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Characterisation and distribution of deposited trace elements transported over long and intermediate distances in north-eastern France using *Sphagnum* peatlands as a sentinel ecosystem

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HIGHLIGHTS

- First characterisation of long-range deposition using sphagnum peatlands in France.
- Cd, Zn, Pb and Cu are predominantly of anthropogenic origin.
- A new synthetic indicator describes the deposition of anthropogenic elements.
- Vosges and Alps are the most affected by anthropogenic deposition.

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ABSTRACT

Trace elements in the form of particulate matter can be transported downwind from their emission sources and may have negative effects on human health and ecosystems. The transport of trace elements is often studied by monitoring their accumulation in mosses. The aim of this study was to characterise and describe the distribution of deposited trace elements transported over long and intermediate distances in north-eastern France, a location far from the main emission sources. We analysed the trace element accumulation in *Sphagnum capillifolium* in 54 ombrotrophic peatlands distributed in six regions of France (Alps, Jura, Massif Central, Morvan, Rhône corridor and Vosges). The concentrations of Al, Cd, Cr, Cu, Fe, Pb, Ti, V, and Zn in the surface were determined in three replicate samples of *Sphagnum* within each peatland. The enrichment factors calculated using Ti as the element of reference clearly exhibited a predominant anthropogenic origin for Cd, Cu, Pb, and Zn, although the concentrations were relatively low compared to those found in other studies. The isolation of the peatlands from any fixed and traffic emission source suggests an intermediate and/or long-distance transport of the pollutants from their emission sources. The structure of the compositional dataset was explored using a covariance biplot. The first score was used as a synthetic indicator of the origin of the deposits and the degree of contamination of each peatland. This new index showed that the Vosges and the Alps were the regions most affected by high enrichment of trace elements, particularly Pb and Cd. The erosion of soils highly contaminated by former mining and smelting activities in the Vosges and the polluted cities and busy highways in the Alps may account for these distributions. The Jura was the least affected region sampled, and the other regions presented intermediate anthropogenic deposits. This study provides valuable information concerning the management and protection of these ecosystems.

1. Introduction

Atmospheric emissions of trace elements in the form of particulate matter in Europe originate primarily from housing and commercial properties (42% of total emissions), industrial

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processes (15%), road transport (14%), and agriculture (10%) (EEA, 2012). These emissions can be transported over long, intermediate, and short distances (defined as >100, 10–100, and <10 km, respectively; Zanetti, 1990) and can be deposited and then resuspended before their final deposition (NRC, 2009). The emissions of trace elements at the European scale have significantly decreased during the last twenty years due to international cooperation for the abatement of air pollution (Ilyin et al., 2013). However, deposition can still occur hundreds to thousands of kilometres downwind of the emission sources, impacting human health and the environment and biomagnifying carcinogenic and neurotoxic substances throughout the food chain (Harmens et al., 2008; Task Force on Health, 2007; Travnikov et al., 2012).

The transport of trace elements is often studied by examining their accumulation on biomonitors, such as mosses or lichens, located far from the emission sources (Harmens et al., 2010; Agnan et al., 2013). Bryophytes, particularly the ectohydric carpet-forming species *Sphagnum* and *Pseudoscleropodium purum*, have been widely used to monitor the atmospheric deposition of trace elements because they obtain most of their nutrients directly from precipitation and dry deposition, with little uptake from substrates (Holy et al., 2009b). Moreover, bryophytes provide a temporally integrated sink, which is useful in the case of low depositions. They are inexpensive to collect and enable higher sampling densities than conventional deposition measurements (Gusev et al., 2009). The studies on the long- and intermediate-range transport of trace elements at the European scale have usually used data from the European moss survey performed at five-year intervals since 1990 (Harmens et al., 2013, 2010, 2008; Ilyin et al., 2013; Schröder et al., 2010; Task Force on Health, 2007; Travnikov and Ilyin, 2005; Travnikov et al., 2012). This moss provides country-specific trace-metal depositions from sources within the same country or from other European countries, intercontinental transport, and wind resuspension (Ilyin et al., 2013; Travnikov and Ilyin, 2005).

Different moss species are often indistinctly used, making the comparison of results difficult. Indeed, trace-element concentrations vary according to a variety of moss species from a variety of ecosystems. In the European Heavy Metals in Mosses Surveys, the preliminary results from Gombert et al. (2004) indicated a significant difference in the accumulations of Cd, Ni, Pb, V, Cu and K between the two major species used. Bioaccumulation depends on several factors, such as species, canopy drip, distance to the nearest emission source, and altitude (Holy et al., 2009a, 2009b; Kleppin et al., 2008). Nevertheless, bioindication using bryophytes and monitoring using stations are complementary methods (Berg and Steinnes, 1997; Berg et al., 2003; Aboal et al., 2010).

