration" class. Manganese concentrations were significantly (KW, $p < 0.05$) higher in mosses compared to lichens in the three sites, as well as Pb and Ni in EPC 08, Cs in EPC 63, and Cu and Ni in SP 11. On the contrary, Al, Fe, Cr, As, Sn and Sb concentrations were significantly higher in lichens compared to mosses for the three sites (KW, $p < 0.05$, except for Al and Cr in SP 11). The rare earth elements concentrations were similar for lichens and mosses for a given site. The REE range fall into the values published in the literature and reported in Dołęgowska and Migaszewski (2013) for Poland, Scandinavia and Canada.

3.2. Trace metal enrichments in mosses and lichens

The enrichment factors (EF) in biomonitors were calculated for each element X following Equation (1) using Al as the normalising element and the local bedrock as the reference (Bargagli, 1995).

$$EF = \frac{(X/Al)_{Biomonitor}}{(X/Al)_{Local\ Bedrock}} \quad (1)$$

The dispersion of EF values calculated in the three sites is presented in Fig. 2. In the three sites, calculated EF were above 2 for both biomonitors for all studied elements except for Fe and V. The calculated enrichment factors for most elements were higher in EPC 08 compared to the other study sites. For lichens, based on the median value (Fig. 2), EF increased following this order: Fe < V < Cr < Cs < Mn < Ni < As < Sn < Cd < Pb < Zn < Cu < Sb. The increase order of EF for mosses was close to the lichen one: Fe < V < Cr < As < Ni < Sn < Mn < Cu < Cs < Sb < Cd < Zn < Pb. If sites were considered individually, EF were significantly higher in mosses compared to lichens in the three sites for Mn, Pb, Cs, Cu, and Ni (KW, $p < 0.01$).

3.3. Association of TM in forest ecosystem compartments

The principal component analysis (PCA) based on TM concentrations in biomonitors and deposition is shown on Fig. 3. The first axis, explaining 40% of the data variance, discriminated biomonitors (lichens, mosses) and deposition (BD and TF). The lithogenic elements with low EF (Al, Fe, Cr or V), as well as two micronutrients, Cu and Ni were the main contributors to this axis. The second axis, which explained only 15% of the data variance discriminated lichens and BD from mosses and TF. Lead, Mn, Zn and Sb were the main contributors for this axis.

The TM signatures were further investigated using the ratios of the normalised concentration to Al (Fig. 4a and b). These ratios were lower in soil and bedrock compared to other compartments in

Table 2
Mean and standard deviation (SD) of the concentration (μg g^{-1}) of the studied TM and REE elements in the different ecosystem compartments.

