Investigation of spatial and temporal metal atmospheric deposition in France through lichen and moss bioaccumulation over one century

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HIGHLIGHTS

- A century of metal deposition was assessed by lichens and mosses in France.
- A regional forest cover-dependent geochemical background signature was evidenced.
- The anthropogenic contribution was low but stronger in the North-Eastern region.
- Changes in the nature of atmospheric deposition were evidenced since the 19th century.
- Pb isotopes traced a conservative specific contamination in SW France over a century.

ARTICLE INFO

Article history:
Received 20 February 2015
Received in revised form 19 May 2015
Accepted 19 May 2015
Available online 27 May 2015

Editor J.P. Bennett

Keywords:
Metals
Lichen
Herbarium
Geochemical background
Lead isotopes

ABSTRACT

Lichens and mosses were used as biomonitors to assess the atmospheric deposition of metals in forested ecosystems in various regions of France. The concentrations of 17 metals/metalloids (Al, As, Cd, Co, Cr, Cs, Cu, Fe, Mn, Ni, Pb, Sb, Sn, Sr, Ti, V, and Zn) indicated overall low atmospheric contamination in these forested environments, but a regionalism emerged from local contributions (anthropogenic activities, as well as local lithology). Taking into account the geochemical background and comparing to Italian data, the elements from both natural and anthropogenic activities, such as Cd, Pb, or Zn, did not show any obvious anomalies. However, elements mainly originating from lithogenic dust (*e.g.*, Al, Fe, Ti) were more prevalent in sparse forests and in the Southern regions of France, whereas samples from dense forests showed an accumulation of elements from biological recycling (Mn and Zn). The combination of enrichment factors and Pb isotope ratios between current and herbarium samples indicated the historical evolution of metal atmospheric contamination: the high contribution of coal combustion beginning 150 years ago decreased at the end of the 20th century, and the influence of car traffic during the latter observed period decreased in the last few decades. In the South of France, obvious local influences were well preserved during the last century.

1. Introduction

Atmospheric deposition of chemicals results from both natural and anthropogenic emissions (Galloway et al., 1982; Nriagu, 1989a). It constitutes the main input of contaminants to natural systems, particularly in sensitive environments, and is responsible for various adverse effects (Lindberg et al., 1982; Ulrich and Pankrath, 1983). A global evaluation of deposition is thus required, but the monitoring network for trace metals and metalloids (*e.g.*, As, Cd, Cu, Pb, or Zn), also called potential harmful elements (PHEs, Plant et al., 1997), remains scarce. It is difficult to set up and maintain long-term monitoring because the metal concentrations are generally low and variable (Adriano, 2001) and atmospheric deposition surveys are expensive and time-consuming. In addition to the conventional physicochemical measurement networks, sensitive organisms like mosses or lichens are known to be a good integrative alternative tool (Rühling and Tyler, 1968; Nieboer et al., 1978; De Bruin and Hackenitz, 1986; Conti and Cecchetti, 2001; Szczepaniak and Biziuk, 2003). Biomonitoring has frequently been exploited as a proxy to evaluate atmospheric contamination through bioaccumulation in industrial (Loppi and Bonini, 2000; Frati et al., 2007), urban (Saeki et al., 1977; Gombert et al., 2004), and forested (Rühling and Tyler, 1973; Steinnes, 1995; Loppi and Pirintsos, 2003) contexts. These studies are aimed at evaluating the deposition levels and estimating the source of contamination. Biomonitoring may also record elements originating from biological recycling, such as Mn or Zn, particularly *via* throughfall, but

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this seems to be reduced for epiphyte lichens compared to terrestrial mosses in forested environments (Gandois et al., 2014). Geochemical tools (such as rare earth elements or stable isotopes) applied to bioaccumulators are also used as tracers to support the understanding of complex processes, such as the origin of atmospheric contaminants (Carignan and Gariepy, 1995; Chiarenzelli et al., 2001; Haack et al., 2004; Spickova et al., 2010).

Nevertheless, the large scale assessment of metal atmospheric deposition through such organisms has been relatively limited in time and space. The Scandinavian moss survey was the pioneer study of country scale biomonitoring (Rühling and Tyler, 1973). On a European scale, the International Cooperative Programme on Effects of Air Pollution on Natural Vegetation and Crops (ICP Vegetation) has evaluated atmospheric deposition using moss monitoring every five years since 1990 (Rühling, 1994; Rühling and Steinnes, 1998; Buse et al., 2003; Harmens et al., 2008, 2010). The last campaign (2010/2011) was carried out at 4500 sites distributed over 25 participating countries (Harmens et al., 2013). The French contribution to this international network – Biosurveillance des Retombées Atmosphériques en Métaux par les Mousses (BRAMM) – observed 526 rural sites. To assess atmospheric deposition prior to this initiative, environmental archives, such as peat bogs, are used (Shotyk et al., 1998; Monna et al., 1999; Forel et al., 2010). However, peat lands are not evenly distributed within and across regions.

To go back further in the past, samples of lichens and mosses preserved in herbaria are particularly helpful (Herpin et al., 1997; Weiss et al., 1999). Comparison between the metals accumulated in the herbarium samples and in current samples provides precious information relating to the historical contamination (Zschau et al., 2003; Rühling and Tyler, 2004; Purvis et al., 2007; Shotbolt et al., 2007). To interpret the data recorded in the old herbarium samples, some precautions are required, such as using a normalized dataset. Despite criticism of such methods for soil samples due to process complexity (Reimann and de Caritat, 2000, 2005; Sucharovà et al., 2012), enrichment factors have proved to be an efficient tool for herbarium material (Purvis et al., 2007; Agnan et al., 2014).

In this study, we aimed to: (1) evaluate the atmospheric deposition of metals in different forested ecosystems with various environmental conditions using bioaccumulation in lichen and moss samples; (2) identify the origins of elements recorded in bioaccumulators distinguishing geochemical background level and local influences using enrichment factors and Pb isotope ratios in combination, as a support of metal concentrations; and (3) assess the evolution of atmospheric deposition over the last century, which is poorly documented. For that purpose, 21 sites spread across various regions of France were selected, of which 13 sites had lichen and moss herbarium samples.

2. Materials and methods

2.1. Study area

Twenty-one deciduous or evergreen forested sites (pine, fir, spruce, oak, and beech forests) were sampled in various parts of France and nearby regions of two neighboring countries, Belgium and Switzerland (Fig. 1). Seven of these sites were from the French International Cooperative Programme (ICP) forest network (http://icp-forests.net) RENECOFOR (Réseau National de suivi des Écosystèmes Forestiers: SP 11, EPC 63, EPC 74, HET 54a, EPC 08, PM 72 and CHS 35), where the atmospheric deposition of major elements has been measured since 1992. The sampling trees were located on the edges of forests of varying density.

The choice for these study sites was driven by the available herbarium samples for historical comparison and the diversity of the environmental conditions: climate conditions (oceanic for the western region, semi-continental for Massif Central, more continental for the North-Eastern regions of Vosges and Ardennes, and mixed climate with

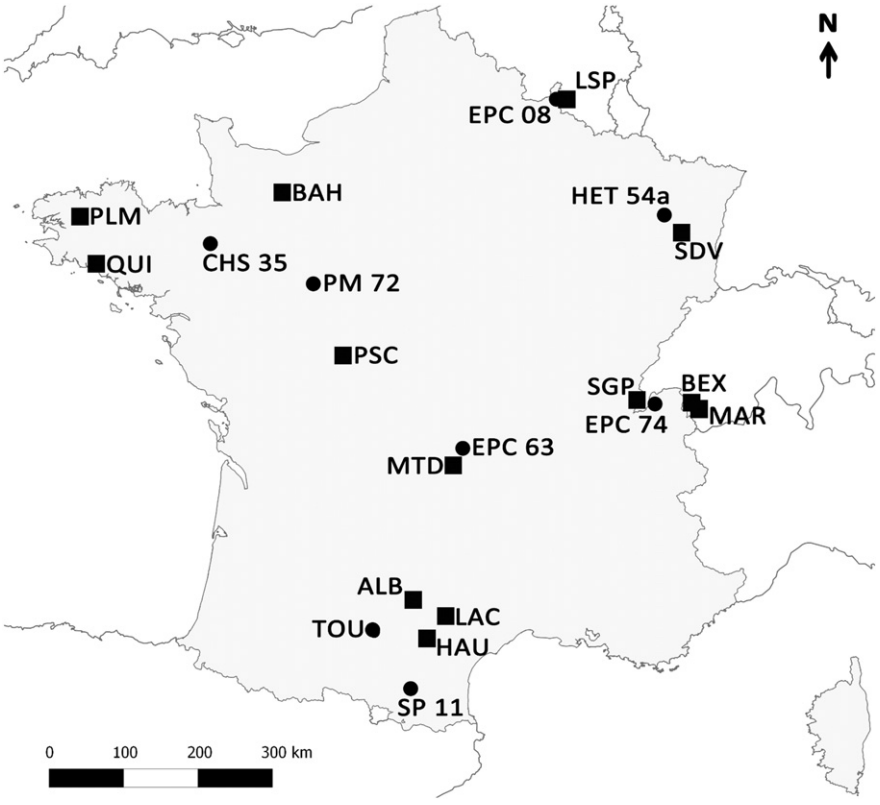

Fig. 1. Study area with the 21 sampling sites in various parts of France and neighboring countries: circles represent current locations only and squares represent both current and historical locations.

altitude influence for the Alps and Pyrenean regions), lithology (alluvia, limestone, sandstone, granite, basalt or schist), or industrial history (Table 1a).