Our study evaluated the long- and intermediate-range transport of trace elements by analysing the elemental concentrations in a single moss species, namely *Sphagnum capillifolium*, collected in northeastern France. *Sphagnum* peatlands are characterised by a set of relatively similar conditions (e.g., waterlogging, anoxic and acidic water, low nutrient contents, and low temperatures) (Rydin and Jeglum, 2006). Furthermore, ombrotrophic peatlands are usually used as a valuable and effective natural archive of atmospheric deposition (Bindler, 2006; De Vleeschouwer et al., 2007). Information on the deposition of trace elements over peatlands can thus be useful for studying the potential changes in the functioning of these sentinel ecosystems and consequently for achieving a better understanding of their ability to mitigate, adapt to, or contribute to climate change (Gorham, 1991; Lunt et al., 2010). Measuring the bioaccumulation of trace elements on living mosses is thus complementary to the conventional physicochemical techniques for acquiring depositional data. Measurements derived directly from living material are an appropriate tool for future studies of the effects of trace-element deposition on ecosystem functionality.

The specific objectives of this study were the following: 1) to characterise the deposition of trace elements in northeastern France by determining the concentrations of trace elements in *S. capillifolium* from isolated peatlands located at long to intermediate distances from potential sources of emission and the network of monitoring stations and 2) to describe the distribution of trace elements among the *Sphagnum*-dominated peatlands sampled in this study.

2. Materials and methods

2.1. Study sites and Sphagnum sampling

Fifty-four ombrotrophic peatlands in six mountain massifs of north-eastern France were selected according to their macroscopic lawns of *S. capillifolium*, an ectohydric species, the lack of a canopy drip in the centre of the peatland, and their distance to atmospheric pollution sources. The altitude of the peatlands varied from 200 m (in the Morvan) to 2035 m (in the Alps). Thirteen peatlands were sampled in the Vosges (altitude: 340 m – 1249 m), eight were sampled in the Jura (altitude: 340 m – 1303 m), five were sampled in the Morvan (altitude: 200 m – 710 m), seven were sampled in the Rhône Corridor (altitude: 770 m–1100 m), nine were sampled in the Alps (altitude: 885 m–2035 m), and twelve were sampled in the Massif Central (altitude: 850 m–1500 m) (Fig. 1). Note that peatland n°18 was considered part of the Morvan. Each peatland was far from any major fixed (industrial and urban) and traffic (highway) pollution sources. The sampled peatlands were on average 49 ± 31 km from any fixed pollution sources and 18 ± 10 km from any traffic sources.

Three peat cores of *S. capillifolium* (diameter 13.5 cm, height 6 cm) 1 m apart were collected in September 2010 from the centre of each peatland. Thirty capitula (0–3 cm) were randomly sampled from each core for the analysis of trace elements. The capitula were collected from the surface to a depth of 3 cm to ensure that the samples correspond to one year of growth (Gerdol et al., 1998; Moore, 1989) such that the concentrations of trace elements represented atmospheric depositions over the period of one year prior to September 2010.

2.2. Analyses of trace elements

The trace elements were analysed in partnership with QUALIO, a laboratory accredited by the French Ministry of Health (COFRAC No. 1-1499). Each moss sample was first dried and crushed in a clean agate mortar to yield a fine, homogeneous powder. A total of 500 mg of homogeneous powder was completely dissolved in a solution of concentrated suprapure HNO_3, HF, and HCl. Blank and certified reference materials (CRMs), namely NIST 1547 – peach leaves, BCR 482 – lichen, and NCS DC 73349, as well as bush branches and leaves were processed with each batch of samples. The solutions, which were appropriately diluted with Milli-Q water, were analysed for Al, Cd, Cr, Fe, Ti, V, and Zn using inductively coupled plasma optical emission spectrometry (ICP-OES) and for Pb and Cu using inductively coupled plasma mass spectrometry (ICP-MS) (Gaudry et al., 2008; Meyer et al., 2010). The concentrations in the blanks were low relative to the elemental compositions of the lichen, whereas the CRM concentrations did not differ from the certified values by more than 15% for all elements analysed when the concentrations were sufficiently higher than the limit of detection (Appendix 1).