		n		Al	As	Cd	Cr	Cs	Cu	Fe	Mn	Ni	Pb	Sb	Sn	V	Zn	La	Ce	Nd	Sm	Yb
EPC 08	Lichen (μg g^{-1})	5	Mean	807.21	0.49	0.47	2.33	0.13	7.04	523.59	41.80	1.81	5.25	0.28	0.64	1.81	83.45	0.574	0.970	0.388	0.076	0.030
			SD	*554.15*	*0.24*	*0.25*	*0.67*	*0.07*	*1.28*	*275.34*	*9.59*	*0.44*	*0.83*	*0.05*	*0.06*	*0.86*	*35.17*	*0.309*	*0.586*	*0.226*	*0.044*	*0.020*
	Moss (μg g^{-1})	4	Mean	197.41	0.13	0.22	1.14	0.18	6.28	241.47	212.42	2.50	9.44	0.21	0.40	1.64	46.05	0.287	0.433	0.189	0.035	0.010
			SD	*27.20*	*0.02*	*0.03*	*0.12*	*0.04*	*0.34*	*27.41*	*68.25*	*0.29*	*1.47*	*0.02*	*0.05*	*0.14*	*0.98*	*0.029*	*0.043*	*0.022*	*0.002*	*0.001*
	Bulk deposition (μg L^{-1})	14	Mean	6.86	0.09	0.09	0.07	0.01	0.88	4.14	3.24	0.44	0.70	0.12	0.10	0.35	12.04	<QL	<QL	<QL	<QL	<QL
			SD	*6.73*	*0.05*	*0.15*	*0.05*	*0.03*	*0.60*	*3.99*	*1.84*	*0.23*	*0.59*	*0.07*	*0.27*	*0.17*	*8.64*	<QL	<QL	<QL	<QL	<QL
	Throughfall (μg L^{-1})	14	Mean	24.47	0.23	0.06	0.15	0.05	1.64	12.65	157.31	0.67	3.09	0.85	20.00	0.40	29.95	0.011	0.020	0.010	<QL	<QL
			SD	*22.08*	*0.50*	*0.08*	*0.11*	*0.05*	*1.34*	*7.58*	*105.61*	*0.62*	*1.96*	*0.41*	*73.68*	*0.16*	*38.24*	*0.006*	*0.012*	*0.007*	<QL	<QL
	Soil and bedrock (μg g^{-1})	5	Mean	77,745.58	44.01	0.42	103.08	5.84	30.11	32,466.44	280.51	11.79	37.11	2.20	3.78	110.16	48.12	26.254	53.208	21.778	4.427	3.495
			SD	*11,504.66*	*6.52*	*0.10*	*9.40*	*0.73*	*4.30*	*2268.72*	*88.46*	*4.42*	*16.42*	*0.29*	*1.36*	*9.28*	*10.15*	*2.017*	*6.560*	*1.944*	*0.414*	*0.143*
EPC 63	Lichen (μg g^{-1})	8	Mean	988.32	0.67	0.07	2.22	0.34	6.88	759.13	25.14	1.26	2.51	0.12	0.33	2.36	30.00	0.815	1.499	0.581	0.106	0.031
			SD	*299.36*	*0.35*	*0.04*	*1.00*	*0.20*	*2.11*	*262.20*	*3.96*	*0.54*	*1.14*	*0.03*	*0.16*	*0.54*	*18.07*	*0.139*	*0.322*	*0.109*	*0.022*	*0.007*
	Moss (μg g^{-1})	12	Mean	386.13	0.14	0.10	0.84	0.64	3.78	280.13	172.81	1.12	2.27	0.06	0.11	1.05	34.72	0.370	0.707	0.300	0.056	0.014
			SD	*139.01*	*0.03*	*0.07*	*0.23*	*0.18*	*0.85*	*101.98*	*39.69*	*0.28*	*0.68*	*0.02*	*0.05*	*0.31*	*13.30*	*0.127*	*0.190*	*0.072*	*0.013*	*0.003*
	Bulk deposition (μg L^{-1})	14	Mean	8.86	0.10	0.06	0.08	0.01	0.84	4.84	3.22	0.62	0.24	0.06	0.04	0.19	43.32	<QL	<QL	<QL	<QL	<QL
			SD	*18.71*	*0.07*	*0.10*	*0.06*	*0.01*	*0.68*	*10.49*	*5.07*	*0.96*	*0.26*	*0.04*	*0.07*	*0.08*	*59.44*	<QL	<QL	<QL	<QL	<QL
	Throughfall (μg L^{-1})	14	Mean	37.29	1.24	0.03	0.27	0.28	1.96	16.43	131.34	0.61	4.09	1.05	0.48	0.36	24.21	0.025	0.060	0.031	<QL	<QL
			SD	*16.10*	*1.89*	*0.02*	*0.15*	*0.26*	*0.78*	*6.81*	*120.42*	*0.29*	*3.16*	*0.72*	*1.11*	*0.14*	*14.73*	*0.008*	*0.021*	*0.014*	<QL	<QL
	Soil and bedrock (μg g^{-1})	5	Mean	94,505.15	11.19	0.57	72.07	3.08	19.95	63,637.53	1648.97	28.91	37.54	1.29	3.39	141.47	140.48	58.426	119.370	42.034	7.432	2.456
			SD	*13,935.28*	*2.90*	*0.13*	*16.71*	*0.44*	*8.29*	*14,176.41*	*204.51*	*9.58*	*30.59*	*1.03*	*0.61*	*42.95*	*13.40*	*14.563*	*20.262*	*11.306*	*1.995*	*0.606*
SP 11	Lichen (μg g^{-1})	5	Mean	2364.13	0.68	0.07	3.69	0.26	4.66	1347.08	29.29	1.72	2.28	0.12	0.38	4.13	22.05	1.354	2.647	1.136	0.216	0.081
			SD	*1054.30*	*0.18*	*0.01*	*1.31*	*0.13*	*0.92*	*595.59*	*14.65*	*0.54*	*1.47*	*0.05*	*0.16*	*1.96*	*9.62*	*0.606*	*1.192*	*0.523*	*0.098*	*0.038*
	Moss (μg g^{-1})	6	Mean	1633.35	0.39	0.17	3.28	0.28	8.20	989.07	97.40	3.25	3.67	0.05	0.14	3.08	24.31	1.006	2.104	1.062	0.224	0.064
			SD	*712.37*	*0.12*	*0.07*	*1.26*	*0.12*	*2.68*	*454.91*	*29.72*	*1.05*	*1.15*	*0.02*	*0.06*	*1.29*	*8.62*	*0.387*	*0.803*	*0.448*	*0.093*	*0.028*
	Bulk deposition (μg L^{-1})	14	Mean	4.23	0.12	0.02	0.09	0.01	1.06	2.43	2.53	0.83	0.23	0.47	0.13	0.27	23.92	<QL	<QL	<QL	<QL	<QL
			SD	*3.04*	*0.08*	*0.02*	*0.06*	*0.01*	*1.05*	*2.15*	*2.07*	*1.04*	*0.16*	*1.19*	*0.31*	*0.19*	*29.42*	<QL	<QL	<QL	<QL	<QL
	Throughfall (μg L^{-1})	14	Mean	50.33	0.24	0.05	0.16	0.02	2.80	22.71	46.76	0.94	7.85	1.53	0.42	0.50	16.41	0.037	0.102	0.051	<QL	<QL
			SD	*27.58*	*0.12*	*0.03*	*0.09*	*0.02*	*1.67*	*7.89*	*16.69*	*0.42*	*3.80*	*0.79*	*0.80*	*0.23*	*13.36*	*0.018*	*0.050*	*0.030*	<QL	<QL
	Soil and bedrock (μg g^{-1})	5	Mean	70,064.38	10.15	0.38	106.50	9.11	17.70	37,905.26	446.71	43.09	24.45	0.72	2.89	109.20	97.45	35.610	69.210	30.408	5.928	2.485
			SD	*6633.53*	*1.03*	*0.10*	*2.88*	*1.37*	*8.75*	*1177.20*	*258.59*	*5.94*	*4.22*	*0.09*	*0.11*	*6.06*	*6.66*	*1.697*	*2.839*	*1.232*	*0.375*	*0.056*

