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Distribution of trace metals in moss biomonitors and assessment of contamination sources in Portugal

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"Capsule": *A national biomonitoring survey with mosses in Portugal demonstrated spatial patterns of several trace elements.*

Abstract

A biomonitoring survey using the moss species [*Hypnum cupressiforme* Hedw. and *Scelopodium touretii* (Brid.) L. Kock] was performed in the whole territory of Portugal, in order to evaluate the atmospheric deposition of the following elements: Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn. The concentrations of the same elements were also obtained in two types of soil samples, collected under the moss and in nearby plots without any plant coverage, and relationships between moss and soil concentrations was investigated using the multivariate statistical method of Co-inertia Analysis. Also, relationships between concentrations in moss and several anthropogenic, geologic, pedologic and environmental parameters were screened using the same method of Co-inertia Analysis. Higher concentrations of Cu, Pb and Zn were found in areas of higher population density, with higher gasoline consumption, while higher values of Fe and Cr occur in the driest region, with lower plant coverage, indicating strong contamination by resuspended soil particles. Results also show good agreement between moss and soil contents, even for elements with high contribution of anthropogenic sources. The spatial pattern in Portugal of element contents in mosses were also detected and discussed in relation to local contamination sources.

Keywords: Atmospheric deposition; Biomonitoring; Co-inertia analysis; Mosses; Soil; Trace elements

1. Introduction

Nutrient needs of mosses are fulfilled by absorption of airborne particles from wet and dry deposition. These ectohydric organisms have primitive tissues without cuticle or waxy layers, enabling water and elements to reach cell wall and membranes, or the cytoplasm by passive or active processes. The substantial cation exchange capacity of bryophytes stems from the fact that cell wall constituents may establish ionic bounds with cationic elements in soluble form, due to negatively charged groups (mostly carboxylic acid groups) that exists in those walls. Elements can also be retained in particles trapped on intercellular spaces. The efficiency of retention of elements by a certain bryophyte species depends on the number and nature of the extracellular binding sites, tissue age and growth conditions (Brown and Bates, 1990).

In result of their biological and ecological properties, bryophytes show several advantages as monitors of atmospheric deposition, as reviewed by Tyler (1990), such as the lack of protective cuticle and thickened cell walls, numerous cell wall constituents with negatively charged groups, mineral nutrition obtained mainly from wet and dry deposition, widespread distribution of several species and simplicity and cheapness of moss biomonitoring methods. Despite some disadvantages identified in the same review (absence of best suited species in urban environments, leakage or incomplete sorption of some elements with lower affinity, difficulty of choosing ideal sampling conditions), a large number of studies have used these organisms for monitoring regional patterns of elemental deposition from the atmosphere (Schaug et al., 1990; Sérgio et al., 1993; Kuik and Wolterbeek, 1995; Berg and Steinnes, 1997a; Pott and Turpin, 1998; Grodzinska et al., 1999;

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Fernández et al., 2000; Gerdol et al., 2000). The concentration of elements assayed in moss tissues can sometimes be interpreted in terms of deposition fluxes, after calculation of calibration models between the biological values and wet deposition data (Berg and Steinnes, 1997b). Other attempts have been made to establish connections between some human diseases and biomonitoring data, with some successful results (Wappelhorst et al., 2000).

Several sources may contribute to the presence of trace elements in mosses: local and long range air pollution sources; natural cycling processes, mainly atmospheric seasalt and biogenic emissions from the marine environment; root uptake and subsequent leaching to mosses by vascular plants; mineral particles, mainly windblown soil dust (Steinnes, 1995; Berg and Steinnes, 1997b). The latter may be particularly important in areas with dry climates, low plant coverage or under erosion risk. Despite the general belief that mosses do not take important amounts of nutrients from the substratum, it should not be neglected as element supply (Brown and Bates, 1990). Therefore, it would be important to investigate the relevance of soil contamination on mosses, in order to discriminate the source for each element. It was observed as an important contamination of mosses by soil dust in arctic areas with low plant coverage (Steinnes, 1995). Several biomonitoring studies interpret the sources of elements uptake based on the grounds of factorial analysis results (Schaug et al., 1990; Kuik and Wolterbeek, 1995; Berg and Steinnes, 1997a; Faus-Kessler et al., 2001), but only few establish relationships between moss contents and actual characterization of sampling site parameters, like lithology, pedology, plant coverage and climatic features. Relations between the trace element contents in mosses and several environmental, geologic and anthropogenic factors, may be established in order to understand the relative importance of each source. This involves the characterization of the study area by all auxiliary available information. The spatial information, retrieved by Geographic Information Systems, and coupled with field studies, can be related to the biological data by multivariate co-ordination methods.

