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Comparing early twentieth century and present-day atmospheric pollution in SW France: A story of lichens

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A B S T R A C T

Lichens have long been known to be good indicators of air quality and atmospheric deposition. *Xanthoria parietina* was selected to investigate past (sourced from a herbarium) and present-day trace metal pollution in four sites from South-West France (close to Albi). Enrichment factors, relationships between elements and hierarchical classification indicated that the atmosphere was mainly impacted by coal combustion (as shown by As, Pb or Cd contamination) during the early twentieth century, whereas more recently, another mixture of pollutants (e.g. Sb, Sn, Pb and Cu) from local factories and car traffic has emerged. The Rare Earth Elements (REE) and other lithogenic elements indicated a higher dust content in the atmosphere in the early twentieth century and a specific lithological local signature. In addition to long-range atmospheric transport, local urban emissions had a strong impact on trace element contamination registered in lichens, particularly for contemporary data.

Keywords:

Lichen
Xanthoria parietina
Herbarium
Trace metals
REE

1. Introduction

Atmospheric deposition of trace metals is considered a major environmental problem as metals are known to have a significant impact on ecosystems (Ulrich and Pankrath, 1983). Their incorporation through the trophic chains is a potential toxicological risk. Anthropogenic atmospheric emissions, in addition to natural ones, shift the balance of natural biogeochemical cycles significantly (Rauch and Pacyna, 2009), requiring the evaluation of these disturbances.

Determination of atmospheric deposition of trace elements – often called Potentially Harmful Elements (PHE) (Plant et al., 1997; Salvarredy-Aranguren et al., 2008) – at local and regional scales, is complex and expensive. Bioaccumulation methods are sometimes used to overcome difficulties in regards to the assessment of PHE deposition (Falla et al., 2000; Wolterbeek, 2002).

Because of their biological and physiological features, some biological organisms are more sensitive than others to atmospheric pollution. Indeed, foliaceous lichens are good candidates for bio-monitoring since they absorb and accumulate atmospheric pollutants more than vascular plants (Loppi et al., 1997). The main reasons for this are: (i) the lack of protective cuticle and root system

(Conti and Cecchetti, 2001); and (ii) their permanent biological activity throughout the year, allowing accumulation even in winter.

The selection of the appropriate species needs to consider the ability to accumulate PHE, their distribution and the availability of relevant data in the literature. Epiphytic foliose lichens such as *Xanthoria parietina* or *Parmelia sulcata* are known for their ability to accumulate trace elements and are often used as air quality indicators (Garty, 2001; Loppi and Bonini, 2000; Nimis et al., 2000). Lichens have been used to evaluate the atmospheric impact of local industry (Loppi et al., 2000; Loppi, 2001; Rusu et al., 2006a; Hissler et al., 2008). However, very few studies have used lichens to evaluate atmospheric deposition of heavy metals on a large spatial scale (Brunialti and Frati, 2007; Nimis et al., 2000) or investigated background levels relative to long-range atmospheric inputs (Garty, 2001).

Historical data on atmospheric metal deposition is particularly scarce. As environmental archives, the lichens and mosses preserved in herbaria represent an important source of historical data. Indeed, a few studies have successfully used such organisms to investigate past contamination (Herpin et al., 1997; Loppi et al., 1998; Purvis et al., 2007; Shotbolt et al., 2007; Zschau et al., 2003).

We hypothesised that: (i) lichens have registered various atmospheric metal contaminants from local and/or long-range emissions, which will be investigated for 13 PHE and Rare Earth Elements (REE) in order to assess the origin of this contamination; and (ii) with industrial development, the registration intensity was

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different in recent decades compared to the early twentieth century, which will be examined using herbarium specimens in comparison with contemporary lichens.

For that purpose, we focused on one chlorolichen species, *Xanthoria parietina* (L.) Th. Fr., collected in 2010 and between 1900 and 1909 (samples from the Sudre herbarium, University of Toulouse) to perform a comparison over one century in four sites located in SW France.

2. Materials and methods

2.1. Study area

This study concerns four stations located in SW France, 70 km east of Toulouse city (Midi-Pyrénées region, Fig. 1). One station is in downtown Albi (50 000 inhabitants); two countryside stations “le Séquestre” and “Castelnau-de-Lévis” are very close to Albi (both 5 km) in the surrounding hills with a scattered settlement; the fourth station called “Hautpoul” is located in the Montagne Noire forest, in a small hamlet 60 km south of Albi (Table 1).

The first three stations are localised on Oligocene sedimentary rocks originating from the dismantling of the Pyrenees mountains, whereas the last (Hautpoul station) is on gneiss interleaved with granodiorites from the Hercynian basement of the Massif Central.

This region is characterised by an oceanic climate with a mountainous influence in Hautpoul. The mean temperature varies from 13 to 10.5 °C and the average annual rainfall ranges from 760 to 1200 mm for the Albi area and Hautpoul, respectively. The main wind direction is E–W for the Albi area and NW–SE for Hautpoul. The Albi area is known for various industries, including a glass factory, an airfield at le Séquestre, a power plant disused since 1988 and a waste incinerator which stopped operating in 1999.

The choice of these stations has been driven by the availability of historical specimens of lichens in the “Sudre herbarium” from the University of Toulouse (Index Herbariorum: TL). The collection is composed of 3000 samples including 1000 different taxa collected at various sites over the whole Midi-Pyrénées region and the Massif Central during 1880–1910. Only a few specimens corresponded to *X. parietina* species located in the areas of interest. All the samples have been stored in newsprint in closets without any conservation treatment. For the relevant stations, samples were collected between 1900 and 1909 for the four sites (Table 1). To overcome the possible variability associated with the site, the 2010 sampling was done at the location noted in the herbarium samples.

2.2. Sampling procedure

For present-day sampling, at every station, an area of around 2500 m² divided into approximately five homogeneous sub-areas, was defined. Several samples were collected from 3 to 5 trees in each sub-area (Table 1). An influence of substrate species on lichen metal concentrations has been documented (Goyal and Seaward, 1981; Debruin and Hackenitz, 1986; Prussia and Killingbeck, 1991). Thus the objective of this protocol was to limit the intra-variability in each station and to increase the representativeness of each studied area.

Sampling was performed at about 1.5 m high on tree trunks to avoid potential contamination by splashing of soil particles during rainfall, with a ceramic knife and latex gloves to avoid any metal contamination (Bargagli and Nimis, 2002). The whole thallus was collected to integrate: (i) the growth rate, which is highly variable and not well-described (Armstrong and Bradwell, 2011); and (ii) the time required to reach an equilibrium between lichen trace metal content and the atmospheric environment (Aboal et al., 2010). Lichen samples were kept in plastic bags and brought back to the laboratory.