2.2. Sampling procedure

Six lichen (*Hypogymnia physodes* (L.) Nyl., *Parmelia sulcata* Taylor (including 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), *Xanthoria parietina* (L.) Th. Fr., *Evernia prunastri* (L.) Ach., *Pseudevernia furfuracea* (L.) Zopf. and *Usnea* sp.) and three moss species (*Hypnum cupressiforme* Hedw., *Pleurozium schreberi* (Brid.) Mitt. and *Scleropodium purum* (Hedw.) Limpr.) were collected from various common tree species (*e.g.*, ash, beech, oak, maple, pine, fir, or spruce) from each site to limit the potential influence of substrate (De Bruin and Hackenitz, 1986; Markert and de Li, 1991; Prussia and Killingbeck, 1991). These lichen and moss species were selected because of their presence in available herbaria and their known ability to accumulate metals. Each site covered an area of 25,000 m^2 including 3–5 sub-sampling sites. This protocol attempted to limit local influence in order to integrate a global and homogeneous signal (Agnan et al., 2013). The lichen sampling was performed on all sides of the tree trunks at a height of approximately 1.5 m to prevent any soil contamination (Bargagli and Nimis, 2002). Approximately ten thalli of at least 2 cm wide were collected using a ceramic knife and latex gloves. The mosses were collected on tree trunks, except for those from the Saint-Dié-des-Vosges stations, where samples were collected on the ground under the canopy like the herbarium samples. Lichen and moss samples were stored in a plastic bag before treatment and analysis.

In addition, 26 historical samples from 1870 to 1964 (herbaria of the University of Toulouse, Index Herbariorum: TL) and 1998 (gift from Mr

Table 1
Description of sampling locations: a. for current samples and b. for herbarium samples (Ep: *Evernia prunastri*, Hc: *Hypnum cupressiforme*, Hp: *Hypogymnia physodes*, Pf: *Pseudevernia furfuracea*, Ps: *Parmelia sulcata*, Psc: *Pleurozium schreberi*, Sp: *Scleropodium purum*, U: *Usnea* sp., Xp: *Xanthoria parietina*).

a.

Region	Station	Code	Coordinates	Lithology	Species	Current samples	Herbarium samples
Midi-Pyrénées	SP 11	SP 11	2°05′40″E/42°52′15″N	Limestome/marble	Xp	5	
	Toulouse	TOU	1°28′15″E/43°33′25″N	Molasse	Xp	8	
	Albi	ALB	2°10′20″E/43°55′50″N	Molasse	Xp	16	3
	Hautpoul	HAU	2°22′30″E/43°28′20″N	Granite	Ps/Xp	8	3
	Lacaune	LAC	2°41′20″E/43°43′25″N	Schist	Ps/Xp	5	1
Massif Central	EPC 63	EPC 63	2°58′05″E/45°45′00″N	Basalt	Ps/Xp	8	
	Mont-Dore	MTD	2°48′40″E/45°33′10″N	Basalt	Ps/Pf/U	14	2
Alps	Saint-Génis-Pouilly	SGP	6°01′00″E/46°16′05″N	Moraine	Xp	5	1
	EPC 74	EPC 74	6°21′00″E/46°13′30″N	Sandstone/schist	Ps/Xp/Ep/Pf	14	
	Bex	BEX	6°58′30″E/46°13′00″N	Limestone/schist	Ps/Xp/Ep/Pf/U	15	2
	Martigny	MAR	6°05′05″E/46°07′25″N	Gneiss	Xp	5	1
Vosges	HET 54a	HET 54a	6°43′10″E/48°30′50″N	Limestone	Ps/Xp/Ep/Hc	14	
	Saint-Dié-des-Vosges	SDV	6°58′15″E/48°17′30″N	Sandstone	Ps/Ep/Psc/Sp	8	2
Ardennes	EPC 08	EPC 08	4°47′50″E/49°57′00″N	Clay loam	Ps/Xp/Ep/Hc	7	
	Louette-Saint-Pierre	LSP	4°55′35″E/49°57′20″N	Siliceous alluvium	Ps/Xp/Ep/Hc	8	1
Armorican Massif	Preuilly-sur-Claise	PSC	0°54′25″E/46°51′30″N	Chalk	Ps/Xp/Ep	8	1
	PM 72	PM 72	0°20′00″E/47°44′25″N	Schist	Hp	4	
	Bazoches-au-Houlme	BAH	0°18′00″E/48°48′55″N	Limestone	Hp/Ps/Xp/Ep/Hc	18	2
	CHS 35	CHS 35	1°32′50″W/48°10′10″N	Clay	Ps	6	
	Quimperlé	QUI	3°33′15″W/47°49′15″N	Granite	Hp/Ps/U	8	3
	Plounéour-Ménez	PLM	3°55′55″W/48°24′05″N	Schist/sandstone	Ps/Ep/U	10	4
					Total:	194	26

b.

Region	Station	Species	Species code	Herbarium	Location	Year
Midi-Pyrénées	ALB	*Xanthoria parietina*	Xp	Sudre	In les Planques, on poplar	1900
		Xanthoria parietina	Xp	Sudre	In le Séquestre	1900
		Xanthoria parietina	Xp	Sudre	On walnut	1900/1909
	HAU	*Xanthoria parietina*	Xp	Sudre	On gneiss	1909
		Parmelia sulcata	Ps	Sudre	On gneiss	1909
		Parmelia sulcata	Ps	Sudre	On gneiss	1909
	LAC	*Parmelia sulcata*	Ps	Sudre	In Ardoisières, on pine	1904
Massif Central	MTD	*Pseudevernia furfuracea*	Pf	Sudre	–	1901
		Usnea dasypoga	U	Sudre	–	1901
Alps	SGP	*Xanthoria parietina*	Xp	Sussey	In Pregnin, on walnut	1998
	BEX	*Evernia prunastri*	Ep	Thomas	In Devens	1870
		Pseudevernia furfuracea	Pf	Thomas	–	1870
	MAR	*Xanthoria parietina*	Xp	Thomas	Between Martigny and Branson	1870
Vosges	SDV	*Scleropodium purum*	Sp	Husnot	Hedge and pasture	1871
		Pleurozium schreberi	Psc	Husnot	On the ground, in a dry wood	1871
Ardennes	LSP	*Hypnum cupressiforme*	Hc	Husnot	On beech	1873
Armorican Massif	PSC	*Xanthoria parietina*	Xp	Aristobile	–	1916
	BAH	*Evernia prunastri*	Ep	Olivier	–	1880
		Hypnum cupressiforme	Hc	Husnot	In front of the Berjou-Cachan station	1873
	QUI	*Hypogymnia physodes*	Hp	Des Abbayes	In Carnoët forest, on bark	1964
		Usnea subflorida	U	Des Abbayes	In Carnoët forest, on bark	1964
		Usnea rubicunda	U	Des Abbayes	In Carnoët forest, on bark	1964
	PLM	*Parmelia saxatilis*	Ps	Des Abbayes	In Roc Trevezel, on rock	1964
		Parmelia omphalodes	Ps	Des Abbayes	In Roc Trevezel, on rock	1964
		Usnea florida	U	Des Abbayes	In Cranou forest	1964
		Usnea ceratina	U	Des Abbayes	In Cranou forest, on bark	1964

Sussey, lichenologist) from the same locations as the current samples were selected to be analyzed to evaluate the evolution of atmospheric deposition over the past century (Table 1b). The absence of indication about precise location and sampling procedure, as well as the reduced amount of available material may constitute a bias for historical data. The samples were carefully separated from conservation sheets, excluding parts of the sample in contact with glue, to avoid any supplementary potential contamination.

2.3. Pre-analysis treatments and analytical procedure

Samples were dried (30 °C for several hours), and lichen and moss species of interest were isolated without a rinsing procedure to avoid losing trapped surface particles (Richardson, 1992; Bergamaschi et al., 2007). The samples were ground in an agate mortar using liquid nitrogen. The powdered samples were preserved in plastic tubes.