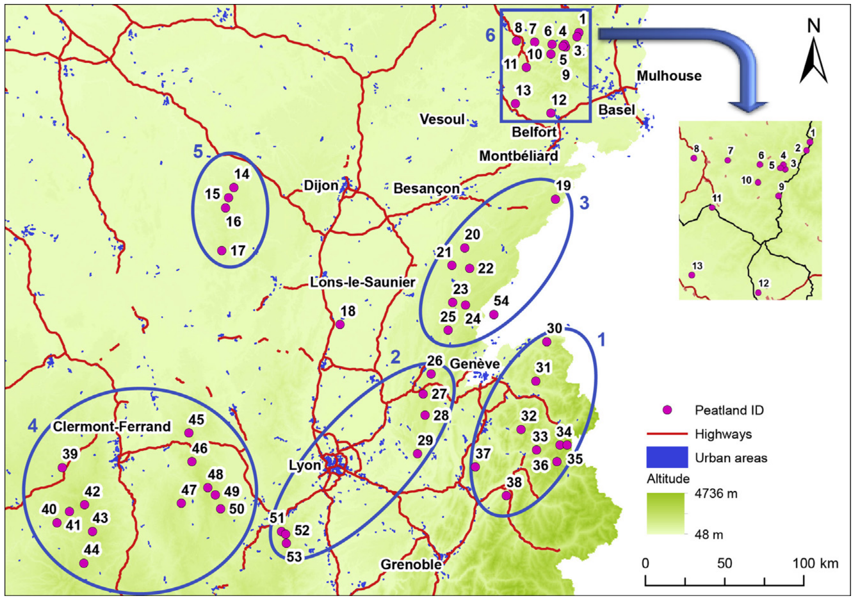

Fig. 1. Location of peatlands. The six regions are outlined in blue: 1) Alps: peatlands 30–38; 2) Rhône corridor: 26–29, 51–53; 3) Jura: 19–25, 54; 4) Massif Central: 39–50; 5) Morvan: 14–18; 6) Vosges: 1–13. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

2.3. Data analysis

Enrichment factors (EFs) were first computed to broadly assess the origins of the trace elements (i.e., natural, anthropogenic, or both). The EF is commonly defined as follows:

$$EF_X = (X/Ti)_{sample} \Big/ (X/Ti)_{ref}$$

where X is the concentration of element X normalised by the concentration of a representative element with no anthropogenic origin (in this case, titanium, Ti). The numerator is the within-sample concentration ratio, and the denominator is the concentration ratio of a material assumed to be unaffected by human activities (i.e., the geochemical background). As a first approximation, the upper continental crust was assumed to be representative of the local background material. Although the use of EFs has been severely criticised due to their intrinsic flaws, i.e., the elemental composition of uncontaminated rocks and soils cannot be considered uniform (Reimann and de Caritat, 2000), EFs lower than 2 generally indicate a substantially natural origin, EFs of 2–5 indicate a notable anthropogenic influence, EFs of 5–10 indicate a high enrichment, and EFs greater than 10 indicate a predominantly anthropogenic origin (Dragovic and Mihailovic, 2009; Zarazua-Ortega et al., 2013). It should be mentioned that, at the scale used in this study, contribution from soils cannot be considered homogeneous because the geological substrate greatly varies. The use of an average abundance for the upper continental crust obviously introduces some unavoidable approximations. Interestingly, in our case, the EFs calculated from the upper continental crust values reported by Wedepohl (1995) and by Krauskopf and Bird (1994) resulted in similar values. Moreover, our aim was only to use EFs to discriminate natural vs. anthropogenic contributions. In this sense, EFs greater than 10 cannot be considered as resulting from natural mineral matter inputs.

The structure of the compositional dataset was explored using a covariance biplot. The trace-element concentrations, $\mathbf{x} = [x_1, x_2, \ldots, x_D]$ for D variables, were first *clr*-transformed (centred log-ratio) to avoid spurious correlations generated by the intrinsically closed nature of the concentration data (Aitchison, 1986), as recommended by Van den Boogaart and Tolosana-Delgado (2013):

$$clr(\mathbf{x}) = \left[\ln\frac{x_1}{gm(\mathbf{x})}, \ln\frac{x_2}{gm(\mathbf{x})}, \ldots, \ln\frac{x_D}{gm(\mathbf{x})}\right]$$

