

# Spatial analysis of metal bioaccumulation in France

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**Abstract.** The European Heavy Metals in Mosses Surveys are performed every five years since 1990. The goal of these surveys is to map the metal and, since 2005, nitrogen concentration in ectohydric mosses throughout Europe. The aim of this study is to present the results of the spatial analyses of metal bioaccumulation data from 536 monitoring sites in France in 2006. In a first step the concentrations of ten metal elements were analysed by means of variogram analysis. Low but existing spatial autocorrelation could be detected, so that raster maps could be produced with help of different kriging procedures. Applying percentile statistics, the kriging estimations were then aggregated to a multi-metal index enabling to comprehensively assess the spatial patterns of the metal bioaccumulation in France. Principal component analysis was furthermore used to derive one component primarily representative for As, Cr, Fe, Ni and V. One other factor shows high correlations to Cd, Cu, Hg, Pb and Zn. Both indices reflect assumed spatial patterns of metal concentrations in background areas throughout France. Nevertheless, the metal accumulation in the mosses is also influenced by local and empirical phenomena as proven by decision tree analysis. Exemplified for Pb it can be shown that next to modelled depositions and urbanisation different moss species can be assumed to have a considerable impact on the metal bioaccumulation.

## 1 BACKGROUND AND AIM

The UNECE Heavy Metals in Mosses Surveys were performed every five years since 1990 in at least 21 European countries. The goal of these surveys is to map the metal and, since 2005, nitrogen concentration in ectohydric mosses throughout Europe (Harmens et al. 2006). In France, the moss survey was conducted 1995 and 2000 (Gombert et al. 2005) and for the third time in 2006. Here, 536 monitoring sites were sampled across the whole French territory (Leblond and Rausch de Traubenberg 2006). The aim of the presented study was to give an integrative overview of the metal bioaccumulation for the entire French territory without geographical gaps. This was to be done by a combination of geostatistical methods as well as multivariate statistics to map the metal accumulation as a whole throughout France. Furthermore, confounding factors of the metal concentration in mosses were to be investigated by means of additional geodata, metadata and decision tree models.

## 2 MATERIAL AND METHODS

Element loads of arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), iron (Fe), mercury (Hg), nickel (Ni), lead (Pb), vanadium (V) and zinc (Zn) measured in the French campaign 2006 were mapped in a 2.5 x 2.5 km<sup>2</sup> raster using variogram analyses and different kriging procedures. At first experimental variograms were calculated using variogram maps (Johnston et al. 2001). Variogram models then were fitted to the experimental variograms and used as the basis for mapping the element loads throughout France. Since all elements showed left skewed distributions they were transformed lognormally preceding the geostatistical analyses. Furthermore, polynomial trend surfaces were calculated and subtracted from the measurement values to account for spatially varying means of the random functions. Kriging was then carried out with the residuals and the residual maps were added to the polynomial maps to derive the surface maps for each of the elements.

The ten surface maps were aggregated in terms of two multi metal indices enabling to describe the overall metal accumulation in mosses throughout France:

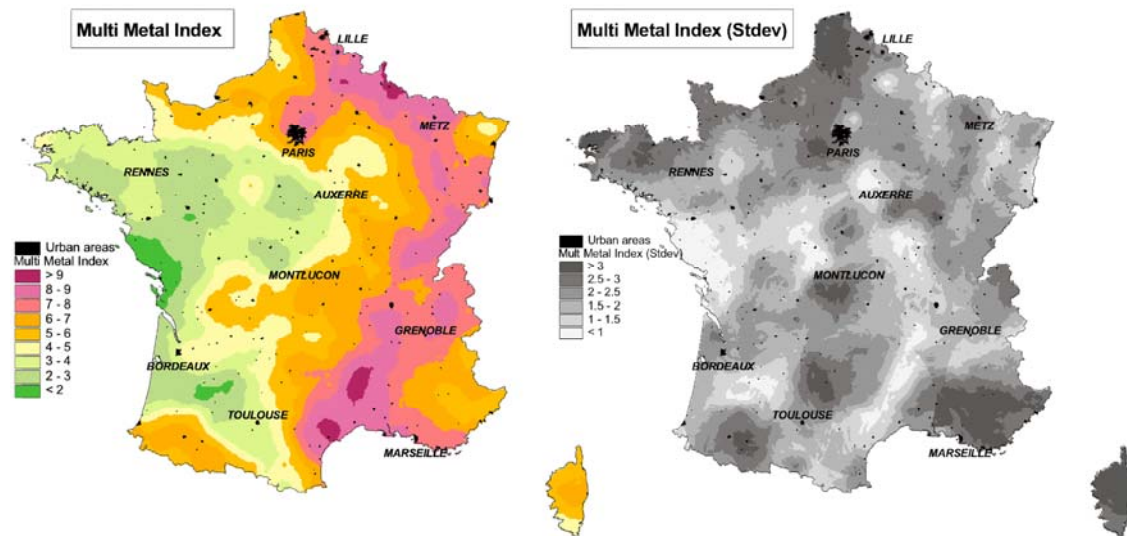
- The first index was first introduced in the German moss surveys and represents the mean rank of each raster cell regarding all elements referred to (Pesch & Schröder 2006). The index reaches from 1 (for low bioaccumulation) and 10 (for high bioaccumulation) and was calculated over all ten element estimations.
- The second index was derived with help of principal component analysis (PCA) where two factors could be derived from the estimated grid values. The first one is strongly correlated with the estimated element loads of As, Cr, Fe, Ni and V (Pearson correlation coefficient > 0.5) explaining 55.2 % of the overall variance. The second one accounts for another 23.7 % of the explained variance and is primarily correlated to Cd, Cu, Hg, Pb and Zn (Pearson correlation coefficient > 0.5).