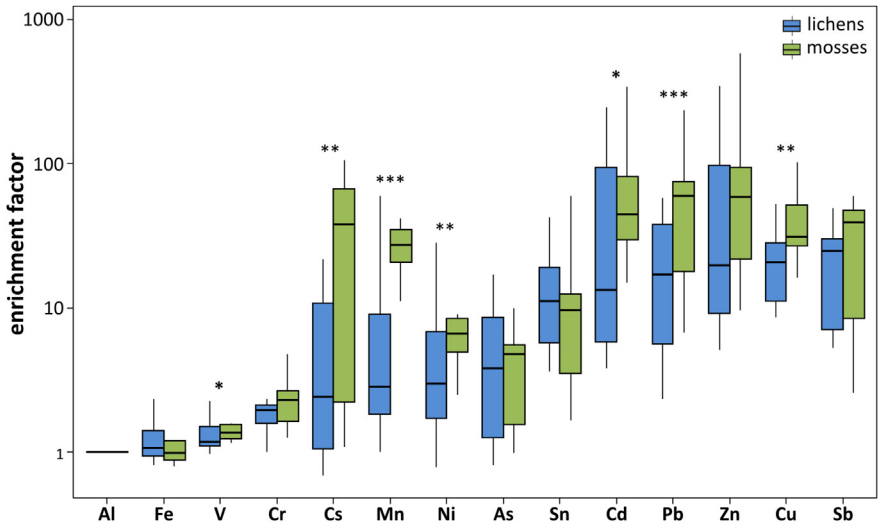

Fig. 2. Boxplot of enrichment factors in lichens ($n = 18$) and mosses ($n = 22$) using Al and local bedrock normalisation (*$p < 0.05$, **$p < 0.01$, ***$p < 0.001$, KW test).