where $gm(\mathbf{x})$ is the geometric mean of the parts: $gm(\mathbf{x}) = (x_1 \ldots x_D)^{1/D}$. Covariance biplots of compositional data represent the relationships among log-ratios of the variables (trace elements) and sites (peatlands) on the same plane (Borgheresi et al., 2013). Covariance biplots have properties that must be addressed for a correct interpretation (Aitchison and Greenacre, 2002; Van den Boogaart and Tolosana-Delgado, 2013): (i) the lengths of links (lines joining two arrowheads) are approximations of the standard deviation of the corresponding log-ratio, and (ii) the angle cosines between links estimate correlations between log-ratios (e.g., a link perpendicular to another indicates that log-ratios among the first set of variables have correlations near zero with the log-ratios among the second set). This modified version of the biplot for compositional data has the interesting feature of being equivalent to the analysis of all pairwise log-ratios (Daunis-i-Estadella et al., 2011). Such a ratioing approach produces results relatively close to those derived from EF calculations. An analysis of variance (ANOVA) was then used to identify possible differences between regions of scores from Component 1 used as a synthetic index of the degree of contamination. A Tukey's pairwise comparison was used to identify significant differences between each pair of geographical areas. Multivariate analyses of variance (MANOVAs) for comparing the multivariate population means of the regional groups could not be performed on the *clr*-transformed data because the covariance matrix was not invertible; thus, we applied an isometric log-ratio (*ilr*) transformation developed by Egozcue et al. (2003):

$$ilr(\mathbf{x}) = \mathbf{z} = [z_1, \ldots, z_{D-1}] \in \mathbb{R}^{D-1},\ zi = \sqrt{\frac{i}{i+1}} \ln\frac{\sqrt[i]{\prod_{j=1}^{i} x_j}}{x_{i+1}},$$

for $i = 1, \ldots, D-1$

MANOVAs, and possibly post-hoc Hotelling's T^2 tests, can then be straightforwardly applied to the *ilr*-coordinates because the covariance matrix of the *ilr*-transformed dataset is not singular (Kovacs et al., 2006). A Bonferroni correction was applied for multiple test designs to maintain the familywise error.

All of the data treatments and statistical procedures were performed using the compositions, FactoMineR, and Hotelling packages of R (R Development Core Team, 2008; http://www.r-project.org/).

3. Results

3.1. Characterisation of atmospheric deposits

First, there is no statistically significant correlation between altitude and the concentrations of trace elements accumulated by *S. capillifolium*. Nevertheless, the concentrations of trace elements varied among the regions (Appendix 2). The peatlands with the highest concentrations of Pb and Cd were along the eastern border of France (Fig. 2), and the peatlands in the Massif Central exhibited the highest Cu concentrations (Fig. 2).

Second, the trace elements measured in *S. capillifolium* had different origins. Al, Fe, and V had EFs of 0.63 ± 0.09, 1.04 ± 0.38, and 1.90 ± 0.43, respectively, indicating natural origins. Cr was notably enriched, with an EF of 3.48 ± 2.85. Cd, Pb (both of which are considered toxic to plants), Cu and Zn (both of which are considered biologically essential for plants) had EFs of 176.4 ± 108.8, 38.5 ± 23.6, 38.2 ± 17 and 72.3 ± 40.8, respectively, indicating a predominant enrichment by anthropogenic sources (Fig. 3). The EFs of the elements enriched by anthropogenic sources were usually higher in the Morvan and the Vosges, whereas the EFs for the elements in the Jura tended to exhibit the lowest values.

3.2. Distribution of atmospheric deposition in northeastern France

The MANOVA of all trace elements indicated that at least one region is significantly different from the others (Wilks's $\lambda = 0.455$, $F = 6.73$, $P < 0.001$). The two-sample Hotelling's T^2 (H-T^2) test

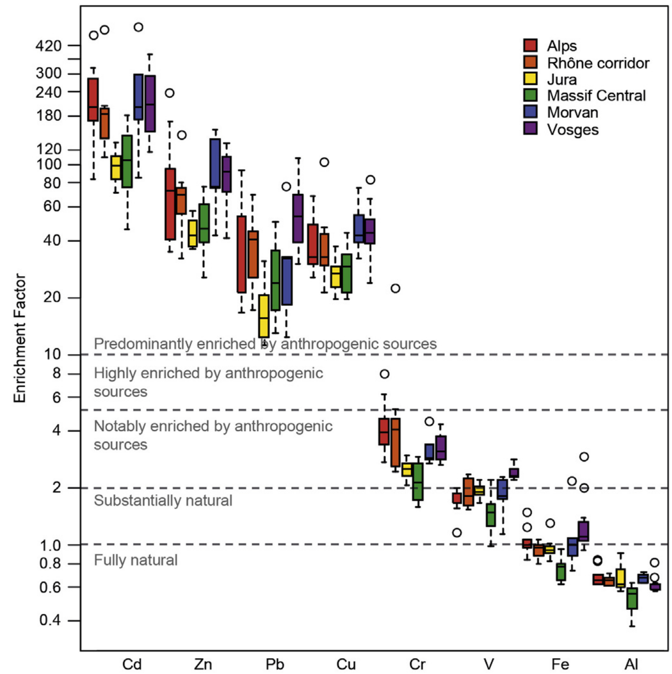

Fig. 3. Boxplot of enrichment factors for each region and trace element using Ti as a reference element (Wedepohl, 1995).

identified significant differences between the Vosges and the Jura, Massif Central, Morvan, and the Alps, and the Massif Central differed significantly from the Rhône corridor and the Alps (Table 1).