The total digestion of the samples was performed in an ISO 7 cleanroom at the Laboratoire Écologie Fonctionnelle et Environnement (EcoLab, Toulouse, France) using a mixture of suprapure acids (HNO_3 and HF) and H_2O_2 (Rusu, 2002). All cleaning procedures used high-purity water (18.2 MΩ cm). Approximately 100 mg of powdered sample was digested using 0.5 mL of 68% HNO_3 and 0.5 mL of 50% HF at 90 °C in a Savillex (Teflon bottle) for 48 h (Agnan et al., 2013). After evaporation, 1 mL of H_2O_2 was added and evaporated at 50 °C, and 1 mL of 68% HNO_3 was added for 48 h at 90 °C. Finally, a 1200-fold dilution was used for spectrometric analysis.

A set of 17 PHEs – Al, As, Cd, Co, Cr, Cs, Cu, Fe, Mn, Ni, Pb, Sb, Sn, Sr, Ti, V, and Zn – was analyzed using ICP-MS analytical platforms: ICP-QMS Agilent Technologies 7500 CE and HR-ICP-MS Thermo Scientific Element XR at the OMP (Observatoire Midi-Pyrénées, Toulouse, France) and ICP-QMS Thermo Scientific Element X-II (laboratory HSM, HydroSciences Montpellier, France). The detection limits were <5 pg g^{-1} for Cu, Cs, Pb, Sb, Sr, and V; <50 pg g^{-1} for Al, As, Cd, Co, Cr, Mn, Ni, Sn, and Zn; and <100 pg g^{-1} for Fe and Ti.

An internal $^{115}In/^{187}Re$ standard of known concentration was added to each sample, and a quality control samples (SRLS 5) was used every eight samples to correct the deviation of the analyzer. The procedure performance of the mineralization was checked for each series of 35 samples by adding two replicates each of certified material: lichen IAEA-336, pine needle SRM-1575a, and peach leaves SRM-1547. No contamination during the digestion procedure was observed through a blank sample analysis (at approximately 1% of the sample concentrations).

The average recovery ($C_{measured}$ / $C_{certified}$ * 100), calculated for each analyte using the three certified materials, was as follows: 100 ± 5% for Al, Fe, Mn, Sr, and Ti, 100 ± 10% for Cd, Cs, Mn, Pb, V, and Zn, and 100 ± 20% for As, Co, Cr, and Ni. Only Sb had a very low recovery (66%), but with a good repeatability between the different series.

The Pb isotope analysis was performed on current and historical lichen and moss samples using ICP-QMS Agilent Technologies 7500 CE (Observatoire Midi-Pyrénées, Toulouse, France) and ICP-QMS Thermo Scientific Element X-II (laboratory HSM, HydroSciences Montpellier, France). Mass bias was corrected using the SRM 981 every 5 or 7 samples by using Galer and Abouchami's (1998) data. The relative standard deviations were performed for 6–10 measurements: 0.21 and 0.18 for $^{208}Pb/^{207}Pb$ and $^{207}Pb/^{206}Pb$, respectively.

2.4. Data treatment

Geochemical background corresponds to concentration levels not influenced by anthropogenic inputs. To determine this non-influenced distribution, we used the calculated distribution function method (Matschullat et al., 2000). This method consists of reducing every single value above the median as a "mirror against the original median value by adding the distance from the individual value to the median to obtain a new value larger than the median". Only the three foliose lichens (*X. parietina*, *P. sulcata*, and *H. physodes*) were considered in order to limit the influence of species (Thöni et al., 1996; Bargagli et al., 2002; Szczepaniak and Biziuk, 2003; Bergamaschi et al., 2007; Basile et al., 2008). The threshold of the geochemical background was determined using the mean (μ) and standard deviation (σ) of this new distribution: $\mu + 2\sigma$.

The enrichment factors EFs (Chester and Stoner, 1973; Atteia, 1994; Loska et al., 1997; Vieira et al., 2004) were calculated for each element X and for all samples (lichens and mosses), using an Al and upper continental crust (UCC) normalization (Taylor and McLennan, 1985):

$$EF = \frac{(X/Al)_{sample}}{(X/Al)_{UCC}}.$$

Statistical treatments were performed using R software. The normality of PHE concentration data was tested with the Shapiro–Wilk test ($\alpha = 0.05$), and significant differences by the Student's or Kruskal–Wallis tests ($\alpha = 0.05$). A log-ratio transformation ('clr' from the rgr package) of PHE concentrations was used for all multivariate analyses. Principal Components Analyses (PCA) were performed using the ade4 package (Dray and Dufour, 2007) and elements were grouped using their relative axis scores (Berg and Steinnes, 1997). Hierarchical classifications were performed using Ward's method. The arbitrary height of 5 or 12 was used as phenon line depending on the maximum height of cluster (<10 or >10, respectively).

3. Results

3.1. Lichen and moss PHE content

3.1.1. Current and historical concentrations

The current lichen and moss samples (Table 2) showed, as a whole, a wide range of PHE content, as observed by their inter-quartile ranges (IQR), which were of the same magnitude as their median values. Differences in concentrations were observed between the species considered, which were related to morphological types (see Supplementary data): the fruticose lichens (*E. prunastri*, *P. furfuracea*, and *Usnea* sp.) generally had the lowest PHE concentrations, unlike foliose lichens (*H. physodes*, *P. sulcata*, and *X. parietina*); moss species had intermediate concentration ranges. Within the *X. parietina* samples, the PHE concentrations differed from site to site: maximum concentrations were observed at TOU, ALB, and LAC (Midi-Pyrénées), MAR (Alps), and EPC 08 (Ardennes), and minimum ones at LSP (Ardennes), PSC, and BAH (Armorican Massif), and BEX (Alps). These concentration levels were in the middle (Al, Fe, Ti, and V), or lower (As, Cd, Cr, Cu, Ni, Pb, and Zn) ranges of contamination given by Nimis and Bargagli (1999). Only some elements were locally in the higher range of concentrations: Mn at MTD (Massif Central), EPC 74 and BEX (Alps), SDV (Vosges), and CHS 35 (Armorican Massif); Ti at SP 11 (Midi-Pyrénées), EPC 63 and MTD (Massif Central), MAR (Alps), and BAH (Armorican Massif); and V at LAC (Midi-Pyrénées).

For historical lichen and moss data (Table 2), the IQR of PHE were systematically higher than for current ones, with the exception of Sr. If we refer to the equivalent sites, the historical/current ratios were >1 and reached 6.5 for Pb, 4.5 for As, 3.0 for Cd, and 2.8 for Sn. Indeed, As, Cd, Co, Cs, Pb, Sb, and Sn were significantly ($p < 0.05$, Kruskal–Wallis test) higher in the herbarium samples. Despite the generally higher concentrations in herbaria, specific trends appeared for each specimen considered without any morphological rule: either higher (*P. sulcata* at HAU, for example), or lower (*H. cupressiforme* at LSP, for example) than their corresponding current sample. This situation was true for all the PHE in an equivalent sample, with a similar ratio between these samples (historical sample/current sample) as described for rare earth elements in lichens by Agnan et al. (2014). Compared to the Nimis and Bargagli (1999) scale, some of our samples were included in the altered environment class ("alteration"), particularly at HAU

Table 2
Median, minimum, maximum, and inter-quartile ranges (IQR) of the 17 PHEs for the current (n = 57) and herbarium (n = 22) data. Each datum corresponds to an average of one species in one station. A Kruskal–Wallis test was performed between current and historical data; the values in bold indicate a p-value < 0.05.

	Current samples (μg g^{-1}, n = 57)				Historical samples (μg g^{-1}, n = 22)				Historical/current (n = 22)	p-Value (Kruskal–Wallis)
	Median	Min	Max	IQR	Median	Min	Max	IQR		
Al	1058.4	225.8	3605.5	918.0	1260.5	136.5	28,007.2	1862.6	1.0	0.076
As	0.4	0.1	3.0	0.3	1.8	0.2	11.1	2.6	4.5	**<0.001**
Cd	0.1	0.1	0.8	0.1	0.3	0.1	1.9	0.2	3.0	**0.009**
Co	0.2	0.1	0.8	0.2	0.3	0.1	7.4	0.4	1.0	**0.041**
Cr	1.8	0.4	6.1	1.5	2.0	0.4	33.9	2.1	1.1	0.115
Cs	0.2	0.1	5.4	0.2	0.3	0.1	5.0	0.5	1.5	**0.010**
Cu	5.2	2.1	12.4	2.4	5.5	2.0	26.1	3.5	1.0	0.784
Fe	616.1	127.6	2226.5	523.2	830.9	86.7	22,870.8	1048.2	1.1	0.063
Mn	61.4	16.8	626.8	100.1	76.9	12.1	1136.9	155.7	1.2	0.519
Ni	1.4	0.5	7.2	1.1	1.6	0.3	16.9	1.8	1.1	0.058
Pb	3.1	0.7	58.1	4.3	20.2	2.2	166.1	20.1	6.5	**<0.001**
Sb	0.2	0.1	0.7	0.1	0.3	0.1	2.1	0.4	1.5	**0.004**
Sn	0.4	0.1	2.2	0.3	1.1	0.3	4.3	1.0	2.8	**<0.001**
Sr	15.2	2.9	63.6	10.9	16.8	3.8	63.0	9.8	1.1	0.470
Ti	62.2	14.8	234.0	67.4	105.0	9.6	1183.1	197.3	1.5	0.061
V	2.0	0.4	6.8	1.8	2.7	0.2	43.4	3.2	1.1	0.084
Zn	30.9	9.7	114.3	21.3	38.9	9.9	136.2	29.2	1.2	0.162

and LAC (Midi-Pyrénées, see Supplementary data). Although the highest historical levels were sometimes reported in herbarium samples (Herpin et al., 1997; Zschau et al., 2003; Shotbolt et al., 2007), such concentration levels have not yet been observed in the literature.