the forest ecosystem in relation to the high Al content in soil. The ratios were lower in biomonitors compared to both bulk deposition and throughfall. For elements contributing to ACP axis 1 (Cu and Ni, Figs. 3 and 4a), the ratios measured in biomonitors aligned with those measured in BD and TF. A decrease of these ratios from BD to TF suggested the direct uptake of these elements by the forest canopy. Ratios in lichens were lower compared to mosses. For elements which contributed to axis 2 (Mn and Zn given as examples, Figs. 3 and 4b), ratios differed in lichens and mosses. For these elements, the TM signature in mosses align with the throughfall one whereas the TM signature in lichens is close to the BD one (Fig. 4b).

3.4. REE signature in forest ecosystem compartments

In order to identify REE origin in biomonitors, we plotted a diagram showing La/Sm vs La/Yb for lichens, mosses and local bedrock (Fig. 5a). The combination of these two ratios allowed discriminating the local bedrocks from the three study sites: the La/Yb ratio is different for the three locations. The La/Sm ratio is similar for SP 11 and EPC 08 (around 6) but is higher for EPC 63 (around 8). In EPC 63 and SP 11, the REE ratios measured in lichens and mosses are close to the bedrock ones. In EPC 08, the signature measured in the biomonitors differs from the local bedrock, with higher ratios measured in the biomonitors. In SP 11 and EPC 63, the light REE ratio (La/Sm) is higher in lichens compared to mosses, and is closer to the one measured in the local bedrock, whereas the La/Yb do not discriminate lichens from mosses. This is not verified in EPC 08 site, where the La/Yb ratio, and not the La/Sm ratio, discriminates lichens and mosses. In all sites, REE ratios measured in lichens are closer to the bedrock ones compared to the one measured in mosses. This is also shown when looking at light REE ratios (La/Ce vs La/Nd) in biomonitors, TF and local bedrock (Fig. 5b–d). In all sites, lichen signatures for these ratios are close to the bedrock one, whereas mosses show an intermediate signature between local bedrock and TF. This is less clear in EPC 08, where the REE signature measured in TF covers a wider range of values.

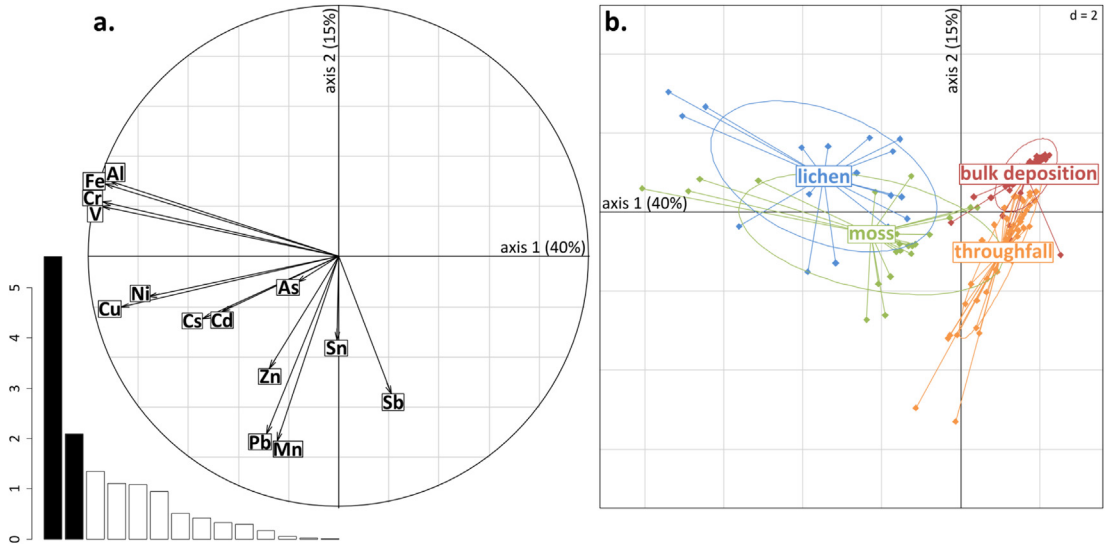

Fig. 3. Two first factors (55% of the data variance) of the PCA analysis by variable (a) and by observation (b) of the TM concentrations in biomonitors (lichens and mosses) and atmospheric deposition (bulk deposition and throughfall).