The dataset was then represented in a covariance biplot (Fig. 4). Components 1 and 2 explained 54.6 and 19.2% of the variance, respectively, i.e., a total of 73.8% for a 2D representation. Variables

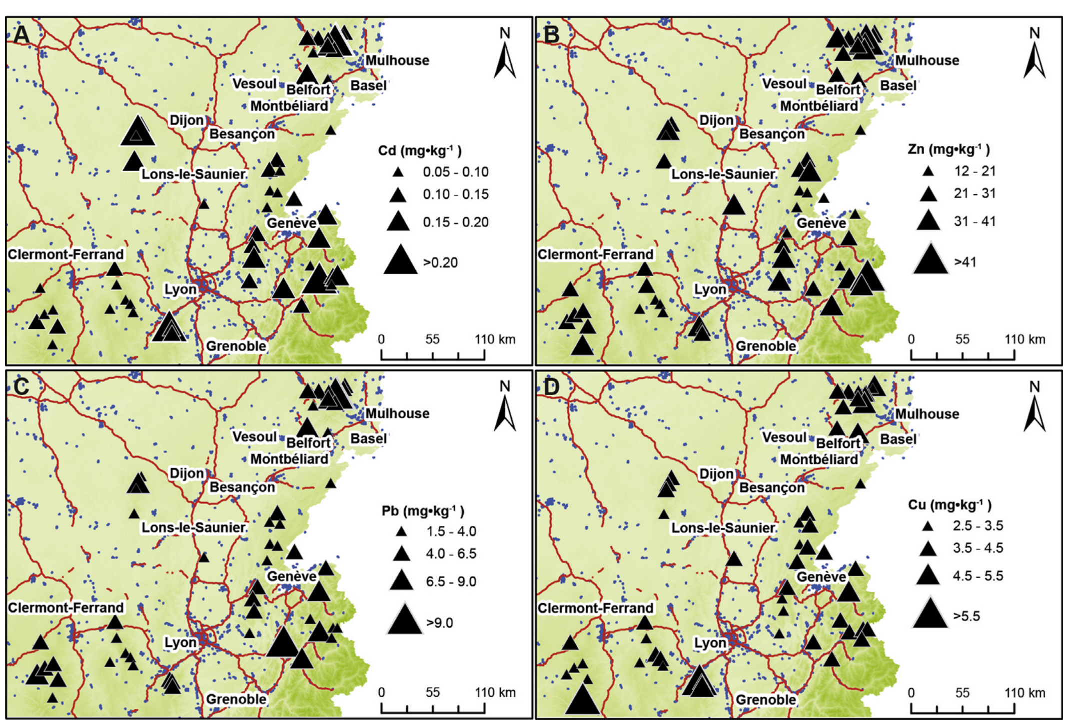

Fig. 2. Concentrations (mg kg^{-1} of dry moss) of the highly enriched trace elements in each peatland: A) Cd, B) Zn, C) Pb, and D) Cu.

concerning the trace elements highly enriched by anthropogenic sources (Pb and Cd) were represented on the negative (left) side of Component 1, and variables concerning the trace elements with predominantly natural origins (Al, Fe, Ti, and V) were represented on the positive (right) side of Component 1 (Fig. 4). The essential elements (i.e., Zn and Cu) acted positively on Component 2, whereas Pb, to a lesser extent, exerted a negative effect on this axis. The log-ratios of Pb/Al and Pb/Ti had the highest standard deviations, as indicated by the lengths of their links (Fig. 4). The peatlands could thus be mainly differentiated in the biplot by the enrichment of Pb relative to Al or Ti. In contrast, the short links for the lithogenic elements Al, Ti, Fe, and V indicated subcompositions of low variance (Fig. 4). Component 1 of the covariance biplot had the highest multiplicative contribution to the Pb/Al, Cd/Al, Pb/Ti, and Cd/Ti log-ratios. The biplot thus allowed the separation of two groups based on the log-ratios of Pb/Al and Cd/Al: sites from the Vosges had higher log-ratios (orthogonal projections on the left side of the Pb—Al and Cd—Al links) than sites from the Jura (orthogonal projections on the right side of the Pb—Al link), whereas the sites from all other regions had highly variable log-ratios (Fig. 4). The ANOVA results suggested that at least one region differed from another ($p = 0.003$) in terms of scores for Component 1. The Tukey's pairwise comparison identified significant differences between the Jura and the Alps, the Rhône corridor, and the Vosges ($p < 0.05$). The scores for Component 1 thus located each peatland along virtual axes, mainly represented by the log-ratios of Pb/Al, Cd/Al, Pb/Ti, and Cd/Ti, i.e., the trace elements of anthropogenic origin. The second component, dominated by Zn and Cu, is probably less informative, although the EFs calculated for these metals clearly indicate a dominant anthropogenic contribution. Zn and Cu are essential nutrients for plants, which recycle them into the root zone. This phenomenon is well known for these metals in peat sequences. It induces metal translocation, and hence generally precludes the reconstruction of past atmospheric deposition (Monna et al., 2004), except in cases with strong pollution (Mighall et al., 2002, Kempter and Frenzel, 2000). Fig. 5 shows the scores for Component 1 for each site, and lower scores (negative) correspond to higher log-ratios of Pb/Al, Cd/Al, Pb/Ti, and Cd/Ti, indicating highly polluted sites.