3.1.2. Geochemical background

The threshold values of PHE accumulated in lichens and mosses from selected French forested sites and the percentages of the sites exceeding these values were calculated for each element using the calculated distribution function (Matschullat et al., 2000, Table 3). A high disparity between elements was observed: more than 28% of sites exceeded the geochemical background threshold for Zn, Mn, Pb, Ti, Cd, and Sr, whereas fewer than 15% of sites were exceeded for Ni, Al, Cr, As, Co, Cu, Fe, Sb, and Sn. According to the Italian classification (Nimis and Bargagli, 1999), the threshold values were classified into four categories: “middle alteration” for Al, Fe, Mn, and Ti, “low naturality/alteration” for Cr, Ni, and V, “middle naturality” for As and Zn, and “high naturality” (Cd and Pb). Here, the terms “alteration” and “naturality” mean “anthropogenically altered environment” and “natural environment”, respectively.

Table 3
Geochemical background thresholds (using the calculated distribution function) and the percentage of exceeding sites for each element.

Element	Geochemical background (μg g^{-1})	Exceeding sites (%)
Al	2320.00	10
As	0.85	14
Cd	0.25	29
Co	0.62	14
Cr	4.23	10
Cs	0.43	19
Cu	9.91	14
Fe	1330.00	14
Mn	66.00	38
Ni	3.18	5
Pb	5.99	33
Sb	0.29	14
Sn	0.75	14
Sr	18.60	29
Ti	130.00	33
V	3.94	19
Zn	44.80	38

3.2. Relationships between elements

The relationships between elements are used to interpret the common origins and/or behaviors of chemicals (Conti et al., 2007; Reimann et al., 2008). A PCA was performed on the PHE concentrations of current lichen and moss samples from all sites (Fig. 2a and Table 4). Based on the relative axis scores (Berg and Steinnes, 1997; Bennett and Wetmore, 2003), the major axis, representing 36% of the data variance, allowed the grouping of Fe, Al, Cr, As, Ti, V, and Co on one side (scores from −0.91 to −0.61), and Mn, Zn, and Cd on the other side (scores from 0.73 to 0.68); Sr and Pb had a light influence on the second axis (15% of the data variance). The first group of elements was strongly linked, as frequently observed in the literature (Shotbolt et al., 2007; Conti et al., 2009). The second axis associated Sb and Sn (scores from 0.91 to 0.68), whereas the third axis (11% of the data variance) distinguished Cu and Ni with negative scores from Cs with a positive one. The link between Cd and Zn was also observed in mosses (Shotbolt et al., 2007), lichens (Brunialti and Frati, 2007), and atmospheric deposition (Gandois et al., 2010). Fig. 2c represents the 107 current observations grouped by the forest density of study sites, with the dense forests in black and the sparse forests in gray. A significant difference ($p < 0.001$, Kruskal–Wallis test) between the two classes appeared along the first axis with more negative scores for sparse forests and positive scores for dense ones.

A second PCA was performed on PHE concentrations from historical samples (Fig. 2b and Table 4). As observed in the current sample PCA, the first axis (46% of the data variance) grouped the same elements with negative scores (between −0.93 and −0.66), excluding As. Cesium also had a highly negative score (−0.68), but differed in the plot along the second axis (15% of the data variance). Cadmium, Pb, Zn, and Cu, with positive values (0.81 to 0.53), were opposite the first group and orthogonal to Mn and Sr, which were also influenced by the second axis. Finally, As and, to a lesser extent, Sb and Sn were grouped together with an influence from the third axis (10%).

Hierarchical classifications were performed on current PHE concentrations to compare the six different regions (Fig. 3). The groups of elements highlighted by the first axis of the PCA (Fig. 2a) were more or less preserved in each dendrogram. However, some links differed from one region to another: (1) the Midi-Pyrénées and Massif Central regions showed a Cu exclusion from the Cd–Zn group (Fig. 3a–b); (2) the Vosges and Ardennes regions presented more complex associations, with As and Co excluded from the Al–Fe group (Fig. 3d–e); (3) the Ardennes region differed by Sb–Sn exclusion from the Al–Fe group and

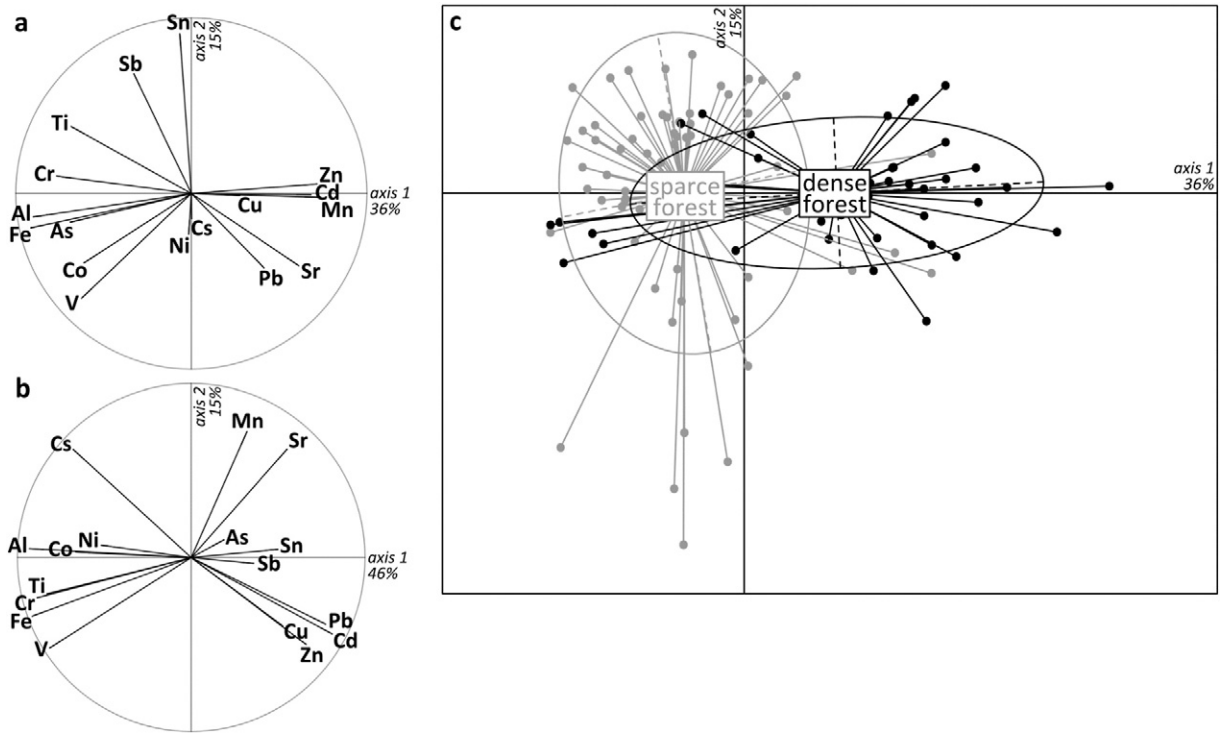

Fig. 2. PCA of log-ratio transformed PHE concentrations in lichens and mosses: current (n = 107, a) and herbarium (n = 15, b) samples, and current observations (n = 107, c).

Pb exclusion from the Cd–Zn group (Fig. 3e); and (4) the Alps and Armorican Massif regions distinguished two different groups very similarly (Fig. 3c and f).

3.3. Enrichment factors

To determine additional sources from the lithology (*e.g.*, anthropogenic and biogenic) and evaluate their evolution over one century, EFs were calculated for each current and historical sample. To limit the influence of species, we focused on foliose lichens. For current data, the EF medians evolved in the following order: Al < Fe < Cr < Ti < Co < Ni < Sr < Cs < V < Sn < Mn < Pb < Cu < As < Zn < Sb < Cd. Specifically, the highest enrichments were observed for Cd at PM 72 in the Armorican Massif (EF = 765 for *H. physodes*), EPC 08 in the Ardennes (EF = 633 for *P. sulcata*), and EPC 74 in the Alps (EF = 570 for *P. sulcata*). Boxplots of 9 of the 17 PHE were performed for each region (Fig. 4).