For the historical samples, lichens were extracted from the herbarium sheets, with the same caution as described above. Particular care was taken to avoid the parts of samples in contact with the glue.

2.3. Pre-analysis treatments and analytical procedure

Lichen thalli were carefully sorted to select only the chosen species before drying at 30 °C. Historical and current samples were carefully ground in an agate mortar with a small amount of liquid nitrogen. The powdered samples were stored in a plastic tube until treatment.

Lichens samples were digested in a cleanroom at the Laboratoire Ecologie Fonctionnelle et Environnement (EcoLab, Toulouse, France) using a suprapure HNO₃/HF/H₂O₂ mixture in Teflon vessels (Rusu, 2002). All the solutions were prepared with high-purity water (18.2 MΩ cm) with a MilliQ-system (Millipore). About 100 mg of lichen thalli was digested using 68% HNO₃ (0.5 mL) and HF (0.5 mL) at 90 °C in a savillex (Teflon bottle) for 48 h. After evaporation, 1 mL of H₂O₂ was added. The final mineralisation step was performed by adding 1 mL of 68% HNO₃ for 2 days at 90 °C. Finally, the samples were diluted 120- and 2400-fold for ICP–OES and ICP–MS, respectively, and stored in a 2% HNO₃ solution before analysis. For each series, the performance of the procedure was evaluated using two replicates of two certified materials (lichen IAEA-336 and pine needle SRM-1575a). Possible contamination during the digestion procedure was assessed with three blank samples (<1% of the sample concentrations for all elements, except for Ti, which was <2%).

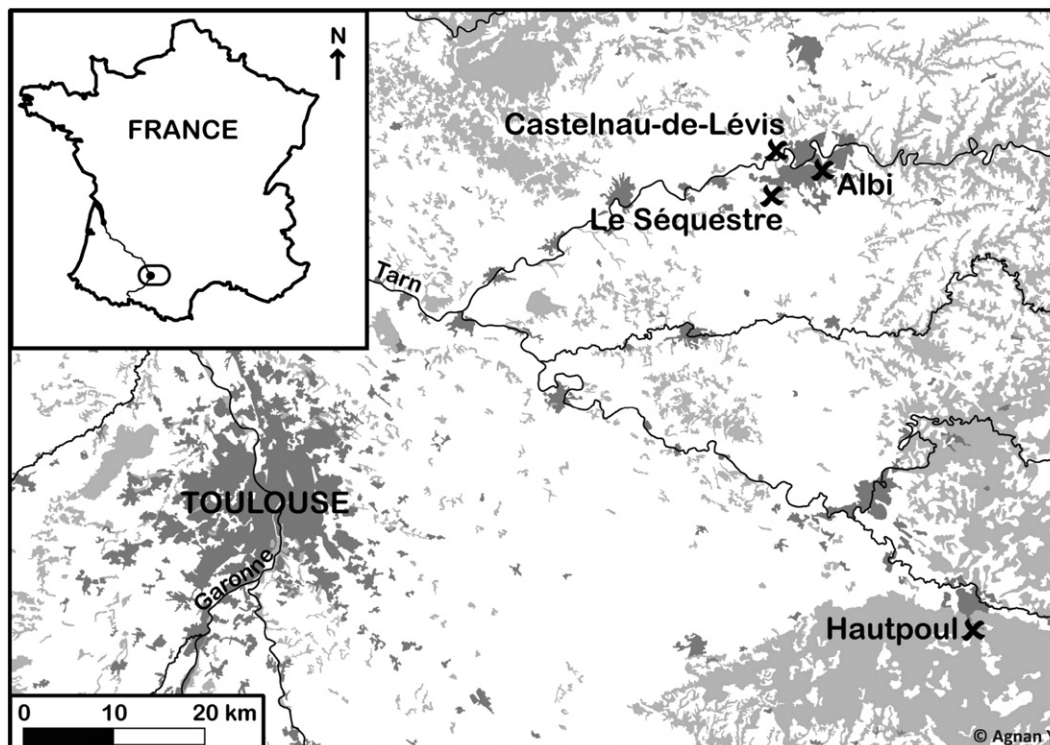


Fig. 1. Map of the studied area (SW of France) and site location (crosses). Urban areas are noticed in dark grey colour and forest areas in light grey colour.

Table 1
Characteristics of the sampling sites for historical and contemporary data.

Area	Samples	Sample location	Altitude	Sampling date	Substrate
Albi	6	2°10'10"E 43°55'40"N	175 m a.s.l.	2010-04-08	Ash, dogwood, sweetgum, fig tree
le Séquestre	7	2°06'30"E 43°54'10"N	220 m a.s.l.	2010-04-08	Elm, ash, oak, cherry tree
Castelnau-de-Lévis	5	2°06'00"E 43°56'30"N	230 m a.s.l.	2010-12-01	Ash, <i>Robinia</i> , <i>Prunus</i>
Hautpoul	4	2°22'35"E 43°26'30"N	520 m a.s.l.	2010-05-27	Ash
Herbaria					
Albi	1	<i>aux Planques, Albi</i>	/	1900	Poplar
le Séquestre	1	<i>au Séquestre</i>	/	1900	?
Castelnau-de-Lévis	1	<i>à Jussens</i>	/	1900	Walnut
Hautpoul	1	<i>à Hautpoul</i>	/	1909-04-06	?

Major elements (Ca, K, Mg, Na, P and S) were analysed by ICP–OES (Thermo IRIS INTREPID II XDL) at the EcoLab laboratory, and trace elements (Al, As, Cd, Co, Cu, Fe, Mn, Pb, Sb, Sn, Ti, V, Zn and REE) by ICP–MS (Perkin–Elmer ELAN 6000) at the OMP (Observatoire Midi-Pyrénées) analytical platform (laboratory Géosciences Environnement Toulouse, France).

During the ICP–MS analysis, $^{115}\text{In}/^{187}\text{Re}$ internal standards of known concentration were added to all samples, and four quality control samples were introduced every eight samples to correct for any analyser deviation. All concentrations were corrected from the recovery ($C_{\text{measured}}/C_{\text{certified}} \times 100$) obtained for each element: around $100 \pm 15\%$ for all the elements, except for Fe, Mn, Pb, Sb and Ti with 121%, 118%, 127%, 80% and 126%, respectively. The detection limits vary around 0.2 mg L^{-1} for ICP–OES and between 1 and $10 \mu\text{g L}^{-1}$ for ICP–MS.