4. Discussion

The objective of this study was to determine the origin (anthropogenic or natural) and distribution of trace elements

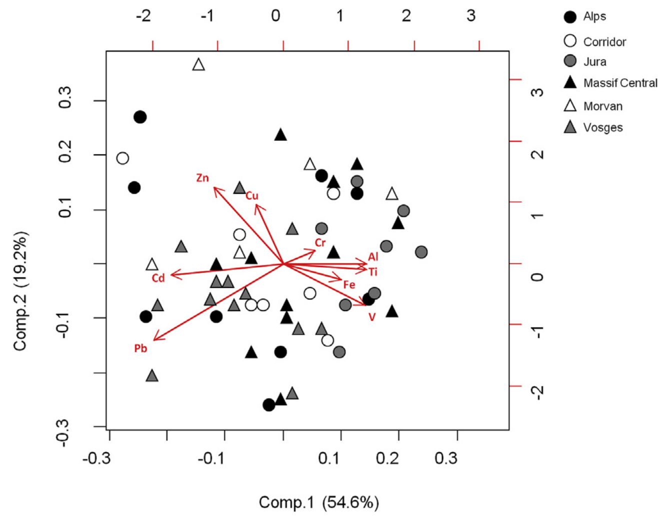

Fig. 4. Covariance biplot (axes 1 and 2) of the peatlands and trace elements concentrations in *S. capillifolium*.

deposited in areas distant from fixed and mobile pollution sources in northeastern France using peatlands as sentinel ecosystems. The concentrations of trace elements accumulated by *S. capillifolium* were generally quite low but slightly higher than the upper concentrations found in various *Sphagnum* species from several supposedly clean ombrotrophic peatlands in northern Finland ($Cu < 3.1$, $Fe < 113$, and $Zn < 20$ mg kg^{-1}; Pakarinen, 1978). Very few studies have reported the concentrations of trace elements in rural areas; thus, comparing our results to those of other studies using *Sphagnum* is difficult. Our concentrations are lower than those found in other *Sphagnum* species in areas under anthropogenic influence. For example, Wojtun et al. (2013) found higher concentrations of Cd (0.3 mg kg^{-1}), Zn (45 mg kg^{-1}), Pb (14 mg kg^{-1}), and Cu (4.7 mg kg^{-1}) in Polish peatlands under the influence of the former Black triangle, the area along the borders of Poland, Germany, and the Czech Republic, which is considered one of the most heavily polluted areas in Europe since the middle of the 20th century (Kucharczak and Moryl, 2010). This study, however, evaluated the trace-element concentrations in other species of *Sphagnum*. The European Heavy Metals in Mosses Surveys, which focused on the long-range transport of pollutants, used five terrestrial species of bryophytes as biomonitors to study the spatiotemporal pattern of heavy-metal deposition in forested areas of France (Gombert et al., 2004; Holy et al., 2009a). The trace-element concentrations in our study indicated that the French peatlands presented in this work presented lower concentrations than the mosses in the French forested areas studied by the European Heavy Metals in Mosses Surveys (Gombert et al., 2004). These differences could be explained by the species effect and by the distance of the sites from the pollution sources. Indeed, all of our sampling sites were located far from traffic sources (18 ± 10 km), whereas some of the sites in the European programme were closer to this type of sources (Gombert et al., 2004).