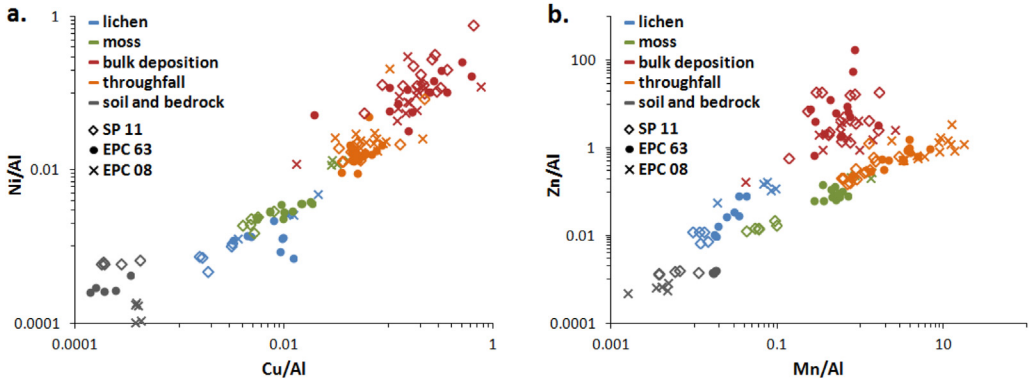

Fig. 4. Trace metal signature in the lichens, mosses, bulk deposition, throughfall and local bedrock: Ni/Al vs Cu/Al (a) and Zn/Al vs Mn/Al (b).

4. Discussion

4.1. Bioaccumulation of TM deposition by lichens and mosses

Since both lichens and mosses are widely used as biomonitors, their respective bioaccumulation capabilities have been investigated in various environmental contexts (Berg et al., 1995; Garty, 2001; Bargagli et al., 2002; Szczepaniak and Biziuk, 2003). In highly contaminated contexts and using transplant of lichen and moss bags (Basile et al., 2008; Bargagli et al., 2002), higher accumulation by mosses was observed. The authors suggest that lichens are more sensitive to environmental factors, like rainfall, and that elements contained in lichens are more likely to be leached. In the context of this study (low contaminated forest ecosystems), higher concentrations of lithogenic elements (Al, Fe, Cr and As) were measured in lichens compared to mosses, the latter being enriched in Mn in all sites, and Pb and Ni in two of the three sites. Higher EF values were calculated for Cs, Mn, Pb and Cu in mosses and therefore higher contamination would be identified if mosses were considered compared to lichens (Fig. 2). This observation supports the fact that terricolous mosses were not influenced by direct elemental transfer from soils, which would have induced high concentration of lithogenic elements in terricolous mosses. The higher concentration for Al, Fe, Cr and As observed for lichens could be related to different mechanisms. Since we sampled corticulous lichens, transfer from the soil cannot explain this enrichment. Tree barks are known to reflect TM atmospheric deposition and accumulate particulate deposition, including lithogenic minerals (Faggi et al., 2011; Gueguen et al., 2012). Transfer from barks or stemflow to lichens has been observed for major elements, but appears limited for trace elements (Prussia and Killingbeck, 1991; Sloof and Wolterbeek, 1993). In the low contamination context of our study, the higher concentrations of lithogenic elements (Al, Fe, Cr) and the relative loss of some TM (Cu, Ni, Fig. 3a) by lichens compared to

