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Spatial analysis of trace elements in a moss bio-monitoring data over France by accounting for source, protocol and environmental parameters

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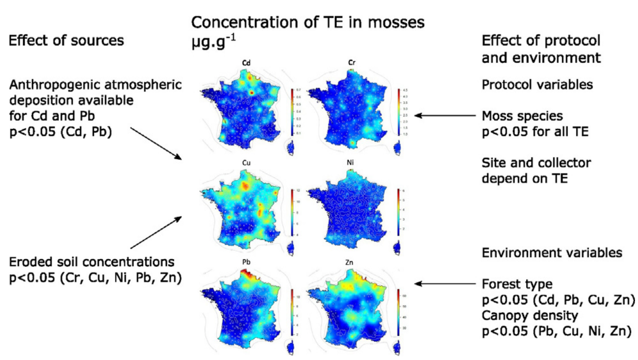
HIGHLIGHTS

- Trace elements (TE) in mosses proxy atmospheric deposition of anthropogenic origin.
- Atmospheric deposition also includes a terrestrial fraction from soil erosion.
- We studied how these sources and other parameters affected TE in mosses.
- Anthropogenic and eroded soil deposition contributed to TE in mosses.
- Moss species and the type of forest also affected TE in mosses.

GRAPHICAL ABSTRACT



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ABSTRACT

Air pollution in trace elements (TE) remains a concern for public health in Europe. For this reasons, networks of air pollution concentrations or exposure are deployed, including a moss bio-monitoring programme in Europe. Spatial determinants of TE concentrations in mosses remain unclear. In this study, the French dataset of TE in mosses is analyzed by spatial autoregressive model to account for spatial structure of the data and several variables proven or suspected to affect TE concentrations in mosses. Such variables include source (atmospheric deposition and soil concentrations), protocol (sampling month, collector, and moss species), and environment (forest type and canopy density, distance to the coast or the highway, and elevation). Modeled atmospheric deposition was only available for Cd and Pb and was one of the main explanatory variables of the concentrations in mosses. Predicted soil content was also an important explanatory variable except for Cr, Ni, and Zn. However, the moss species was the main factor for all the studied TE. The other environmental variables affected differently the TE. In particular, the forest type and canopy density were important in most cases. These results stress the need for further research on the effect of the moss species on the capture and retention of TE, as well as for accounting for several variables and the spatial structure of the data in statistical analyses.

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1. Introduction

Air pollution has been a public health and environmental concern handled by European authorities for decades, by implementing legislation and mitigation strategies, for example with the Directive on Ambient Air Quality and Cleaner Air for Europe (Directive 2008/50/EC). Among atmospheric pollutants, some trace elements (TE), such as As, Cd, Cr, Ni, are particularly carcinogenic according to the International Agency for Research on Cancer (Straif et al., 2009), and Pb is a general toxic especially for children and also for the environment (Buekers et al., 2009; International Agency for Research on Cancer, 2004; Jakubowski, 2011; Pourrut et al., 2011). Atmospheric thresholds have been established for some TE to prevent health outcomes in Europe. However atmospheric TE remain very delicate and expensive to measure on a fine grid at national scales. To make up for the scarcity of measurements, modeling of TE atmospheric deposition and bio-monitoring of TE are now broadly used (Szczepaniak and Biziuk, 2003; Travnikov and Ilyn, 2005). With respect to TEs, bio-monitoring is a technique aiming at providing data on the exposure of organisms or parts thereof to air pollution by measuring their TE content. Mosses are particularly suited for bio-monitoring (Markert et al., 2003). Moss bio-monitoring cannot substitute classical measurements of atmospheric concentrations or deposition, yet its main advantages are the relatively moderate cost by sample and the possibility to sample moss theoretically everywhere in terrestrial ecosystems.

In Europe, the ICP-Vegetation (International Cooperative Programme on Effects of Air Pollution on Natural Vegetation and Crops) under the UNECE framework has managed moss bio-monitoring surveys from several countries since the 1990s (one survey every 4–5 years). Major findings involve adequacy between atmospheric deposition of Cd and Pb with concentrations in mosses (Harmens et al., 2012; Schröder et al., 2010) and assessments of temporal trends over Europe (Harmens et al., 2015). Recently, the question of the uncertainties of the values due to the protocol sampling as well as the environmental conditions was raised (Dołęgowska and Migaszewski, 2015). Indeed, mosses are living organisms, so their physiology varies with their environment. In addition, many features of the bio-monitoring protocol were found to induce variability in the biomonitoring data (Fernández et al., 2015), and a recent attempt was made to quantify the uncertainty associated with the protocol used by the ICP-Vegetation in the case of France (Lequy et al., 2016). This stresses the need to account for such variables in the statistical analyses. Previous attempts were made by other studies to analyze the possible determinants of the Cd, Hg, and Pb concentrations in mosses, at the European or national scale, generally by using CART-trees (Holy et al., 2010; Schröder et al., 2010). The authors found out that the main predictor of Cd and Pb in mosses was indeed atmospheric deposition, and, for Pb, another main predictor was the distance to the nearest Pb source. On the other hand, they did not found that the tested environmental conditions were important predictors. Yet it is of primary importance to carefully evaluate which and to what extent environmental parameters affect TE concentrations in mosses. This would facilitate interpreting moss bio-monitoring data, especially when pooling data from different countries that show contrasted environments, as encountered between Northern/Southern or Eastern/Western Europe.