Even though the peatlands were distant from the pollution sources, the EFs indicated a clear anthropogenic origin of Cd, Zn, Pb, and Cu. The average distances of 49 and 18 km from fixed and mobile emission sources, respectively, suggested that these elements had been transported intermediate and long distances from their sources. Gombert et al. (2004) reported similar findings for Pb, Cd, Cu, and Zn ($EF > 20$) and for Cr and Fe ($EF < 5$), and the EFs for French mosses in forested areas suggested highly probable anthropogenic sources for Pb, Cd, Cu, and Zn originating from

Table 1
Hotelling's T^2 (H-T^2) test, degrees of freedom (*df*), *p*-value, and Bonferroni correction for each pair of regions for all analysed trace elements. Asterisks indicate significant differences between pairs of regions based on the sequential Bonferroni correction *p*-value.

Region	H-T^2	*df*	*p*	Bonferroni correction
Vosges-Morvan	14.217	9	0.000002*	0.0036
M. Central-Vosges	10.309	16	0.00001*	0.0033
Vosges-Jura	10.966	12	0.0001*	0.0038
Vosges-Alps	6.758	13	0.0010*	0.0042
M. Central-Rhône	7.569	10	0.0020*	0.0045
M. Central-Alps	5.682	12	0.0035*	0.0050
Jura-M. Central	4.486	11	0.0093	0.0056
M. Central-Morvan	4.603	8	0.0223	0.0063
Vosges-Rhône	3.334	11	0.0273	0.0071
Jura-Alps	2.210	8	0.1323	0.0083
Jura-Rhône	1.808	6	0.2508	0.0100
Jura-Morvan	1.753	4	0.3114	0.0125
Morvan-Alps	1.133	5	0.4609	0.0167
Morvan-Rhône	1.289	3	0.4827	0.0250
Rhône-Alps	0.567	7	0.7797	0.0500

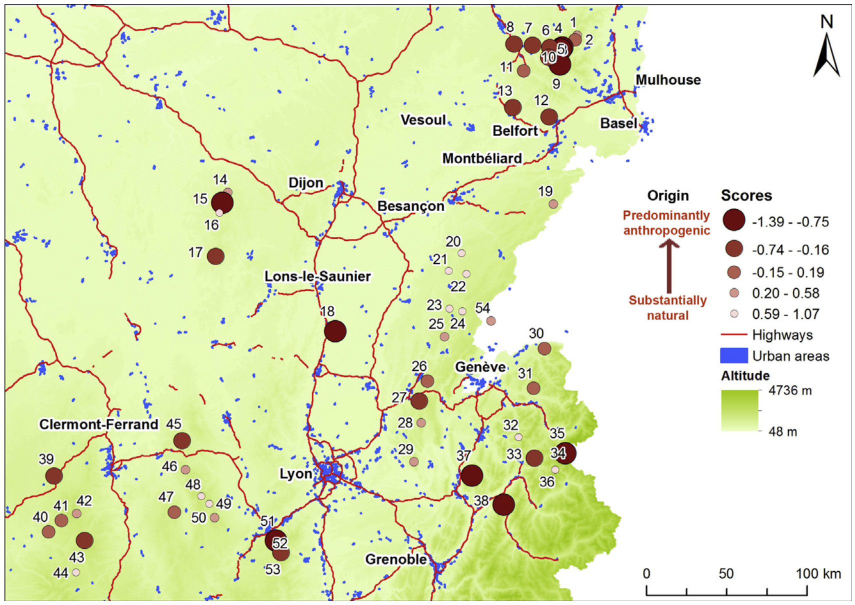

Fig. 5. Scores of Component 1 of the biplot (synthetic index of contamination) for each peatland.

industrialised and urbanised areas and a lithogenic origin for Cr and Fe. Similar findings have also been reported for Cd, Zn, Pb, and Cu in two species of lichens from five sites in France located far from any local sources of contamination (Agnan et al., 2013). The elevated EFs reported by Agnan et al. (2013), which are comparable to those obtained in our study, indicate a high pressure from anthropogenic sources. In contrast, our EFs for V, Al, and Fe, which also comparable to those obtained in other studies, showed a clear lithogenic origin for these elements. The EFs for the Morvan and Vosges were generally higher than those found in other areas for trace elements of anthropogenic origin, likely due to lower concentrations of Ti, particularly in the Morvan, combined with higher concentrations of the anthropogenic elements in the Vosges.