2.4. Data treatment

The normality of the data distribution was checked by the Kolmogorov–Smirnov test. It was non-normal for As, Cd, Mn, Pb, Sb, Sn, V and Zn. Consequently, the correlations were evaluated using the non-parametric Spearman correlation coefficient with SigmaStat software. The correlations between all the elements were displayed as a whole using a dendrogram allowing separating the elements into groups according to their closest Euclidean distance with Minitab software.

Enrichment Factors (EFs) are often used to evaluate the intensity of metal contamination in soil or river sediments (Bur et al., 2010; Hernandez et al., 2003) and in lichens (Bergamaschi et al., 2002; Rusu et al., 2006b; Vieira et al., 2004) to assess the anthropogenic atmospheric contribution. The EF is calculated as follows:

$$EF = \frac{(X/\text{Ref elt})_{\text{sample}}}{(X/\text{Ref elt})_{\text{Ref mat}}}$$

with X: metal of concern, Ref elt: reference element from natural origin, and Ref mat: reference material from natural origin.

Some studies (Reimann and de Caritat, 2005; N'Guessan et al., 2009) have indicated the potential influence of the chosen reference element and of the reference material on EF interpretation. However, to insure the comparison with previous studies, the authors selected the Upper Continental Crust (Taylor and McLennan, 1985) as the reference material (representative of the lithogenic origin) and aluminium as the reference invariant element (Gandois et al., 2010; Vieira et al., 2004).

3. Results

3.1. PHE and REE concentration ranges

3.1.1. Current concentrations

The current PHE (Table 2) could be ranked according to their decreasing concentrations: $\text{Al} > \text{Fe} > \text{Ti} > \text{Zn} > \text{Mn} > \text{Cu} > \text{Pb} > \text{V} > \text{As} > \text{Sn} > \text{Sb} > \text{Co} > \text{Cd}$, with the exceptions of Pb and Sn (Albi), Co and V (le Séquestre), V (Castelnau-de-Lévis), and Co and Mn (Hautpoul). The metal concentrations were in the middle-range of the values found by Bargagli and Nimis (2002) for Italian lichens

Table 2
Current and past concentration ranges of PHE in lichens (in $\mu\text{g g}^{-1}$) from the four stations. The italic figures are the standard deviations. The values in bold (%) indicate the evolution trend between past and present concentrations: (past – present)/present.

	Albi			le Séquestre			Castelnau-de-Lévis			Hautpoul		
	Present	Past	Past trend	Present	Past	Past trend	Present	Past	Past trend	Present	Past	Past trend
Al	1319.98 633.73	1153.41	–13%	1217.16 390.47	5901.22	+385%	1456.85 446.12	2254.74	+45%	1550.15 194.46	10 272.78	+563%
Fe	884.94 479.59	688.22	–22%	697.02 216.55	3166.52	+354%	846.66 274.58	1464.61	+54%	953.79 107.83	4855.45	+409%
Ti	110.36 62.62	49.84	–55%	87.11 31.32	294.20	+238%	86.66 36.69	147.17	+176%	53.36 10.76	418.24	+684%
Zn	30.86 9.55	31.18	+1%	19.02 3.71	44.61	+135%	23.03 2.86	30.18	+15%	26.17 1.03	79.73	+205%
Mn	21.53 11.66	16.33	–24%	14.98 4.16	60.59	+305%	18.73 3.96	73.14	+51%	48.55 36.97	111.60	+130%
Cu	6.49 2.56	4.90	–25%	4.74 1.33	14.02	+196%	7.83 3.20	5.87	–25%	4.69 0.51	6.52	+39%
Pb	8.38 3.87	9.38	+12%	1.93 0.65	24.47	+1165%	2.60 1.27	20.33	+372%	4.31 1.44	19.47	+352%
V	2.92 1.54	2.11	–28%	2.31 0.72	9.25	+300%	3.02 1.15	4.21	+60%	2.63 0.29	12.13	+360%
As	1.29 0.64	4.58	+254%	0.53 0.16	11.08	+2004%	0.58 0.22	3.24	+564%	0.49 0.07	6.39	+1211%
Sn	2.19 1.25	0.46	–79%	0.50 0.14	1.69	+235%	0.43 0.12	0.96	+566%	0.14 0.03	2.66	+1749%
Sb	0.67 0.37	0.21	–69%	0.21 0.06	0.62	+194%	0.29 0.09	0.55	+388%	0.11 0.02	0.36	+217%
Co	0.41 0.18	0.41	+1%	0.28 0.09	1.16	+317%	0.37 0.14	0.61	+74%	0.35 0.05	2.52	+619%
Cd	0.14 0.08	0.22	+63%	0.04 0.01	0.25	+478%	0.09 0.05	0.30	+204%	0.10 0.03	0.36	+259%

from a large range of air quality conditions. However, some differences were observed among the stations. The coefficient of variation (standard deviation divided by the mean) indicated little variation between stations (29–50%) for Al, Co, Cu, Fe, Ti, V and Zn. The most significant variation was for As, Cd, Mn, Pb, Sb and Sn (65–117%), the greatest variation being observed for Sb and Sn with the highest values for these two elements in Albi, whereas for the first group of elements, no specific concentration trend could be observed.

The REE concentrations (Table 3) showed the same order of magnitude as found in the literature (Aubert et al., 2006; Spickova et al., 2010) in similar environmental conditions. The highest REE concentrations were predominantly observed in Hautpoul (like Al and Fe), whereas the lowest ones were located in le Séquestre.

3.1.2. Past concentrations

The past PHE concentrations (Table 2) were always enriched compared to the current ones, except for Albi. On average, concentrations in historical samples were around five-times higher in Hautpoul and le Séquestre and two-times higher in Castelnau-de-Lévis, whereas concentrations were rather close to current data in Albi. The concentrations ranked in the following order: Al > Fe > Ti > Mn > Zn > Pb > Cu > V > As > Sn > Co > Cd > Sb, except for As, Cd and Zn (Albi), As (le Séquestre) and V (Hautpoul).

The REE concentrations across the stations (Table 3) followed the same trend as for PHE, except for Albi where the past REE concentrations were lower than present. Concentration variations were similar for all the REE within a given station.

