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Preliminary results of atmospheric trace metal deposition in Portugal quantified by moss biomonitoring

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Abstract

The atmospheric deposition of trace metal in Portugal was assessed by moss monitoring. Concentrations of Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn were quantified in samples of *Hypnum cupressiforme* and *Scleropodium touretii* collected in the whole country after acid wet digestion and atomic spectrometry analysis. Distribution maps of the elements was drawn after ordinary kriging estimation and the analysis of the patterns obtained allowed the identification of some local contamination sources. Among them, urban and road traffic, mine exploration, power plants and metal industries were identified as principal fonts for some elements. Particular attention was given to soil as source for moss contamination as dust, which may be of major importance in areas with mediterranean characteristics, in which a large part of the country is included.

1 Introduction

Mosses have been widely used as biomonitors of atmospheric deposition, not only of trace elements,[1,2,3] but also of organic compounds,[4] because they show a set of morphological and ecological features that make them well suited for that type of studies. These ectohydric organisms have primitive tissues without cuticle or waxy layers, enabling them to acquire most of the nutrients from the air by wet or dry deposition. They also can accumulate nutrients in concentrations considerably higher than their physiological needs, trapped as particles in the surface or intercellular spaces, or bound in soluble form to the cationic exchange sites of the cell wall. The capacity of retaining toxic elements in the mentioned forms may be considered as a mechanism of tolerance to high concentrations of such elements.[5]

The reproduction of atmospheric deposition by moss biomonitors was assessed by a set of studies comparing direct measurements of atmospheric deposition, measured with bulk deposition gauges, with values obtained in moss samples.[3,6] In such studies, regression models where obtain to transform moss concentration values absolute deposition rates.

Some advantages may be point out to the use of these organisms in the assessment of trace element deposition, when compared to classical sampling methodologies. The spatial density of the sampling network can be easily increased, being limited only by the presence of the organism. Even when the moss species is not present in the study area, transplants can be used to overtake this difficulty.[6] Other advantage is a strong reduction in the sampling costs, because there is no need for the installation, operation and maintenance of sampling stations.

Several sources may contribute to the content of trace elements in mosses, according to Berg and Steiness:[3] local and long range air pollution sources; natural cycling processes, mainly atmospheric seasalt and biogenic emissions from the marine environment; root uptake and subsequent transfer to mosses by leaching from vascular plants; mineral particles, mainly windblown soil dust. The last factor can be of large importance, in particular, in areas where the plant cover of the soil is sparse.

A moss biomonitoring network was implemented on a national scale in Portugal, with determination of eight heavy metals: Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn. The main goals of the study are: to qualify and quantify the deposition rate of such elements at a national scale; to identify local and long range contamination sources; to interpret the regional patterns of metal concentration with relation to the geographic distribution of urban and industrial activities and; to follow the evolution of the deposition rate, comparing the present data set with previous similar studies developed in Portugal in 1992.[7] This paper presents the preliminary results of the sampling campaign developed in Portugal, showing cartography made by geostatistical methods.

2 Material and Methods

Moss samples were collected between December 1996 and December 1998 in a monitoring network set up on a national scale, with a total of 169 sampling sites (Figure 1). The moss species chosen for the study were *Hypnum cupressiforme* Hedw. and *Scleropodium touretii* (Brid.) L. Kock. The former is a widespread, carpet forming species occurring in neutral or acid substrates, in areas with

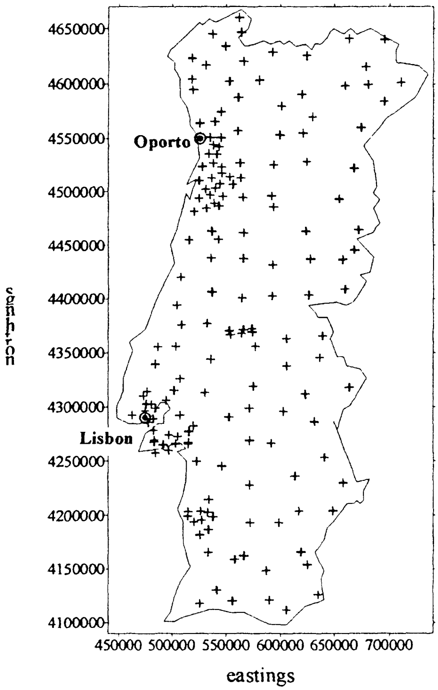

Figure 1: Portugal map showing moss sampling sites.
The two principal urban areas are also indicated.

average precipitation not less than 600 mm/year.[8] It can easily be found in the northern part of the country. In the southern, the latter species was selected because it is more resistant to drought and direct exposure to sunlight.