Table 4
First three component loadings (C1, C2, and C3) from PCA for each element from current and herbarium samples. The main axis is represented by bold numbers.

Element	Current samples			Element	Herbarium samples		
	C1	C2	C3		C1	C2	C3
Fe	−**0.91**			Al	−**0.93**		
Al	−**0.90**			Fe	−**0.92**	−0.34	
Cr	−**0.77**			Cr	−**0.89**	−0.23	
As	−**0.69**			Ti	−**0.83**	−0.21	
Ti	−**0.68**	0.38	0.29	V	−**0.81**	−0.52	
V	−**0.63**	−0.60		Cs	−**0.68**	0.62	0.30
Co	−**0.61**	−0.40	−0.31	Co	−**0.66**		
Sr	**0.61**	−0.41		Sb	**0.36**		0.31
Cd	**0.68**		−0.35	Sn	**0.50**		0.43
Zn	**0.72**		−0.43	Cu	**0.53**	−0.39	−0.36
Mn	**0.73**		0.35	Zn	**0.66**	−0.50	−0.25
Pb	0.41	−**0.42**		Pb	**0.77**	−0.38	
Sb	−0.33	**0.68**	−0.40	Cd	**0.81**	−0.44	0.12
Sn		**0.91**		Sr	0.55	**0.62**	
Cu	0.28		−**0.61**	Mn	0.32	**0.73**	−0.49
Ni		−0.23	−**0.26**	Ni	−0.52		−**0.60**
Cs			**0.78**	As			**0.71**

Some regional disparities in EF were observed: Cs enrichment in the Massif Central, Mn enrichment in the Armorican Massif, Cd, Sb, Sn, and Zn enrichment in the Armorican Massif, Vosges, and Ardennes, and Pb enrichment in the Vosges and Ardennes. As a whole, the samples from the Ardennes were the most enriched for Cd, Cu, Sb, Sn, and Zn, whereas those from the Midi-Pyrénées, Massif Central and Alps regions frequently had the lowest PHE enrichments (Cd, Cu, Pb, and Zn).

The EF for historical samples was compared to those of the current samples, and the historical/current EF ratios were calculated for each site by time period (Fig. 5). With the exception of As, Cd, Cs, Cu, Pb, Sb, and Zn for the SDV site, EFs were higher in the past for most PHEs (As, Cd, Cs, Cu, Mn, Pb, Sb, Sn, and Zn, $p < 0.05$, Stutent's t-test) during the first period (1870–1880). The two alpine sites (BEX and MAR) had EF ratios <1 for Cd and Cu, and for Mn, Sb, Sn, and Zn from at least one of these stations. Except for Pb, Sb, and Sn, the Northern regions (LSP, SDV, and BAH) had the highest enrichments in the past.

For the 1900–1916 period, the EF ratios were still high, particularly in the Massif Central (MTD) and Armorican Massif (PSC) for As, Cd, Pb, Sb, and Sn ($p < 0.05$, Student's test). In the Midi-Pyrénées region, the three sites behave differently: the EF ratio >1 for Cd, Cu, Mn, and Zn in HAU, compared to ALB and LAC. Nevertheless, it is worth noting that the most enriched elements in this period were the same ones as in the last period (*i.e.*, As, Cd, Pb, Sb, and Sn).

During the last half century, the two Brittany sites had similar trends for six PHEs, with a clear enrichment of As, Pb, and Sn in 1964. The ratio was lower for Cu and Mn (QUI) and Cs (PLM) than in the previous two periods. Finally, the alpine 1998 period revealed a different pattern than those observed for the other periods. Only Cu, Mn, Pb, and Sb showed significant differences ($p < 0.01$, Student's test), with a ratio <4.

3.4. Lead isotope ratios

The Pb isotope ratios were investigated for current (n = 50, Fig. 6a–b) and historical (n = 17, Fig. 6c–d) lichen and moss samples from 15 different sites. The average data were 1.159 ± 0.009 for $^{206}Pb/^{207}Pb$, 2.430 ± 0.029 for $^{208}Pb/^{207}Pb$, and 18.132 ± 0.207 for $^{204}Pb/^{206}Pb$. These values were close to those found for lichens from urban and

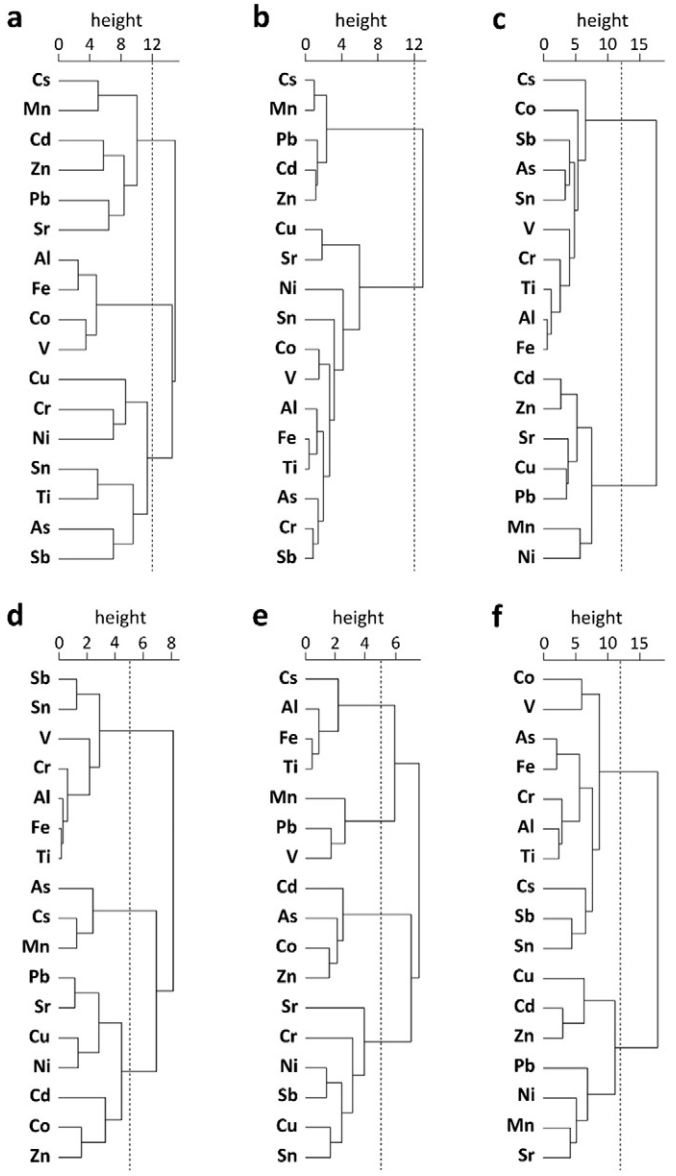

Fig. 3. PHE hierarchical classifications (Ward's method) by study region based on log-ratio transformed current foliose data: a. Midi-Pyrénées (n = 36), b. Massif Central (n = 9), c. Alps (n = 20), d. Vosges (n = 7), e. Ardennes (n = 7), f. Armorican Massif (n = 28). The phenon lines (dotted lines) are arbitrary of 5 and 12 depending the maximum height of the cluster.

forested areas (Doucet and Carignan, 2001; Monna et al., 2012; LeGalley et al., 2013). In Fig. 6, the $^{208}Pb/^{207}Pb$ *vs.* $^{206}Pb/^{207}Pb$ are plotted, and data are identified by region and by biomonitor morphology (foliose lichens, fruticose lichens, and mosses). The current data (Fig. 6a) fitted mainly on a linear trend ($y = 0.90x + 1.39$, $r^2 = 0.93$) and were located between two major end-members selected after testing different European signatures found in the literature (natural rocks, urban emissions, industrial emissions): the potential natural pole represented by Miocene sediments (Monna et al., 1995) and the anthropogenic pole illustrated by the Swiss gasoline (Chiaradia and Cupelin, 2000). This line is very close to the European Standard Pollution (ESP, $y = 1.10x + 1.17$) line, which reflects the European pollution level as a whole (Haack et al., 2002). The samples from the Armorican Massif, Massif Central, and Ardennes were closest to the gasoline ratios, whereas the samples from the Midi-Pyrénées region (SP 11) and Vosges were located close to the natural sediment ratios. Foliose lichens showed $^{206}Pb/^{207}Pb$ ratios slightly higher than fruticose lichens at BEX, the only site containing both morphologies. Nevertheless, samples from three sites were excluded from this general trend: SEQ, ALB, and HAU, which were all from the Tarn department (Midi-Pyrénées region). No European isotope data, such as urban dust or industrial emissions, were found to explain these signatures (Monna et al., 1997; Véron et al., 1999; Chiaradia and Cupelin, 2000; Carignan et al., 2005). The last two samples (ALB and HAU) followed another linear relationship ($y = 1.52x + 0.62$, $r^2 = 0.87$), for which no species specificity was observed. If the natural sediment could be assumed as one of the end-members, the other end-member was not identified and was far from the gasoline pole mentioned above. Finally, the remaining site (SEQ) was not along this trend and was characterized by particularity high $^{208}Pb/^{207}Pb$ ratios (2.48–2.51), as observed in local molasses bedrock with values >2.5 (Bur et al., 2009).