Atmospheric deposition of TE has not only direct anthropogenic sources such as industrial and traffic emissions, but more natural sources, such as wind erosion of soil, which can also be contaminated by TE (Nriagu and Pacyna, 1988). Besides, some environmental parameters can be of major importance for moss physiology, such as the forest type, the edaphic conditions, the elevation and many more parameters that have never been tested over France.

The objectives of this paper are to highlight (i) the effect of several variables (source, protocol features and environmental parameters), and (ii) the relative importance of these variables on the TE concentrations in mosses over France. To do so, spatial models will be used to take into account the spatial structure of TE concentrations in mosses and provide information about the role of each variable on moss concentrations.

2. Material and methods

2.1. The TE data

The French contribution to ICP-Vegetation is the BRAMM programme (Bio-monitoring of TE atmospheric deposition by mosses). The data used in the present article consists of the 2011 survey of BRAMM, which was described by Lequy et al. (2016). Briefly, 449 sites homogeneously distributed over France, including sites on Corsica Island, were collected (Fig. 1). Five moss species were sampled, *Hylocomium splendens* (Hedw.) Schimp., *Hypnum cupressiforme* Hedw., *Pseudoscleropodium purum* (Hedw.) M. Fleisch., *Pleurozium schreberi* (Brid.) Mitt., and *Thuidium tamariscinum* (Hedw.) Schimp., respectively, and are referred to as Hs, Hc, Pp,Ps, and Tt hereafter. The specificity of BRAMM is a sampling in exclusively afforested areas in the 2011 survey. Indeed, the 5 moss species recommended by ICP-Vegetation are typically mosses that thrive at best in forest ecosystems. For this reason, collecting them in another ecosystem may affect their physiology and TE content. Samples were analyzed by ICP-MS at the INRA-USRAVE laboratory, Bordeaux, France. The TE analyzed in this study are Cd, Cr, Cu, Ni, Pb, and Zn.

2.2. The covariates of the statistical model

2.2.1. Protocol variables

In addition to TE concentration for each sampling site, various metadata were included in the database: protocol information (sampling month, collector, and collected moss species) and environmental parameters (forest type, canopy density, altitude, distance to the sea, and distance to major highway).

Forest type included conifer, mixed, and broad-leaved forests. The sampling months consisted in the three sampling months May, June, and July. Seven collectors distributed over France had sampled mosses in 2011. Canopy density was visually estimated by collectors to fit in classes (5–15%, 15–25%, 25–50%, 50–75%, and 75–100%). This data was converted to a numeric vector (0.08, 0.18, 0.38, 0.63, and 0.88) to test the effect of an increasing canopy density on TE concentrations. Elevation was measured by altimeter. Distance to the sea was computed by GIS software and converted into a two-factor variable: a threshold distance of 40 km was set and sites closer and further to the sea were converted into a two-class <40 km or >40 km factor. Distance to the closest highway was also computed by GIS and treated as numeric to test the effect of an increasing distance from highways.

2.2.2. Predicted soil concentrations

To assess the effect of eroded soil as a possible source of TE in mosses, the concentrations of six TE (Cd, Cr, Cu, Ni, Pb, and Zn) in the top agricultural soil were estimated, at the location of the moss sampling sites to proxy erosion of local agricultural soil, using a geostatistical model based on to the results of the French soil monitoring network (Saby et al., 2011). For this, the geological and continuous spatial variations are described, respectively, by the fixed and random effects of a linear mixed model (LMM). A robust algorithm was used to account for local anomalies that lead to observations which are spatial outliers with respect to the LMM. Trace metal content measurements from total and partial extraction with Ethylenediaminetetraacetic acid (EDTA) were used because they can bring different insights in TE spatial distribution and origin (Saby et al., 2009).

2.2.3. Modeled atmospheric deposition

Atmospheric deposition of Cd and Pb were provided by MSC-E of EMEP (Co-operative Programme for Monitoring and Evaluation of Long-range Transmission of Air Pollutants in Europe). Deposition fluxes of these metals over territory of France were simulated with spatial resolution 50×50 km^2 using chemical transport model MSCE_HM (Travnikov and Ilyin, 2009; Travnikov and Ilyn, 2005). It is a regional-

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