The sampling sites were generally located at least 500 m from main road or populated areas, or 100 m from rural houses. On each site, samples were collected using plastic gloves and bags within a 50 x 50 m area and combined to a composite sample. All moss samples were kept in a refrigerator before cleaning and separation of the green part. Afterwards, samples were dried and kept in plastic bags until further treatment.

Moss samples were dried overnight at 40°C and dry weight (d.w.) was determined. Afterwards, *ca.* 2.5 g of moss went through a digestion in 30 ml concentrated nitric acid at 65°C for 72 h, until almost complete evaporation. The residue was then diluted with nitric acid 1 M and filtered to a final volume of 25 ml. The concentration of Cd, Cr, Cu, Fe, Mn, Ni, Pb, and Zn was determined by atomic absorption spectrometry.

Basic statistics parameters were determined for all elements and mapping was performed by geostatistic methods. Statistical outliers were scrutinised according to standard procedures.[9] Experimental variograms were determined for a set of directions and, after iterative fitting, spherical models were used in the estimation of element concentration by ordinary kriging.[10]

3 Results and discussion

The statistic parameters determined for all elements are presented in Table 1. The results show considerable variability for all elements, with the distribution of all elements skewed to the positive side of the histogram. This indicates the presence of extreme maximum values in the data set, which may result from contamination sources at the local scale. This local variance contributed for the high nugget effect observed in experimental variograms of most variables, which is also reflected in the spherical models used in the kriging estimation (Table 2).

Figure 2 shows the maps of metal concentration in moss obtained by ordinary kriging estimation. The pattern changes considerably between elements, however it can be observed that the major urban and industrial nucleuses, centred in Lisbon and Oporto towns, reveal high concentrations for almost elements. Apart from the intense road traffic existent in those areas, there is an intense occupation of industries of variable dimension and activity.

High concentrations of cadmium were found in the areas west and south of Lisbon (Figure 2A). In the former area, results from soil analysis also revealed high values,[11] while in the latter, the use of fertilisers in rice production or other crops may be accounted as contamination source. Another font for this element could be intensive stone mine exploitation of sedimentary rocks,[12] that exists west and south of Lisbon.

The distribution pattern of chromium shows the existence of high values in the south area of Portugal (Figure 2B). This area corresponds to the driest region

Table 1: Basic statistics determined for the complete data set of every trace element determined on moss samples.

	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn
n	169	164	167	167	169	167	167	167
Average	0.81	2.77	8.70	1845.21	188.08	11.51	20.52	48.84
Std. Dev.	0.54	2.53	6.10	1779.13	155.79	7.77	14.85	29.23
Median	0.71	1.96	7.38	1207.75	147.82	9.55	16.77	40.44
Max	3.53	13.95	41.62	9429.65	948.76	44.35	105.81	211.09
Min	0.04	0.04	0.40	82.98	4.03	0.83	1.71	13.72
1ºquartile	0.48	1.03	4.88	687.37	85.58	6.05	10.27	31.17
3ºquartile	0.98	3.66	10.72	2254.00	248.47	14.62	26.96	59.79

Table 2: Parameters of the spherical models used in the kriging estimation of moss concentration.

Parameters	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn
C_0	0.1	3.0	7	490000	6000	20.0	70	300
C_1	0.2	3.5	30	2675000	18000	40.5	160	550
Range (m)	60000	90000	80000	70000	80000	40000	60000	40000
Anisotropy	1.00	1.00	2.67	1.17	2.67	1.00	1.50	2.67

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of the country, with highest erosion processes, which may result in higher contamination of mosses by soil particles suspended by wind or rain drops. Geochemical analysis performed in the south part of Portugal showed high concentrations of chromium in the soil, in particular in the south-west region.[11] This element has already been considered to be mainly of soil origin in other biomonitoring studies.[1,13,14]

Copper shows high concentrations in the urban areas, but also elevated values were observed in the south, were active and abandoned mines for copper, lead, zinc and pyrite exploration are located (Figure 2C). In the north, principal sources are active metal smelter industries and cultivation of vineyards, in which copper–containing pesticides were used for more than fifty years. Also a coal-fired power plant may be considered as point source in the north-west region.

The distribution of lead clearly shows contamination by antropogenic sources, like road traffic and urban pollution in the Lisbon and Oporto regions, though the values observed are lower than the concentration obtained in previous studies in the area, which can be a consequence of the reduction in the consumption of leaded gasoline (Figure 2D).[15] However, other sources, like metallurgic industries, may account for the values observed in the Lisbon area. The high values observed in the centre of the country were obtained in samples collected in the vicinity of new motorway junctions, where new road traffic took place.

Iron concentration in soils is considerable high in the south part of Portugal, as a result of several mineralizations known in the area (Figure 2E). Like, chromium, iron concentration observed in mosses is likely to reflect contamination by soil particles.[1] Other factor that may contribute to the contamination by iron is the low plant cover and high erosion rate in the area. The high values observed in the north-east region could have the same origin.