3.2. Relationship between the elements

To identify sources and behaviours of the elements, correlations were performed for all current samples taken together. The

Spearman correlation coefficients (Table 4) indicated three main groups with significant positive ρ value ($\rho > 0.7, n = 24, p < 0.01$): (i) Al, Co, Fe, Mn, V and REE (sum of REE concentration); (ii) Cd, Pb and Zn; and (iii) As, Sb, Sn and Ti. Copper was only significantly related to Co and V.

Dendrograms were performed on current and past data (Fig. 2) to get an overview of the relationships between the elements. Five groups could be distinguished on the current data ($n = 24$, Fig. 2A). The first group, including Al, Co, V, Fe, Ti and REE, corresponded to a significant homogeneous unit with 93% inner similarity. The second one included As, Sn, Sb and Pb (similarity coefficient 95%). The three remaining groups concerned Cu, the tandem Cd–Zn, and Mn, which was isolated from the other elements (with 20% distance). A random sampling with one sample by each station ($n = 4$) was performed to check the potential influence of the number of replicates in each station. The resulting dendrogram was almost equivalent (data not shown).

Consequently, this allowed the authors to run the dendrogram based on historical samples despite their limited number ($n = 4$, Fig. 2B). The past dendrogram indicated four groups of elements: the first one was an extremely robust group composed of Al, Fe, Sn, Ti, V, Co, REE and Zn (with 98% similarity), and three pairs Cd–Mn, As–Cu and Pb–Sb (with 97% similarity each). The comparison of the two dendrograms underlined some major differences. The robust unit Al, Co, Fe, REE, Ti and V remained unchanged between past and present, except Sn and Zn, which were included in this group in the past. Lead and Sb were also unchanged, in contrast to Mn–Cd and As–Cu, which were dislocated in the current sample, isolating Mn from the other elements.

3.3. Relationships between element ratios for current and past data

The relationships between As, Cu, Pb, Sb and Sn were particularly investigated (Fig. 3) in order to understand their sources

Table 3 Current and past concentration ranges of REE in lichens (in $\mu\text{g g}^{-1}$) from the four stations. The italic figures are the standard deviations. The values in bold (%) indicate the evolution trend between past and present concentrations: (past – present)/present.

	Albi			le Séquestre			Castelnau-de-Lévis			Hautpoul		
	Present	Past	Past trend	Present	Past	Past trend	Present	Past	Past trend	Present	Past	Past trend
La	1.18 <i>0.37</i>	0.95	–19%	0.97 <i>0.23</i>	3.97	+309%	1.04 <i>0.64</i>	1.82	+75%	1.35 <i>0.35</i>	9.05	+569%
Ce	2.46 <i>0.78</i>	1.89	–23%	1.93 <i>0.48</i>	7.90	+309%	2.06 <i>1.39</i>	3.68	+78%	2.57 <i>0.66</i>	18.28	+610%
Pr	0.26 <i>0.09</i>	0.22	–17%	0.22 <i>0.06</i>	0.92	+315%	0.24 <i>0.15</i>	0.43	+83%	0.29 <i>0.08</i>	2.12	+620%
Nd	1.00 <i>0.33</i>	0.84	–17%	0.83 <i>0.25</i>	3.40	+311%	0.89 <i>0.57</i>	1.61	+80%	1.09 <i>0.26</i>	8.10	+643%
Sm	0.19 <i>0.06</i>	0.15	–23%	0.16 <i>0.06</i>	0.66	+323%	0.17 <i>0.12</i>	0.30	+73%	0.20 <i>0.03</i>	1.57	+702%
Eu	0.04 <i>0.02</i>	0.03	–28%	0.03 <i>0.01</i>	0.13	+304%	0.04 <i>0.02</i>	0.07	+56%	0.03 <i>0.00</i>	0.21	+555%
Gd	0.19 <i>0.08</i>	0.17	–14%	0.15 <i>0.05</i>	0.61	+296%	0.19 <i>0.11</i>	0.33	+71%	0.19 <i>0.03</i>	1.60	+729%
Tb	0.02 <i>0.01</i>	0.02	–22%	0.02 <i>0.01</i>	0.07	+280%	0.02 <i>0.01</i>	0.04	+59%	0.02 <i>0.00</i>	0.20	+781%
Dy	0.13 <i>0.05</i>	0.11	–17%	0.11 <i>0.02</i>	0.41	+291%	0.12 <i>0.08</i>	0.18	+52%	0.12 <i>0.01</i>	1.07	+798%
Ho	0.02 <i>0.01</i>	0.02	–8%	0.02 <i>0.00</i>	0.07	+286%	0.02 <i>0.01</i>	0.03	+44%	0.02 <i>0.00</i>	0.20	+870%
Er	0.07 <i>0.03</i>	0.06	–18%	0.05 <i>0.01</i>	0.21	+287%	0.07 <i>0.04</i>	0.09	+41%	0.06 <i>0.01</i>	0.55	+867%
Tm	0.01 <i>0.00</i>	0.01	–27%	0.01 <i>0.00</i>	0.03	+341%	0.01 <i>0.01</i>	0.01	+37%	0.01 <i>0.00</i>	0.08	+883%
Yb	0.06 <i>0.02</i>	0.06	–1%	0.05 <i>0.01</i>	0.21	+285%	0.06 <i>0.03</i>	0.09	+49%	0.05 <i>0.01</i>	0.50	+872%
Lu	0.01 <i>0.00</i>	0.01	–19%	0.01 <i>0.00</i>	0.03	+343%	0.01 <i>0.01</i>	0.01	+46%	0.01 <i>0.00</i>	0.07	+830%

Table 4Spearman correlation coefficient (ρ) for current data in lichens ($n = 24$). The p -values are in italic (in bold if $p < 0.01$).