The $^{208}Pb/^{207}Pb$ ratios were plotted against the inverse of the Pb enrichment factors (1/EF(Pb), Hernandez et al., 2003; N'Guessan et al., 2009, Fig. 6b). Two different linear trends were clearly identified: (1) a first trend including the majority of the stations identified above and (2) a second linear trend corresponding to the three Tarn sites (SEQ, ALB, and HAU). ALB and HAU had the lowest $^{208}Pb/^{207}Pb$ ratios and high Pb enrichments, whereas SEQ was characterized by lichens with high $^{208}Pb/^{207}Pb$ ratios and a low Pb enrichment factor. The first linear relationship was used to determine $^{208}Pb/^{207}Pb$ ratios, which corresponded to a mean anthropogenic end-member of 2.43, whereas the second relationship indicated an anthropogenic ratio of 2.34.

The historical data were grouped by time period (Fig. 6c). Aside from the Tarn samples, the 1870–1916 herbarium Pb ratios fitted a new linear relationship ($y = 0.94x + 1.38$, $r^2 = 0.98$) almost parallel to that of the current samples and intersecting the Swiss coal signature (Chiaradia and Cupelin, 2000). However, this line shifted to higher $^{208}Pb/^{207}Pb$ ratios. This trend was particularly true for the 1870–1880 samples, with homogeneous $^{208}Pb/^{207}Pb$ ratios of 2.46, whereas others samples were more dispersed (Fig. 6d). For the three Tarn sites, the historical sample ratios converged with their current characteristics: SEQ with high $^{208}Pb/^{207}Pb$ ratios, and ALB and HAU plotted on the current relationship with higher $^{206}Pb/^{207}Pb$ ratios. The 1998 sample was close to the gasoline end-member.

4. Discussion

4.1. Origins of metals in atmospheric deposition: background vs. anthropogenic sources

The present study aimed to investigate atmospheric deposition of metals through different spatial scales (site, regional, and country) in France. On the country scale (Fig. 2a–b), the chemical elements that accumulated in current lichen and moss samples were linked as followed: (1) a group of elements strongly linked together, and generally originating from oxides or clay minerals (Al, As, Co, Cr, Fe, Ti, and V), also called lithogenic elements (Pacyna, 1986; Nriagu, 1989b); (2) several groups of metals arising from various mixed sources (both natural and anthropogenic), such as Cd–Mn–Zn, Pb–Sr, Sb–Sn, Cu–Ni, and Cs. We noticed that the lithogenic group explained an important part of the data variance (36% for the first axis), and most of these elements were consistent between the different regions (Fig. 3). This result indicated that, with a few exceptions, these elements had a common lithogenic origin on the country scale, and behaved in a similar way in terms of the bioaccumulation process, as previously highlighted through the rare earth elements, which are also strongly linked to bedrock weathering (Agnan et al., 2014). We can assume that the weak density of vegetation observed in sparse forests allows a better accumulation of lithogenic elements brought by dust (Fig. 2c). Conversely, the canopy limits direct dust deposition and allows a higher bioaccumulation of: (1) elements recycled by vegetation through foliar leaching, such as Mn or Zn (Heinrichs and Mayer, 1977; Lovett and Lindberg, 1984; Rea et al., 2001; Ukonmaanaho et al., 2001; Gandois et al., 2010, 2014), or (2) more mobile elements such as Cd (Baker, 1997; Colbeck, 2008).

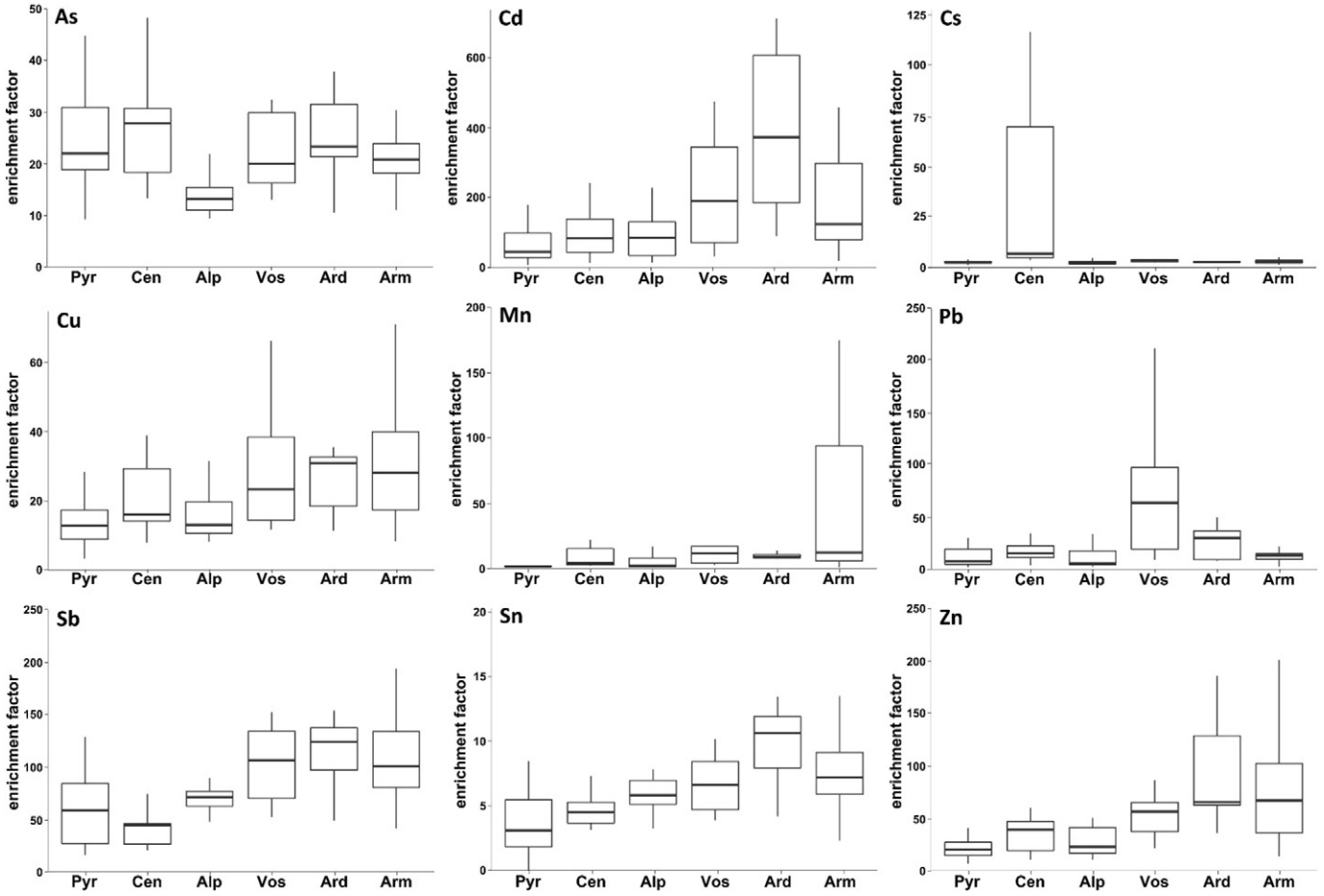

Fig. 4. Enrichment factor boxplots of 9 PHE in foliose lichens for the six regions: Midi-Pyrénées (Pyr), Massif Central (Cen), Alps (Alp), Vosges (Vos), Ardennes (Ard), Armorican Massif (Arm).

Common chemical behavior explains the frequent association between Cd and Zn without any common origin (Fig. 3).

To evaluate the sites where PHE exceeded the "natural" threshold, we used the geochemical background of foliose lichens. Between 5 and 38% (20.4% on average, Table 3) of the sites showed an exceedance, which could be considered as characteristic of the overall French forested environment. Indeed, a non-negligible percentage of exceedance was found for supposedly less anthropogenic elements (10% for Al, 14% for Fe, 19% for V). This phenomenon could be explained by: (1) the variability of concentrations in bioaccumulators, particularly as related to the forest density (Garty, 2001); and (2) a potential influence of short-distance contamination linked to the proximity of urban areas to some sites (*e.g.*, ALB, TOU, or MAR). The geochemical background values were consistent with values found on the European scale (Nimis and Bargagli, 1999). However, compared to contaminated sites, the thresholds of anthropogenic elements were mostly included in "naturality" classes, as a result of the low contamination levels of these elements in the studied sites. However, the lithogenic elements were sometimes classified in the "alteration" class, suggesting that these PHE appeared with low differences in concentrations between background and polluted areas on the European scale (Harmens et al., 2013), unlike anthropogenic elements.