To statistically evaluate the metal loads in the mosses the decision tree model Classification and Regression Trees (CART – Breiman et al. 1984) was applied. Decision tree models are used to identify latent structures in datasets consisting of large numbers of objects that are described by a multitude of variables with different scale dignities. They aim at computing an explanation or prediction model for a variable of interest (the target, response or dependent variable – here the element loads in the mosses) from a given set of variables assumed to have an influence on this variable (predictor or independent variables – here site specific metadata on e.g. moss specific criteria and available geodata on modelled depositions, land use,

altitude and precipitation). The algorithms thereby rely on the consecutive segmentation of the entire data set (root node) into subclasses or sub-nodes. CART subdivides the sample by selecting that predictor with the highest increase of homogeneity (improvement) of the response variable.

### 3 RESULTS

Figure 1: Mult metal index map for France

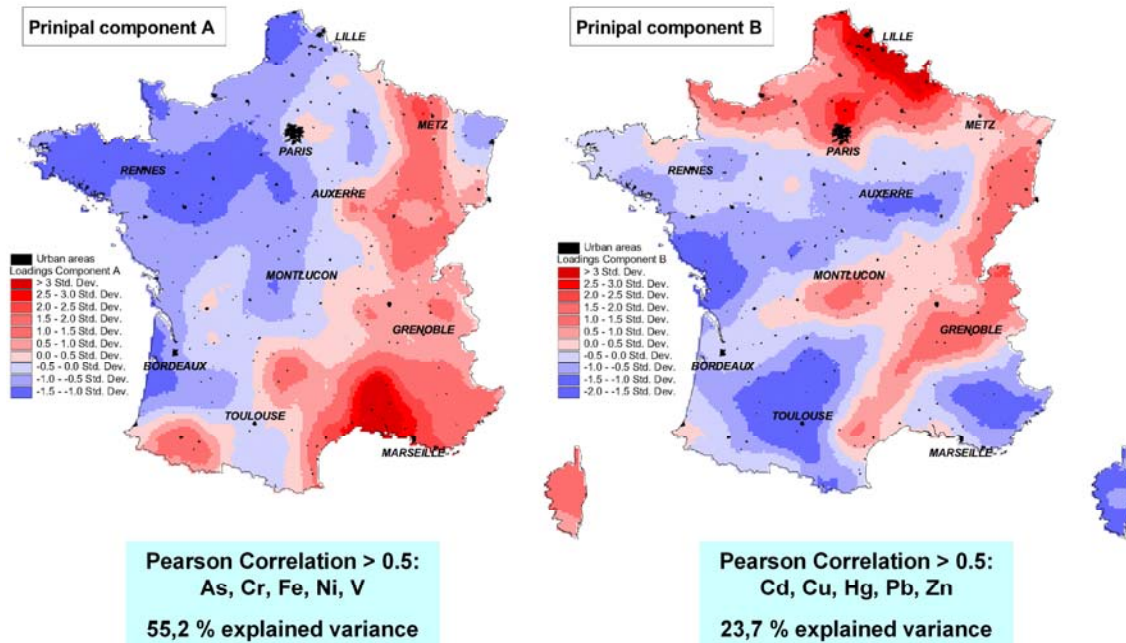


The results of the multi metal index calculations are illustrated in Figures 1 and 2. Figure 1 (left) thereby depicts the index which was calculated with help of percentile statistics. It can be seen that high index values of above eight can mostly be found in regions characterised by urban agglomerations like the area around Paris, along the Rhône River and in the Rhône delta around Marseille. Furthermore, high index values are found near the border to Belgium, a region traditionally characterised by industrial activities. Figure 1 (right) furthermore illustrates the standard deviation of all ten element specific indices to describe their variability.