	Al	As	Cd	Co	Cu	Fe	Mn	Pb	Sb	Sn	Ti	V	Zn	REE
Al	—	0.505 <i>0.012</i>	0.178 <i>0.400</i>	0.827 0.000	0.689 0.000	0.932 0.000	0.784 0.000	0.440 <i>0.031</i>	0.199 <i>0.347</i>	0.084 <i>0.691</i>	0.643 0.000	0.945 0.000	0.549 0.006	0.954 0.000
As	—	—	0.375 <i>0.070</i>	0.699 0.000	0.637 0.000	0.496 <i>0.014</i>	0.383 <i>0.064</i>	0.715 0.000	0.831 0.000	0.773 0.000	0.817 0.000	0.623 0.001	0.501 <i>0.013</i>	0.477 <i>0.019</i>
Cd	—	—	—	0.558 0.005	0.353 <i>0.089</i>	0.383 <i>0.064</i>	0.515 0.010	0.778 0.000	0.362 <i>0.081</i>	0.203 <i>0.338</i>	−0.009 <i>0.963</i>	0.300 <i>0.152</i>	0.763 0.000	0.291 <i>0.165</i>
Co	—	—	—	—	0.770 0.000	0.886 0.000	0.794 0.000	0.742 0.000	0.451 <i>0.027</i>	0.318 <i>0.128</i>	0.597 0.002	0.908 0.000	0.749 0.000	0.810 0.000
Cu	—	—	—	—	—	0.652 0.000	0.545 0.006	0.460 <i>0.024</i>	0.595 0.002	0.334 <i>0.108</i>	0.643 0.000	0.817 0.000	0.483 <i>0.017</i>	0.597 0.002
Fe	—	—	—	—	—	—	0.890 0.000	0.574 0.003	0.154 <i>0.468</i>	0.054 <i>0.799</i>	0.514 0.010	0.924 0.000	0.632 0.000	0.939 0.000
Mn	—	—	—	—	—	—	—	0.632 0.000	0.080 <i>0.706</i>	−0.020 <i>0.924</i>	0.311 <i>0.137</i>	0.780 0.000	0.737 0.000	0.865 0.000
Pb	—	—	—	—	—	—	—	—	0.536 0.007	0.469 <i>0.021</i>	0.366 <i>0.078</i>	0.537 0.007	0.804 0.000	0.543 0.006
Sb	—	—	—	—	—	—	—	—	—	0.886 0.000	0.718 0.000	0.357 <i>0.085</i>	0.333 <i>0.110</i>	0.150 <i>0.478</i>
Sn	—	—	—	—	—	—	—	—	—	—	0.707 0.000	0.211 <i>0.318</i>	0.200 <i>0.345</i>	0.032 <i>0.879</i>
Ti	—	—	—	—	—	—	—	—	—	—	—	0.698 0.000	0.243 <i>0.250</i>	0.559 0.005
V	—	—	—	—	—	—	—	—	—	—	—	—	0.590 0.002	0.885 0.000
Zn	—	—	—	—	—	—	—	—	—	—	—	—	—	0.610 0.002
REE	—	—	—	—	—	—	—	—	—	—	—	—	—	—

and their behaviours. Indeed, these elements were significantly correlated (Table 4) and the concentrations differed greatly between past and contemporary samples. To ensure an optimal comparison, all the elements were normalised to Al in order to limit the influence of the high concentrations often observed in the historical samples.

According to the dendrograms, Sn and As were more distant in the past (84% versus 97% at present, Fig. 2). The relationship Sn/Al versus As/Al (Fig. 3A) showed two distinct positive linear trends for past and present samples. Despite a smaller number of historical samples, it could be observed that the contribution of Sn was less obvious in the past compared to As. In contrast, the linear relationship for the current samples was stronger and the slope was two orders of magnitude larger, indicating a high contribution of Sn. Nevertheless, the order of data distribution for the different sites was similar.

Unlike the previous elements, Sb and Pb were relatively closely related both in the past and in the present (Fig. 3B). Past samples

were characterised by a higher Pb/Al, namely in Castelnaud-de-Lévis and Albi, whereas current samples had higher Sb/Al for the countryside stations near Albi and particularly in urban Albi. Curiously, Hautpoul current data fell on the regression line of the whole past samples.

Cu/Al was plotted versus Pb/Al, both were not very significantly linked during the two periods (Fig. 3C). However, three trends could be distinguished: (i) a positive trend for past samples with a relative increase of Pb/Al; (ii) two trends for current data with a slope of 1:1 for Hautpoul and Albi samples, and a positive relationship with double the Cu/Al value relative to Pb/Al for le Séquestre and Castelnaud-de-Lévis.

Finally, As/Al was related to S/Al (Fig. 3D). As previously shown for other metals, a significant positive linear regression was observed in the past, with the highest As/Al in Albi, whereas the relationship for current data was not significant. Indeed, a very large variation of S/Al and a very low As/Al ratio was observed for current data within each station.

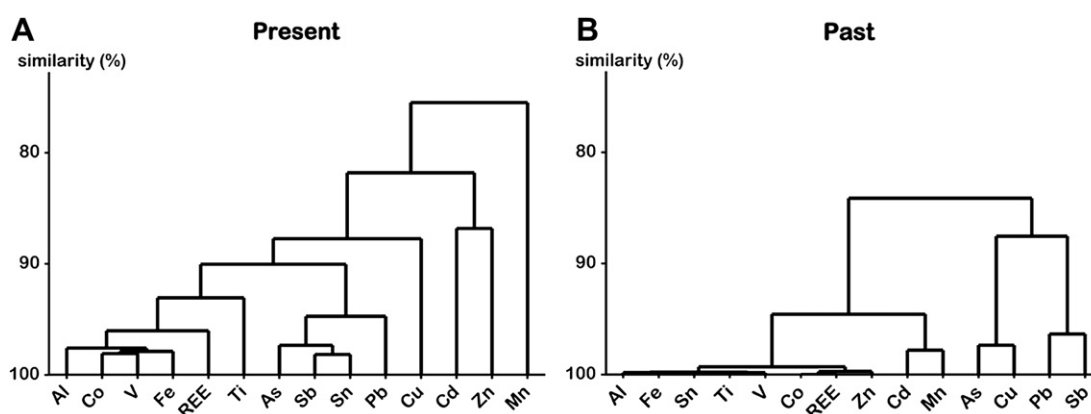


Fig. 2. Dendrogram based on Euclidean distance between elements registered in lichens. (A) Current data ($n = 24$) and (B) Past data ($n = 4$). The ordinate axis shows the percentages of similarity between the groups.