Despite the national trend, some differences were observed from one region to another (Figs. 3 and 4). Most of the PHEs (Cd, Cu, Pb, Sb, Sn, and Zn) were more enriched in the three Northern regions (Vosges, Ardennes, and Armorican Massif, Fig. 4), as was also evidenced in the soil surface horizons from the North-Eastern part of France (Hernandez et al., 2003). We assume that both soil and lichen concentrations revealed atmospheric deposition of contaminants. This contamination could be related to the regional distribution of anthropogenic activities: historical mining (Sainte-Marie-aux-Mines, La Croix-aux-Mines), metallurgic activities, or local factories (Baccarat crystal glassworks in the Vosges, Peugeot-Citroën automotive industry in the Ardennes, and a high density of industries in France and its neighbor countries in these areas). In contrast to Cd and Zn, Pb has low solubility (Colbeck, 2008). Its atmospheric transport is therefore preferentially carried out by particles, and Pb could originate from a transboundary industrial region like Belgium or the Ruhr Valley in Germany (Harmens et al., 2008). This different origin explains the opposite distribution of Pb and Cd–Zn in the Vosges and Ardennes dendrograms (Fig. 3d–e).

The Pb isotope ratios (Fig. 6a–b) confirmed the Pb contamination in LSP illustrated by the proximity with the anthropogenic end-member (Chiaradia and Cupelin, 2000). The origin of this global contamination had a $^{208}Pb/^{207}Pb$ signature of 2.43. In the Midi-Pyrénées, a heterogeneous pattern was observed: only SP 11 followed the previous general trend with a wide dispersion, whereas the three stations from the Tarn department (ALB, SEQ and HAU) had local signatures. The sedimentary bedrock molasse was also characterized by typically high $^{208}Pb/^{207}Pb$ ratios (>2.5, Bur et al., 2009), which could explain the natural end-member of this region, as observed in the lowest Pb-enriched site (SEQ, Fig. 6b). A $^{208}Pb/^{207}Pb$ signature of 2.34 with a high EF was determined and attributed to an anthropogenic source for the Tarn region. However, although ALB and SEQ were geographically close (approximately 6 km away), ALB showed similar Pb signatures as HAU (approximately 54 km away). Several main activities have occurred in this region over more than a century: the exploitation of the Carboniferous coal field of Carmaux-Albi (Monnié, 1929) until the end of the 1950s, the tannery industry since the middle of the 19th century (although

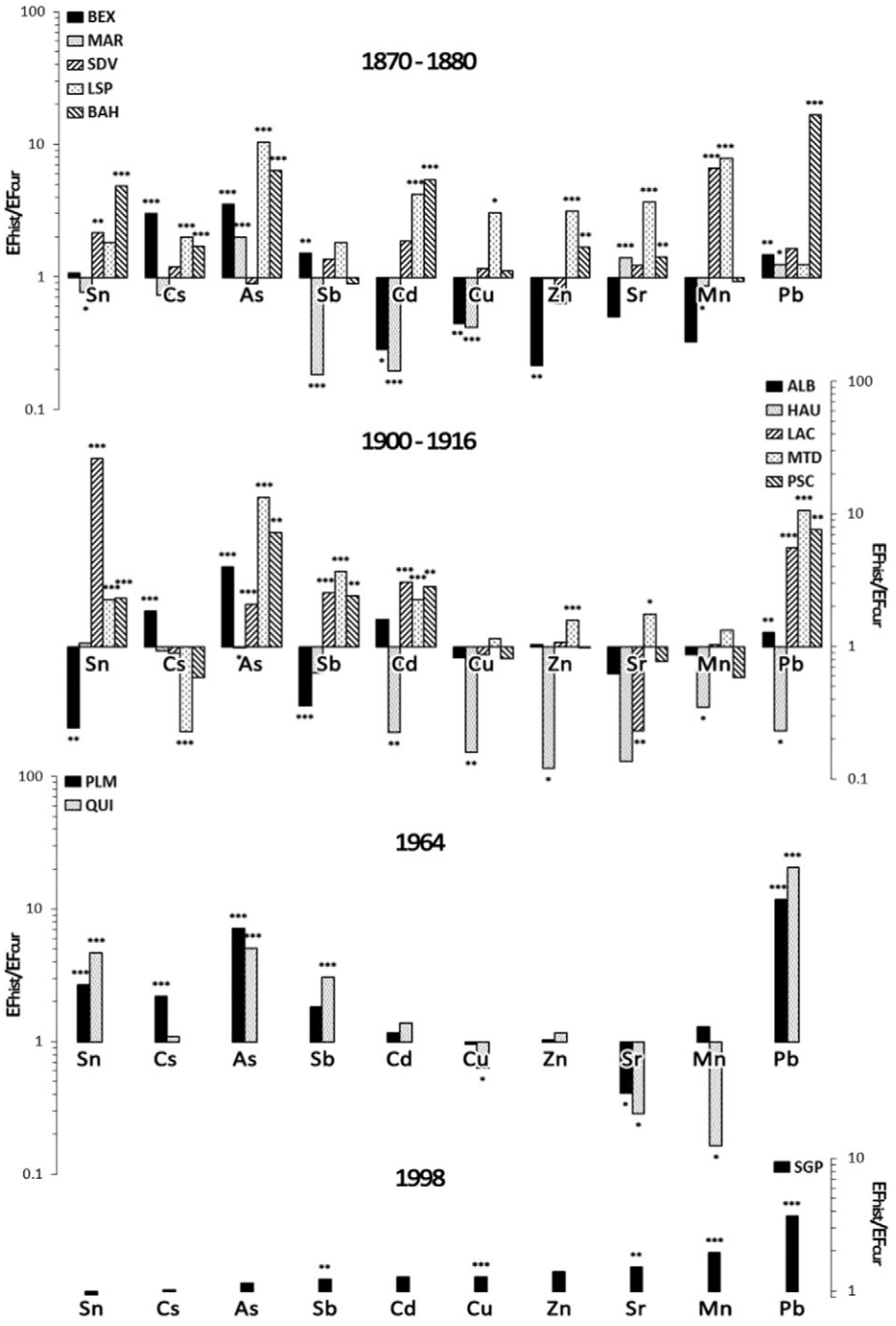

Fig. 5. Ratios of historical/current EF for different sites from each period: 1870–1880, 1900–1916, 1964, and 1998. The comparison between historical and current EF was performed using Student's test (*p < 0.05, **p < 0.01, ***p < 0.001).

no contamination of Cr, the typical PHE linked to these activities, was observed), and metallurgic activities. No similar signature in the literature was observed in urban areas (Monna et al., 1997; Véron et al., 1999; Carignan et al., 2005). The $^{208}Pb/^{207}Pb$ ratios of European coal from United Kingdom (Farmer et al., 1999), Switzerland (Chiaradia and Cupelin, 2000), or Spain (Díaz-Somoano et al., 2007) are greater than 2.41. The exception is the Cenozoic Spanish coal basin ($^{208}Pb/^{207}Pb = 2.28–2.39$), but, from a geological point of view, the Cenozoic Spanish field could not be linked to the Carboniferous Tarn field. To date, it is not possible to clearly identify this local source.