The study reported here is part of the survey of the atmospheric deposition of metals measured by mosses, performed in several European countries every 5 years. The results of the first national survey using mosses, performed in 1992/1993 were reported previously (Sérgio et al., 1993), as well as another survey using epiphytic lichens (Freitas et al., 1999). The aims of the paper are: to present the results of the 1997/1998 Portuguese survey, and interpret the spatial patterns in terms of common and local contamination sources; to compare and discuss the importance of soil and moss elemental contents using multivariate Co-inertia Analysis; to study and discuss the importance of several types of elemental sources by establishing relationships between anthropogenic, geologic, pedologic and environmental parameters and moss contents by multivariate Co-inertia Analysis.

2. Material and methods

2.1. Sampling and analysis

Moss samples were collected on 178 sites, located in 30×30 km grid, set up at a national scale, but intensified in large urban or industrial areas to a 10×10 km grid (Fig. 1). Sampling took place between December 1996 and December 1998. Some variability may have been introduced in the data as a result of temporal variations, however, the field work did not follow a pre-determined spatial sequence, which resulted in a more or less random sampling scheme. Therefore, temporal variability should affect all areas equally, and not promote any differences between regions.

The species collected were the pleurocarpous mosses *Hypnum cupressiforme* Hedw. and *Scleropodium touretii* (Brid.) L. Kock. The former is a carpet forming species occurring in neutral or acid substrata, in areas with average annual precipitation higher than 600 mm. It can be easily found in the northern and central part of the country. In the south, the latter species was used because it is more resistant to drought and to direct exposure to sun light. The use of different moss species may contribute to increase overall variability of results, and would imply the use of corrective factors among them (Fernández et al., 2000). The need for correction was tested by comparing the element concentration in samples from 13 sites, where it was possible to collect both species. Results of analysis of variance have shown

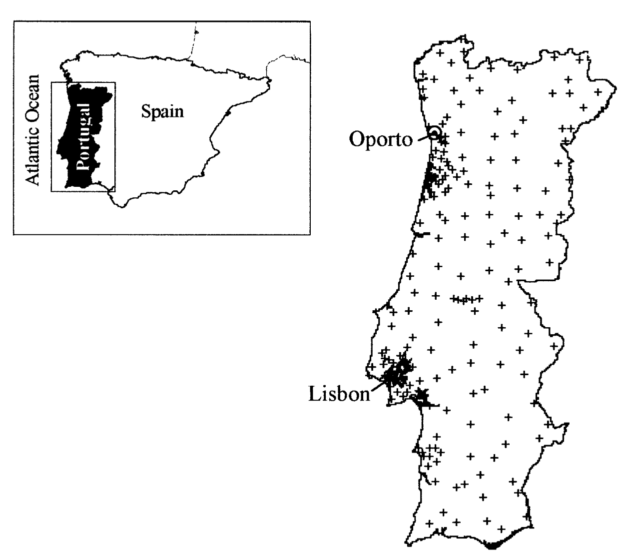

Fig. 1. Map of Portugal showing moss sampling sites. In the two principal urban areas sample density was intensified.

no significant differences ($P<0.05$) between the two species, for all elements, therefore data from both was used without correction.

At each site, a composite sample was collected within a 50×50 m area, using plastic gloves and bags to avoid handling contamination. Each plot was at least 500 m away from main roads or populated areas, and 100 m from rural houses. The characteristics recorded in each site were exposition, aspect, type and percentage of plant coverage, moss substratum, humus level and rock outcrops.

All moss samples were kept in a refrigerator before cleaning and separation of the green part, used for analysis. After cleaning, samples were dried and preserved in plastic bags until digestion. Digestion of biological material was done by wet ashing with nitric acid, following the procedure used in previous campaigns (Sérgio et al., 1993). Before digestion, samples were dried overnight at 40 °C and dry weight (dry wt.) was determined. Approximately 2.5 g of moss was digested in 30 ml of concentrated nitric acid ultra pure 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 and Ni was determined by graphite furnace atomic absorption spectrometry and the concentration of Cu, Fe, Mn, Pb and Zn was determined by flame atomic absorption spectrometry. As this study was part of an international program, it used the moss reference material, provided by the Finnish Forest Research Institute, for quality control assessment. The deviations from reference material were generally within the range 2–10% (Rühling and Steinnes, 1998).