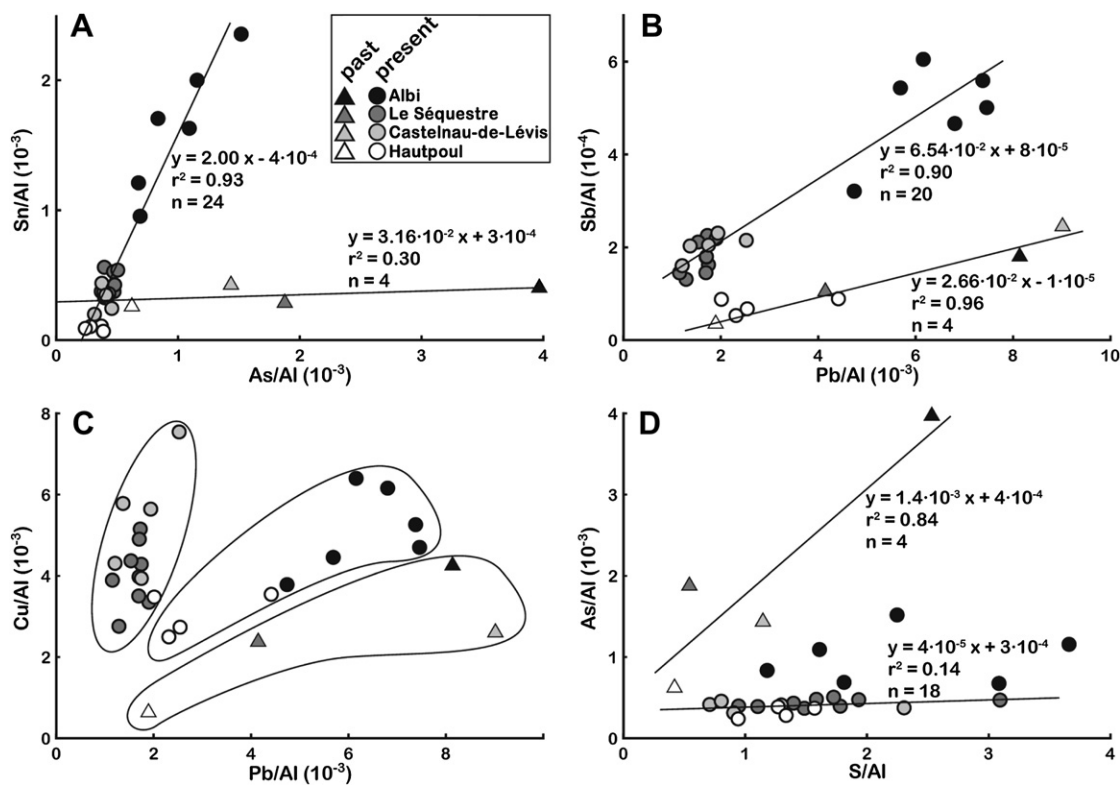


Fig. 3. Relationships between element concentration ratio in lichens for Albi (in black), le Séquestre (in dark grey), Castelnau-de-Lévis (in light grey) and Hautpoul (in white). Triangles symbolize the historical data and circles the current ones. The regressions were indicated even if non-statistically significant for discussion purpose (see text).

3.4. Enrichment factor

The enrichment factor (EF) was calculated for past and present PHE data (Fig. 4) to minimise the influence of generally elevated concentrations in the past (Purvis et al., 2007). The standard deviation of historical data could not be calculated by the single sample on each location. Whatever the station, three groups of elements could be distinguished according to their enrichment level: (i) Al, Co, Fe, Mn, Ti, V and, to a lesser extent, Mn, with no enrichment ($EF < 2$); (ii) Cu, Sn, Pb and Zn with moderate to high EF values; and (iii) Sb, Cd and As, which were the most enriched PHE with the EF reaching 200. The reference material probably has an influence on the intensity of the enrichment (N'Guessan et al., 2009; Reimann and de Caritat, 2005), thus only differences between sites should be considered. Overall, EFs increased as follows: Hautpoul < le Séquestre \approx Castelnau-de-Lévis < Albi.

For the first group of elements, there was no significant change between past and current samples except for Mn. Some elements (e.g. As, Cd and Pb) showed lower contemporary EFs than in the past, except in Hautpoul. Other elements, such as Cu, Sb, Sn and Zn exhibited opposite trends with increased EFs compared to the past.

3.5. Present and past patterns of REE

The distribution patterns of REE were normalised to PAAS (Post-Archean Australian Shale, Fig. 5). All the profiles showed a strong depletion with reference to the PAAS (from 0.5 to 0.02). In all the stations, the following can be observed: (i) a stable light REE (LREE) pattern; (ii) an enrichment for middle REE (MREE); (iii) a depletion for the heaviest REE as indicated by the ratio Gd/Lu (1.69–2.38); (iv) a positive Gd anomaly as already observed in the lichen species *Evernia prunastri* (Aubert et al., 2006); and (v) two light negative

anomalies for Ho and Nd. A positive anomaly is observed for Tm in current data from Albi. The current REE profiles were in the same range around 0.05, in contrast to historical data, which varied greatly from Albi (around 0.02) to Hautpoul (around 0.25), as observed previously for the PHE concentrations. Remarkably, past and present REE profiles followed exactly the same pattern, which is site-specific. REE anomalies were calculated to evaluate the specificity of each station:

$$\frac{Eu}{Eu^*} = \frac{Eu}{(Sm + Gd)/2}$$

Current and past Eu anomalies were as follows: 1.07 and 0.95 for Albi; 0.97 and 0.96 for le Séquestre; 1.08 and 0.98 for Castelnau-de-Lévis; and 0.78 and 0.63 for Hautpoul, respectively.

4. Discussion

The results obtained in this study for trace elements concentration in lichens allow: (i) comparison of contamination levels between the early 20th and early 21st centuries, and (ii) consideration of the origin of the elements (naturally or anthropogenically derived) and how this has changed between these two points in time.

4.1. Level of concentrations and its comparison over one century

The 2010 lichens showed no extreme contamination, being within the range of what Bargagli and Nimis (2002) proposed as "natural". Elements such as Sb or Sn were not taken into considerations in this reference. As a whole, the observed concentrations were in the range of those described by Purvis et al. (2007). However, the high enrichment observed in all the stations for the