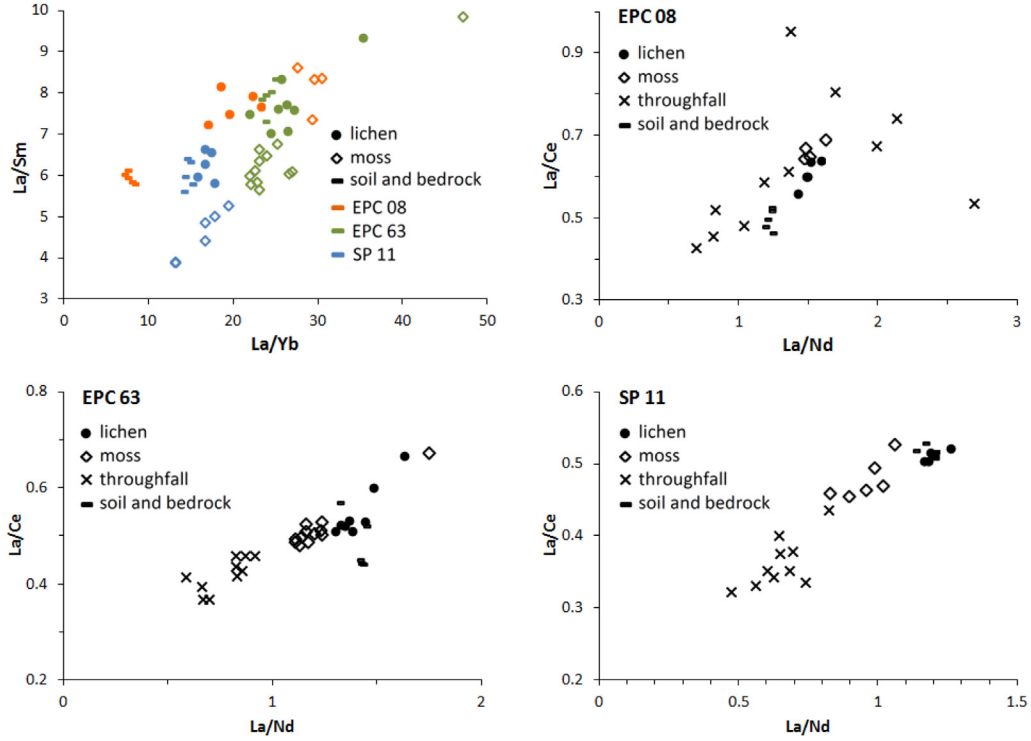

Fig. 5. La/Sm vs La/Yb ratio in lichens, mosses and soil and bedrock for the three studied sites (a) and La/Ce vs La/Nd ratio in lichens, mosses, throughfall and soil and bedrock for EPC 08 (b), EPC 63 (c) and SP 11 (d).

mosses and deposition were more likely due to higher selective accumulation of lithogenic elements by lichens or longer accumulation time. In the case of mosses, the concentrations of TM in biomonitors vary with time and selective loss of elements has been observed (Boquete et al., 2011). The longer life span of lichens and therefore the longer accumulation time compared to mosses could explain their higher concentration of lithogenic elements (Catinon et al., 2009).

4.2. Spatial integration of biomonitors

The REE ratios (La/Sm vs La/Yb) have been used to investigate the origin of TM deposition in environmental archive, like peat (Aubert et al., 2006). In this study, distinct values of the La/Sm vs La/Y ratios were observed for the soils and bedrocks of the three studied sites, allowing the identification of the local dust signature (Fig. 5a) for the different mountainous massifs. This specific signature was recorded by both mosses and lichens, highlighting a regional integration of TM atmospheric deposition by biomonitors. Trace metal dispersion range depend on the chemical form during emission and transport (Chester et al., 1993; Desboeufs et al., 1999; Colbeck, 2008). While some TM can be transported for long distance, the influence of TM emissions hotspots like cities and factories rapidly decrease within kilometres (Aznar et al., 2008; Cloquet et al., 2006).

In the Pyrenees (SP 11), higher concentration of Al and Fe and REE were measured in mosses and lichens compared to the other sites, in accordance with the high deposition of these elements in this area (Gandois et al., 2010). This is potentially related to the former mining activity in the area. In the North-East of France (EPC 08, Fig. 4a and b), REE signatures in TF was more dispersed, and higher La/Sm ratios were measured in biomonitors compared to the local soil and bedrock (Fig. 4b). Higher La/Sm ratio could indicate industrial deposition, as measured in particulate matter originating from steel plants by Gueguen et al. (2012). In this site located in an industrial area, higher EF compared to other sites were recorded by both lichens and mosses for many elements (Zn, Sr, Pb, V, Cr, Ni, Sn and Co), reflecting relatively more anthropogenic metallic atmospheric deposition already evidenced (Gandois et al., 2010) and registered in surface layers of the soils (Hernandez et al., 2003).