The concentration of manganese in the moss samples of the south (Figure 2F) seems to reflect mainly the soil chemistry, which is confirmed by the observation of high values of this element in soil analysis for that area, and may be related to mineralizations occurring in the region.[9] However, high values observed in the centre and south-west coast could be a consequence of the activity of coal fired power plants installed in that sites. The high values observed in the north-east region may reflect, on the other side, contamination caused by intensive mining activity that was carried out in that area in the second half of this century.

Nickel release to the environment is mainly due to coal and oil combustion.[2,14] It can also have origin on crustal material (soil), leading to high concentrations in plants, in areas where serpentine formations are present. In Portugal, two regions with serpentine formations are present, one well known in the north-east,[16] where high concentration have been quantified in the moss (Figure 2G), and some small patches in the south of the country, near Beja.[17] Principal sources for the values obtained in the moss survey are metal industries located in the Lisbon area. Also the coal-fired power plant located in the south-west coast may have some influence, although in the south area, high values were obtained also in geochemical analysis, indicating that could occur contamination of moss by soil particles. However, these high values seem to be independent of the soil type or known mineralizations.[11]

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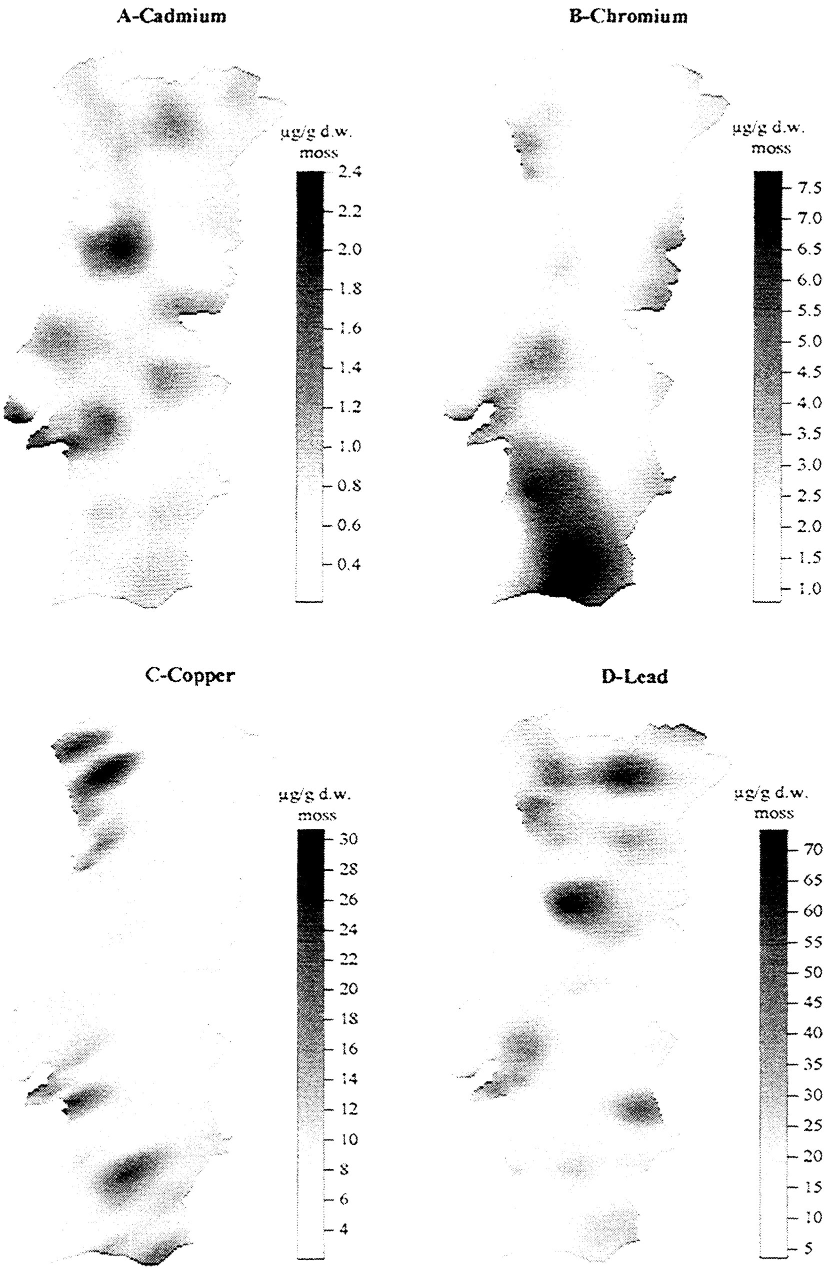

Figure 2: Maps of metal concentration in mosses obtained by ordinary kriging (continued).