Figure 2 depicts the spatial distribution of the factor scores of component 1 and 2 calculated by means of PCA. Principal component 1 representing the elements As, Cr, Fe, Ni and V predominantly shows high scores in the Rhône delta around Marseille and along the Rhône River. All of these five elements are emitted by the burning of coal and fuels. Therefore component 1 might be representative for areas with high densities of e.g. coal energy plants and oil refineries. Nevertheless these elements, especially Fe, are also indicative for the possible contamination of the sampled mosses with soil particles. Component 2 mainly representative for Cd, Cu, Hg, Pb and

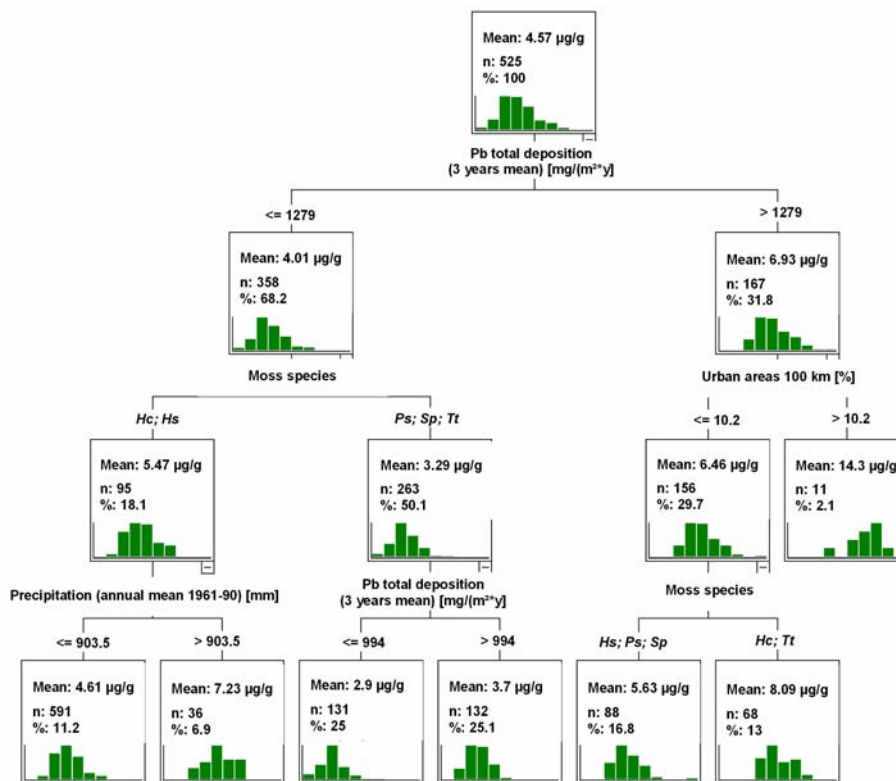
Zn especially shows high scores in areas with high population densities like in the areas around Paris and Lyon. All of the elements are emitted by emissions related to urban activities. This especially holds true for Cu and Zn that are amongst others emitted into the atmosphere by the abrasion of automobile tires and brake pads.

Figure 2: PCA scores for PCA 1 and 2 for France



The results of the evaluation of the metal loads in the mosses are exemplarily shown in Figure 3 in terms of the CART decision tree calculated for the Pb concentrations in the sampled mosses. As can be seen modelled deposition was selected as the most associated factor to the Pb loads in the mosses to split the entire data set into two subnodes. Together with the ratio of urban areas around the monitoring sites and estimated annual precipitation the modelled deposition occurs again in lower tree levels. As can be observed the moss species were selected as a splitting variable indicating that empirical aspects and sampling criteria have an effect on the Pb loads in the mosses.

Figure 3: CART Decision tree for Pb measured in the French moss survey 2006



## 4 CONCLUSION AND OUTLOOK

The calculated index maps give a comprehensive overview of the metal bioaccumulation in France without geographical gaps. They allow to assess the spatial patterns of potential environmental stress as a consequence of atmospheric metal deposition. The presented metal integrating approach should be applied on data from past French moss surveys and on those to come. Additionally, the decision tree analyses should be carried on to examine possible changing boundary conditions of the metal accumulation in mosses over time.

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