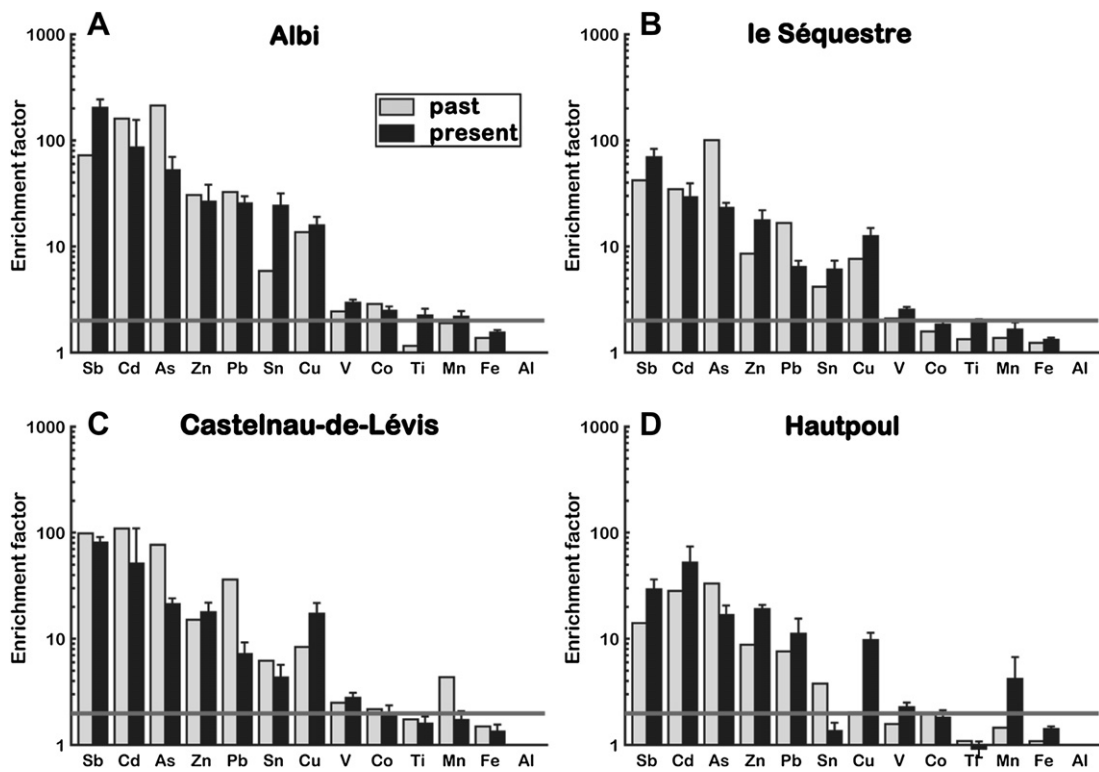


Fig. 4. Enrichment factor normalised to UCC and relative to Al for past data (in grey) and current data (in black, with standard deviation). The grey line indicates the limit for a significant enrichment ($EF > 2$).

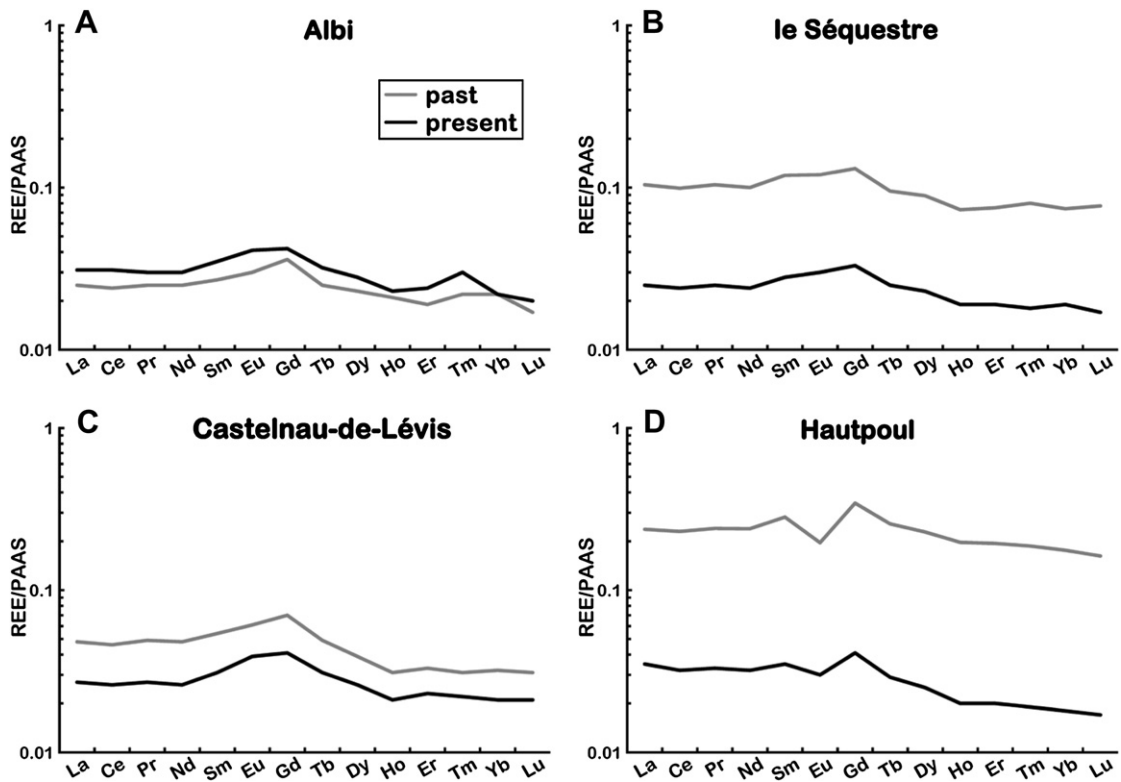


Fig. 5. Distribution patterns of REE for past data (in grey) and current data (in black) normalised to the PAAS in lichens from the four stations: Albi (A), le Séquestre (B), Castelnau-de-Lévis (C) and Hautpoul (D).

elements from Sb to Cu (Fig. 4) indicates a significant background contamination from regional to global atmospheric contributions. The increasing PHE concentrations shown by *X. parietina* from the Hautpoul rural station to Albi city indicate a clear local industrialisation influence impacting the atmosphere. Between these two opposite stations, le Séquestre and Castelnau-de-Lévis have intermediate concentration patterns reflecting their location close to Albi.

The herbarium lichens indicated, as a whole, higher historical concentrations for PHE as well as for REE (Tables 2 and 3), particularly for the stations far from Albi city (seven-times higher on average). This shift might be related to a more intense atmospheric dust deposition at the beginning of the twentieth century as registered in peat bog (De Vleeschouwer et al., 2009; Shotyk et al., 2002). However, this difference is not observed at the Albi station, and there is no obvious explanation; this needs further investigation for confirmation in other regions in France. The remarkable correlations between past and current REE distribution patterns, and their local signatures (e.g. the Eu anomaly), strongly indicate that herbarium lichens are valuable resources for determining past REE, and by extension, PHE deposition. In particular, this observation refutes the hypothesis suggested by Purvis et al. (2007) regarding dust contamination during storage. If dust contamination had occurred, it would likely have produced an REE signature common to the four herbarium samples rather than one that is common to sampling location.