The regional environmental context could also explain the anomalies observed in the concentration and enrichment data. In addition to the dust record in sparse forests, the Southern regions were characterized by the highest concentrations of lithogenic elements: *e.g.*, the average foliose lichen concentrations of Al were 1612 μg g^{-1} for the Midi-Pyrénées, Massif Central and Alps, and 831 μg g^{-1} for the Vosges, Ardennes and Armorican Massif. This difference might result from climatic conditions on a large scale: the Southern sites were closer to the Mediterranean region, with a drier and dustier environment, and also influenced by regional dust, confirming the recent findings on bioaccumulation in mosses reported by the BRAMM network (Rausch de Traubenberg et al., 2013). The lithology would also act as an important player to explain the local anomalies: the Sr and Ti enrichment in the Massif Central could obviously be linked to the nature of the local basalt. For example, the Ti/Al ratio in the Massif Central basalt was 5.7-fold higher than in UCC (Chauvel and Jahn, 1984). Manganese was also found with high enrichment in MTD,

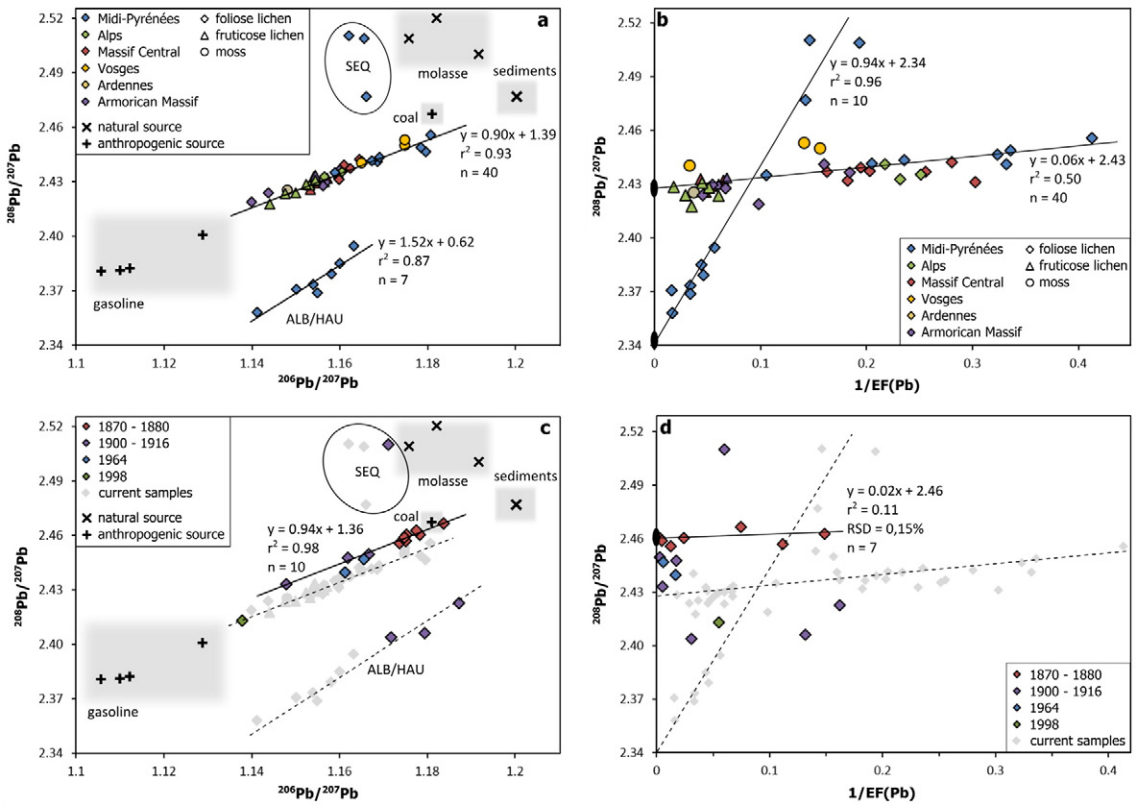

Fig. 6. Lead isotope ratios: $^{208}Pb/^{207}Pb$ *vs.* $^{206}Pb/^{207}Pb$ of current (n = 50, a) and historical (n = 17, c) samples, and $^{208}Pb/^{207}Pb$ *vs.* 1/EF(Pb) of current (n = 50, b) and historical (n = 17, d) samples. Literature data are added: Miocene sediments (Monna et al., 1995) and Pyrenean molasse (Bur et al., 2009) for natural signatures, and Swiss gasoline and coal (Chiaradia and Cupelin, 2000) for anthropogenic signatures.

as a result of its abundance in mineral veins, including in the pumice substrate (Guerin and Perseil, 1996). As observed for REE, the bioaccumulators therefore recorded local metal signatures from the regional lithology (Agnan et al., 2014).

4.2. Evolution of metal atmospheric deposition over the last century: changes in the nature of contamination

The metals registered in lichen and moss samples preserved in herbaria differed from those of their corresponding current samples. First, Cs was associated with lithogenic elements, as it easily adsorbed to clay minerals (Kabata-Pendias, 2010); however As was less influenced by lithogenic association (Fig. 2b). Moreover, biological recycling was restricted to Mn–Sr, while Zn and Cd were more indicative of the anthropogenic signature, together with Pb and Cu. These differences implied distinct origins over time. Despite the non-exclusive anthropogenic sources highlighted by EF, a normalized method is required for interpreting the herbarium samples (Agnan et al., 2014). As a whole, regarding the historical EF normalized to current ones (Fig. 5), the number of elements with significant enrichment in the past decreased over time: 9 for 1870–1880 (n = 5), 7 for 1900–1916 (n = 5), 5 for 1964 (n = 2), and 4 for 1998 (n = 1). Nevertheless, a geographical pattern was observed: the Northern regions (*e.g.*, MTD, LSP, PSC, and BAH) were generally the most impacted regions. The PHEs that were strongly enriched (As, Cd, Pb, Sb, and Sn), particularly during the late 19th century and the beginning of the 20th century, were specific to mining activities and coal combustion contributions (Finkelman, 1999; Chen et al., 2013), as also observed in various European peat bogs (Krachler et al., 2003; Cloy et al., 2005, 2009). This finding was confirmed by 1870–1880 Pb isotope data, which converged to a $^{208}Pb/^{207}Pb$ ratio of 2.46, typical of the coal signature (2.47, Chiaradia and Cupelin, 2000). The wide dispersion observed for the 1900–1916 period indicated potential additional sources and required other end-members; unfortunately, the low number of samples did not allow us to determine these sources. Both local industrial pressure and other sources explained the geographical differences observed for other PHE (such as Cu or Zn).

Unexpectedly, the three Tarn stations showed the same isotope Pb ratios as current samples: low $^{208}Pb/^{207}Pb$ ratios for ALB and HAU and *vice versa* for SEQ (Fig. 6c). This consistency over time dismissed modern contamination: only a local lithological origin or local industries active over a century ago that continue to operate could explain these specific characteristics. In addition, coal contribution modified the $^{208}Pb/^{207}Pb$ ratios and made the determination of a signature more complex than present-day (Fig. 6d). Surprisingly, in this same region, the EF ratios were lower than in other regions (Fig. 5), particularly in ALB, which could be explained by the current contamination described by Agnan et al. (2014).

Finally, the influence of coal combustion decreased gradually over time, but still made its mark in the mid-20th century, as the EF ratios were also significant for As, Pb, Sb, and Sn in 1964. However, the maximum values for Pb EF ratios (10 to 20) during this period implied an additional source. Lead was added to gasoline as an antiknock additives starting in 1920 (Miquel et al., 2001), peaking at the end of 1960s (Goodsite et al., 2001), and was legally abandoned in Europe (directives auto oil 98/69 and 98/70). However, the total elimination of leaded gasoline in France occurred in January 2000. This event explains how the EF was still as high as 4 in the 1998 sample (Fig. 5), although the Pb isotope ratios showed a high gasoline influence (Arnaud et al., 2004; Forel et al., 2010, Fig. 6c).

5. Conclusions

The atmospheric deposition of metals was assessed in forested ecosystems over various regions of France through lichen and moss

bioaccumulation. The concentration levels showed, as a whole, low contamination, and the determination of geochemical background indicated that elements classified as anthropogenic elements (*e.g.*, Cd, Pb, Zn) were weakly altered compared to the Italian scale. This result is due to the multiple origins of these elements, including various local human activities and the influence of biological recycling. However, elements mainly originating from natural dusts (*e.g.*, Al, Fe, Ti) were incorporated at a relatively homogeneous level of concentrations between contaminated and background sites on European scale. It appeared that the density of the forest canopy influences the accumulation of these dusts and associated elements by lichens and mosses. Each region/site was obviously characterized by a group of metals related to the local context (anthropogenic activities and/or lithology). The lichens from the North-Eastern region exhibited a substantial contamination, whereas dust deposition related to the drier climate and atmospheric dust clouds were thought to influence the composition of samples from the Southern regions. The historical evolution of atmospheric contamination was demonstrated by EF and Pb isotope ratios of herbarium samples compared to current samples. The high global influence of coal combustion recorded since 1870 decreased gradually during the 20th century, whereas the contamination from car traffic obviously registered during the end of the 20th century has decreased in the last several decades. Lead isotopes also evidenced a well-maintained contamination pattern over a century in the Southern regions of the country. Even if the sources were not clearly identified, they were thought to be from local anthropogenic activities.

Acknowledgments

This project benefited financial support from ADEME (French Agency for Environment). The authors would like to thank Paul Seimandi and Dominique Mazau from the University Toulouse III for kindly providing herbarium samples. Frédéric Candaudap, Aurélie Lanzanova, David Baqué, Marie-José Tavella, Carole Boucayrand, Manuel Henry and Jonathan Prunier thanked for their assistance during the ICP analyses and the cleanroom dissolution procedure. The authors also thank Gaël Le Roux for his help in the treatment of ICP-MS isotope data. Thanks to two anonymous reviewers for their relevant comments. Yannick Agnan was funded with an ADEME fellowship.

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.scitotenv.2015.05.083.

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