4.3. Influence of vegetation on biomonitor records

Both TM rand REE ratios in biomonitors highlighted the higher influence of throughfall on moss composition compared to lichens. Mosses were enriched in Mn compared to lichens, and in some sites, in Pb, Ni, and Cu (Fig. 2). The Mn/Al and Zn/Al ratios in mosses aligned with the throughfall ones, and showed a relative enrichment in Mn compared to Zn (Fig. 4b). In forested ecosystems, throughfall composition reflects processes occurring on the canopy, including elemental recretion, direct uptake, as well as accumulation and leaching of dry deposition (Lindberg and Lovett, 1992; Probst et al., 1992; Balestrini et al., 2007; Gandois et al., 2010). The Mn enrichment of mosses reflects the already observed high Mn cycling in forested ecosystem and recretion by the canopy (Petty et Lindberg, 1990; Gandois et al., 2010), and highlights the influence of canopy on moss record (Schilling and Lehman, 2002). Trace metals that are mostly deposited in the form of dry deposition, including Al, Fe and Pb, are enriched in TF, as a consequence of dissolution of accumulated dry deposition on the canopy. For these elements, TF is a proxy of both wet and dry deposition (Hou et al., 2005; Gandois and Probst, 2012). In mosses, the REE ratios reflected both TF composition and the local bedrock (Fig. 5), while lichen closely reflected the local bedrock composition. This add to the evidence that in forested ecosystems mosses also reflect the influence of accumulation of dust deposition on forest canopy and following dissolution and leaching in TF. The integration of TM from other sources than atmospheric deposition to mosses has been highlighted by Steinnes (1995), and included transfer from vascular plants, direct uptake from soil, and ion exchange with deposition. All these reasons have been cited by Aboal et al. (2010) to explain the lack of correlation between TM content in mosses and atmospheric deposition measured in BD. Our results suggest that in forest ecosystems, the lack of correlation between mosses and BD is related to the canopy influence, mosses reflecting TF composition. Depending on the considered element, this includes recretion by the canopy or dissolution of accumulated dry deposition. When compared to lichens, mosses reflect the local below-canopy environment and integrate wider spatial influence due to dust deposition. In survey networks, mosses are collected under the forest cover to assess TM deposition (Harmens et al., 2012). This study confirms that below canopy collected mosses do not reflect bulk deposition.

5. Conclusion

This study combined the TM and REE signatures in biomonitors (mosses and lichens) and in various compartments of the forest ecosystem (bulk deposition and throughfall, soil and bedrock), in order to study the elemental transfers between compartments.

The similar REE ratios measured in soil and local bedrock and biomonitors for each mountainous area showed that lichens and mosses integrated a regional atmospheric signal, including both soil derived and industrially influenced atmospheric deposition. Based on EF, comparable contamination diagnostics could be addressed using lichens and mosses, with the exception of Cs, Mn, Ni, Pb and Cu. Different accumulation of TM by lichens and mosses were attributed to a different influence of forest ecosystems on the two biomonitors. Mosses reflected the TF composition whereas lichens were less influenced by the forest canopy. These organisms were enriched in micronutrients highly cycled in forested ecosystems and leached by the forest cover, like Mn. In contrast to lichens, mosses were also enriched in element likely transported in the form of dry deposition (Cs, Pb, Cu, REE), which accumulate on forest canopy. They are more influenced than lichens by the local undercanopy environment and integrate a wider spatial signal in relation to dust deposition on the canopy. When collected in forested ecosystems, mosses reflect both atmospheric deposition and canopy influence.

Acknowledgements

This project benefited from a financial support by ADEME (French Agency for Environment) and received logistic support from the ONF (French Forest board). The authors warmly thank the ONF staff for great help during field work, Manuel Nicolas for acceded to the RENECOFOR data, Frédéric Candaudap (GET, Université de Toulouse, UPS-CNRS-IRD) for ICP-MS analysis assistance.

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