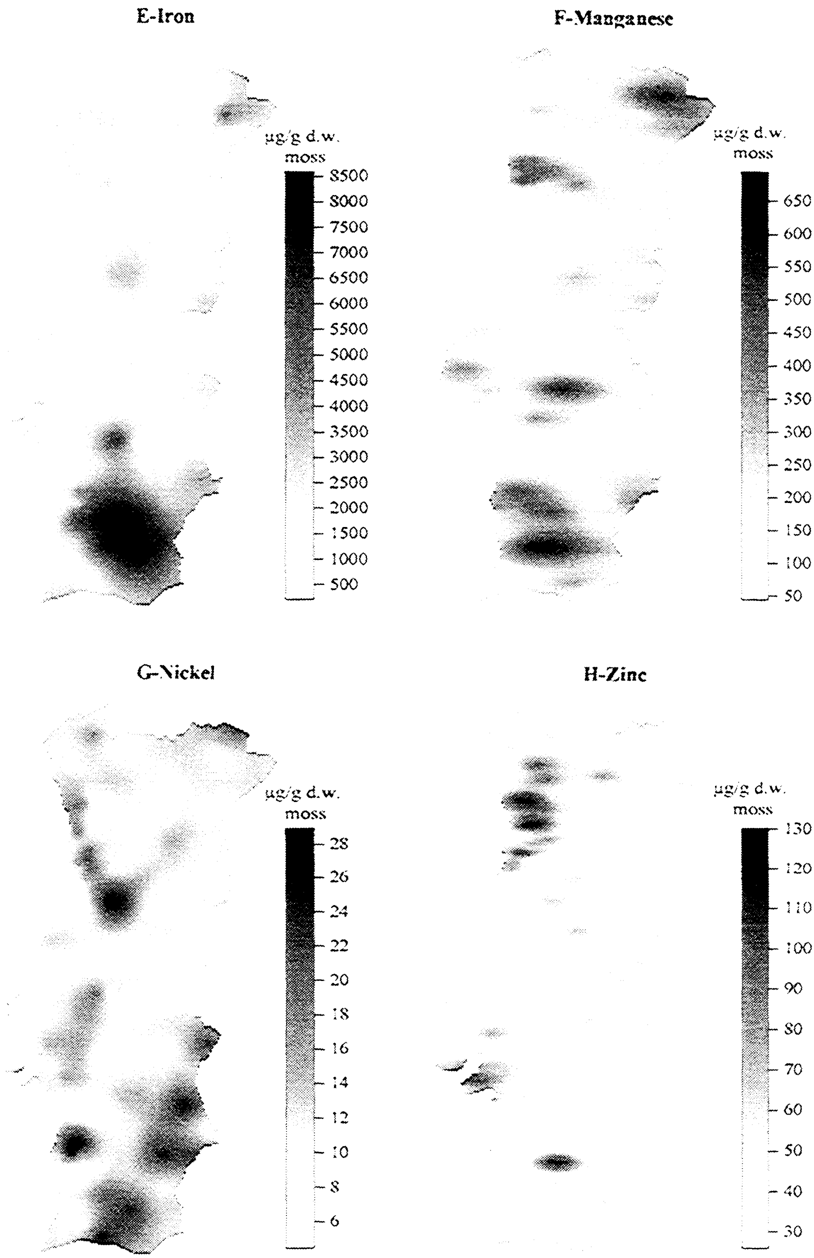

Figure 2: Continued.

High concentrations of zinc were observed in Lisbon and Oporto urban areas, that could have as sources the metal industries installed in that regions (Figure 2H). Another contamination source was identified in the south, were mining activity has taken place in the last decades.

Of all sources of moss contamination by trace metals, soil particles seem to be one of the most important for almost all elements analysed. In mediterranean areas, the ecological conditions of the environment where the samples were collected must be considered to fully understand this observation. The plant cover of the country in natural or semi-natural areas is often sparse, in particular in the south region, which correspond also to the driest climate and high erosion rate of the soil. In addition to these factors, the dry deposition is normally high, in comparison to European northern countries, and the leaching events by precipitation are less frequent. All these conditions may then contribute to high contamination of moss samples by dust of soil origin.

4 Final remarks

In this preliminary report, the atmospheric deposition of trace metals measured by moss monitoring program in Portugal can be associated with the following sources:

- Copper, lead and zinc are associated with metal industries, mining and road traffic. Also pesticide addition to vineyards may contribute as copper source to the environment;
- The concentration of iron, chromium, manganese, nickel and cadmium in the moss seems to be influenced by contamination by soil particles. This is particularly evident the first two elements. Other local sources were mentioned as point sources for manganese and nickel, like coal-fired power plants and oil refineries.

The importance of soil contamination in the mediterranean condition will now be assessed by the implementation of soil analysis, characterisation and mapping of ecological conditions at moss sampling sites.

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