The evaluation of the accumulation of trace elements in the 54 peatlands sampled in the present study also enabled us to identify a pattern of atmospheric depositions in north-eastern France. Minor but proximal sources, as well as other factors, such as rainfall or exposition, which are difficult to estimate, may lead to notable intra-regional variability. Despite these uncertainties and the low concentrations measured, it should be noticed that Fig. 5, which summarizes the pollution indices, exhibits a robust geographical structuration and significant inter-regional differences. Peatlands from the Vosges were significantly different from those in the Massif Central and the Jura, as demonstrated by the log-ratio of Pb and Cd versus Al and Ti. Very high concentrations of anthropogenic Pb were also found by Forel et al. (2010) in the subsurfaces of peatlands in the Vosges (>200 mg kg^{-1}) several kilometres from the former emission sources. Metal production in the Vosges Massif has been documented since the 10th century (Fluck, 2000), with intensive prospecting and mining particularly during the 15th and 16th centuries (Fluck and Weil, 1975). Mining operations in the Vosges finally ended in the mid-20th century, but the millennium of mining activity has introduced large amounts of Pb near the mines (Forel et al., 2010). The high concentrations of Pb in the Vosges could not only be due to the aeolian erosion of contaminated soils at the regional level but also to a possible cross-border transport of Pb from Germany (Harmens et al., 2008). In contrast, the peatlands in the Jura presented the lowest log-ratios for Pb and Cd versus Al and Ti, which differed significantly from those found in the Alps. The differences between these two regions could be due to a combined effect of the different distances to main transportation routes and industrialised areas, the amount of pollution emitted by these sources, and the frequency and speed of dominant winds from the emission sources. The peatlands in the Alps may be influenced by usually highly polluted cities, such as Grenoble, where winds from the southern part of the valley strongly interfere with the up-valley wind pushing the polluted air mass upward (Chemel and Chaxel, 2007), whereas peatlands in the Jura are generally farther from the main transportation routes and large cities. Similar results have been reported for the multi-metal index used to integrate data of metal bioaccumulation in mosses from all of France (Holy et al., 2009a). Holy et al. (2009a) found that Lorraine, Alsace (both of which are bordered by the Vosges), the Rhône valley, and the French Alps were the most contaminated regions in the country.

The MANOVA of trace elements indicated significant differences among the regions investigated in this study. These differences, though, were not the same as those identified by the biplot because they were mainly due to the different lithogenic compositions of each region. The differences between the Massif Central and the other regions may be due to the predominantly volcanic nature of the geological substratum of this region.

The biplot Component 1 score for each peatland (Fig. 5) can be used as a synthetic indicator of the origin of the deposits and the degree of contamination of each peatland. Various methods have been applied for the calculation of multi-element indices (Grodzińvska, 1978; Grodzińska et al., 1999; Holy et al., 2009a), either using the mean concentrations of accumulated elements in bryophytes or using rank numbers derived from the 10th percentiles of the measurements for each element (multi-metal index computation). Schroeder and Pesch (2007) used a complex index based on the bioaccumulation of metals (calculated using the geostatistics and percentiles from monitoring data) and ecoregionalisation in Germany (based on 21 geographical categories). Our synthetic indicator is easier to obtain and use than the index developed by Schroeder and Pesch (2007) for the management and protection of natural environments because it does not require information on environmental parameters (e.g., soil texture, precipitation, and evaporation) to define ecoregions. It only uses the concentrations of the accumulated trace elements in a statistical treatment designed especially for compositional data. Moreover, the specificity of the regions defined by Schroeder and Pesch (2007) hinders the comparisons of results from different countries.

Our indicator shows that the Alps and the Vosges are the most contaminated regions, whereas the Rhône corridor and the Massif Central are moderately affected. These findings agree with those reported by Holy et al. (2009a) for the Alps and the Vosges but not for the Jura and the Massif Central, which had high multi-metal indices even though these regions are among the least industrialised in France. Our results differ because our index (score 1) is not only based on the concentration of anthropogenic deposits but also on the compositional structure of the data.

5. Conclusions

To the best of our knowledge, this study provides the first examination of the deposition of trace elements in peatlands located far from pollution sources in France. The peatland ecosystem could be used as a sentinel ecosystem. The observed contaminant concentrations were low but could be used to determine the origin of the deposits (natural or anthropogenic) and the distribution of the trace elements. The Vosges peatlands were the most contaminated by elements of anthropogenic origin, whereas those in the Jura were the least contaminated. Our data provide valuable information for improving the management and protection of these ecosystems of paramount importance. These peatlands are sensitive to climate change, and this sensitivity can be easily modified by the presence of atmospheric contaminants (Barnard et al., 2005; Smith, 1997). Our data can also be incorporated into models of atmospheric pollutant dispersion and provide new values for constraining elemental deposition over a large scale. This study can also become a key element for the evaluation of policies undertaken to reduce pollutant emissions. Further studies should be planned to enrich the database of other types of atmospheric contaminants, such as polycyclic aromatic hydrocarbons, and to monitor these deposits in peatlands on an annual basis.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.atmosenv.2014.11.041.

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