Some PHE are more enriched (e.g. Sb and Sn) in recent lichens supporting the emergence of these elements in the atmosphere as shown in peat bogs (Shotyk et al., 2002). Arsenic and Pb are nearly always more concentrated in the herbarium lichens as has been found in other herbarium-based studies using mosses and lichens (Purvis et al., 2007; Shotbolt et al., 2007).

4.2. Contributions of elements and comparison over time

4.2.1. Natural influences

Six of the PHE (Al, Co, Fe, Mn, Ti and V) and the REE group are strongly correlated over time (Figs. 2 and 4) and space (Fig. 4). This supports the results frequently found in other lichen studies (Bargagli et al., 2002; Basile et al., 2008; Szczepaniak and Biziuk, 2003). These elements are known to originate mainly from mineral weathering (Nriagu, 1989; Pacyna, 1986). These strong correlations confirm their common lithogenic origin, through the regional geochemical background. Conversely, the exclusion of Sn and Zn from this group in current data supports the idea of a new additional source supposed to be anthropogenic, whereas the natural (Fig. 4) but complex environmental behaviour of Mn (Pacyna, 1998; Pacyna and Pacyna, 2001) might explain why it is out of the lithogenic group in the dendrogram (Fig. 2).

Concerning REE (Fig. 5), their strong link to the lithogenic group (Table 4 and Fig. 2) is consistent with their natural origin. They are efficient tracers of the regional influence (similar profiles among the stations and a positive Gd anomaly on the whole). Nevertheless, the local lithogenic influence could be recorded in lichens as shown with the negative Eu anomaly in the granitic station of Hautpoul, an anomaly well-known for these bedrocks (Aubert et al., 2002; Weill and Drake, 1973). As a summary, the behaviour of those “natural” elements support the idea that lichens are very good indicators of dust originating from local weathering processes as well as from long-range atmospheric transport.

4.2.2. Anthropogenic sources and their comparison over time

Contrary to the lithogenic group, a second set of elements including As, Cd, Cu, Pb, Sb, Sn and Zn had a larger variability among the studied stations and over time. This might be related to mixed

natural and anthropogenic sources. In most cases: (i) the level of concentration allows classifying the stations from the most rural (Hautpoul) to the most urban (Albi); and (ii) the comparison of the enrichment across one century allows distinguishing a set of dominating contaminants of the last century (As, Cd or Pb) from the contemporary one (Cu, Sn or Sb).

The enrichment for As, Cd and Pb in the past (Fig. 4) was more prevalent close to the urban area (Albi, Fig. 3). The significant relationship between As/Al and S/Al (Fig. 3D) indicate a probable convergent origin for these elements. Indeed, sulphur emissions, currently in decline in Europe (Berge et al., 1999; Granier et al., 2011), resulted mainly from coal combustion (Manahan, 2009), as other elements such as As, Cd and Pb (Pacyna, 1987). This source of elements was also most likely in this study area, because of coal activities at the beginning of industrial development (coal mining and coal-fired power station in Carmaux, northeast of Albi).

The variable trend observed for Pb over time between the stations can be explained by the evolution of the different sources of Pb over one century.

The same enrichment observed for the three stations in the Albi area (average EF = 29) and the lowest enrichment in Hautpoul (EF = 8) in the past, indicate a more diffuse pollution around Albi. From the early twentieth century to the present, lead gasoline was significantly impacted upon the atmosphere composition (von Storch et al., 2003), but this contribution has decreased since lead gasoline was forbidden in 2000. The lower Pb enrichment observed in current lichens suggests that they indicate the rather recent atmospheric conditions, which appear to be less impacted than at the beginning of the last century. However, the highest enrichment observed in Albi can be related to the increasing anthropogenic activities. In Hautpoul, the unexpectedly high enrichment compared to the past can be explained by the proximity of a small car park. The correlation between Pb as well as Cu, Zn and REE (Table 4) indicates a certain affinity with atmospheric particles (Gandois et al., 2010; Gandois and Probst, 2012).

The Cd–Zn link, commonly found in the literature in various organisms (Brunialti and Frati, 2007; Gandois et al., 2010; Nimis et al., 2000), is also observed in the current data (Fig. 2). This behaviour might be explained by their physicochemical likenesses despite their distinct origin and biological affinity (Zn is an essential element whereas Cd has no known biological functions). In contrast with more recent times, this link was weaker in the past, probably due to two combined causes: (i) a global geochemical background of Cd explained by a more homogenous enrichment in the past (Fig. 4), and (ii) a weaker past anthropogenic pressure for Zn and thus a more important lithogenic contribution (Fig. 2B). In the past, the “sources” factor outweighs the “environmental behaviour” factor and thus severs the link between these two elements.

The emergence of some PHE in Albi – like Sb and Sn (Fig. 4) – seems to be related to a local influence. As mentioned by Wu and Biswas (1993), high temperatures promote volatile speciation of Sn. The non-correlation between Sn and REE indicated a non-particulate affinity for this element. This might support the idea of a high temperature process (such as waste incineration) as a Sn source. The enrichment observed for these PHE in the neighbouring stations (le Séquestre and Castelnau-de-Lévis) might be explained by the contamination influence of Albi under the prevailing wind. The context of a higher atmospheric dust content can explain the lower enrichment observed in the past for Sn (Figs. 3A and 4), as also confirmed by the strong relationship between Sn and other lithogenic elements during that period (Fig. 2B).

Lichens can therefore reliably trace the origin of contamination, from both current and historical samples, using geochemical tools, particularly to overcome the low number of herbarium samples and the large variability in concentration.

5. Conclusion

In this paper, metal concentrations registered in contemporary and historical lichens originating from the SW of France have been compared. Within one century, the chemistry of atmospheric deposition was modified by man-made activities. Despite the limited number of herbarium samples, historical data – supported by geochemical tools – indicated that the atmosphere was mainly impacted by coal combustion in the areas studied with As, Pb and Cd. Both local and long-range influences contributed to the past atmospheric environment, which was characterised by a higher dust content as shown by lithogenic elements such as Sn and REE. In contrast, present-day lichens indicated emerging contamination (like Sn, Sb, Pb and Cu) from long-range transboundary contamination and local anthropogenic activities (e.g. waste treatment, car traffic), which mainly impacted urban Albi and its surrounding countryside. As illustrated by REE, weathering of local bedrock influences the particulate deposition registered in lichens. In the study area, in addition to the long-range transboundary transport, the lichens have recorded a significant contribution of urban activities, which was particularly obvious in contemporary data.

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