In the same moss sampling sites, two kinds of soil samples were collected, one under the sampled moss, being its substratum, and other of free soil, directly exposed to deposition, without any type of plant or plant litter. Each one of the soil samples were collected to represent the whole layer between 0 and 15 cm deep, using plastic tools. Soil samples were air dried in the laboratory, cleaned from leaves and other plant material, sieved in 2 mm and 75 µm sieves and stored in plastic bags. The material was afterwards submitted to acid digestion using the same procedure of moss digestion and the same chemical elements were determined by atomic absorption spectrometry.

2.2. Statistical analysis and mapping of element concentrations

After determination of basic statistic parameters and histograms for all elements in mosses, values were log transformed before further processing, to make linear the relationships between variables. Interpolation maps were built after spatial structure analysis of variables, fitting of model variograms and interpolation of element concentration by ordinary kriging, using Isatis (version 3.2) software (Geovariances, 2000). The relationship between concentration of elements in mosses and in soil samples, as well as between moss values and several environmental, geological and anthropogenic was investigated by using the multivariate linear ordination method known as Co-inertia Analysis (Dolédec and Chessel, 1994) using ADE-4 software (Thioulouse et al., 1997). The table of auxiliary variables was built using data collected on site and public information available online on population statistics (INE, 2000), energy consumption (Anonymous, 1998) and environmental atlas (DGA, 1998). All geographical information was introduced, processed and mapped in Arc/Info and ArcView GIS information systems (ESRI, 1998a, 1998b). The methodology implemented in the geographic information systems assigned to each sampling site the value of the parameter in region where it is included [municipality level for energy consumption and Territorial Units of Statistics (NUTS III) for population statistics]. For the variables obtained from the Environmental Atlas, the value corresponded to the class in which the sampling site was included.

3. Results and discussion

3.1. Relationship between element concentration in mosses and soils

Table 1 shows basic statistic parameters for all metals determined on mosses. In all elements it detected high variability of values, as revealed by the high coefficients of variation, and the distribution is asymmetrical, as concluded by the skewness exhibited in Table 1. The same was observed on the soil samples, as well as in the biplots between moss and soil samples, therefore a logarithmic transformation was performed to all variables, prior the correlation analysis, in order to reduce the influence of extreme values in correlations.

For assessing the relationship between element contents in mosses and soil data, the Co-inertia Analysis was selected, because it stresses the interdependence between variables in two sets. This inter-table ordination method extracts the common variability between tables by finding pairs of factors with maximum covariance. It results in the simultaneous ordination of variables, which consequently displays the relationships present in data. A more detailed description of this method can be found in Dolélec and Chessel (1994), where its advantages in regard to other techniques can also be found.

The correlation between moss contents and soil type contents (under-moss soil and free-soil) are presented in Table 2. All elements show significant correlation ($P<0.01$) between the concentration in the moss and in

Table 1
Summary of statistics obtained for the concentration (μg/g dry wt.) of all elements determined in Portuguese mosses

	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn
Mean	0.79	3.86	9.10	1934.29	187.51	13.54	21.77	52.48
S.D.	0.54	8.99	7.49	2026.65	154.10	23.18	22.80	59.52
Coef. Variation	0.68	2.33	0.82	1.05	0.82	1.71	1.05	1.13
Minimum	0.04	0.04	0.40	82.98	4.03	0.83	1.71	12.97
Maximum	3.53	107.26	52.01	11 193.61	948.76	254.46	191.17	709.79
Median	0.70	1.95	7.38	1204.62	152.14	9.50	16.67	40.43
1st Quartile	0.44	1.00	4.88	663.85	85.58	5.96	10.12	29.02
3rd Quartile	0.98	3.78	10.72	2381.35	246.05	14.50	26.86	58.95
Quartile range	0.54	2.78	5.84	1717.50	160.47	8.54	16.74	29.93
Skewness	2.02	9.20	3.17	2.28	1.81	8.34	4.68	8.13

Table 2
Correlation coefficient between moss and soil concentration ($n=152$)

	Moss							
	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn
Under-moss soil								
Cd	0.14	0.13	0.12	0.01	−0.12	0.04	0.08	0.16
Cr	0.10	0.40*	0.26*	0.43*	0.18	0.25*	0.06	0.09
Cu	0.22*	0.26*	0.52*	0.32*	0.02	0.28*	0.35*	0.38*
Fe	−0.04	0.21*	0.19	0.50*	0.38*	0.28*	0.14	0.00
Mn	0.09	0.28*	0.07	0.44*	0.47*	0.23*	−0.03	−0.07
Ni	0.11	0.41*	0.29*	0.41*	0.18	0.35*	0.07	0.09
Pb	0.13	0.01	0.19	−0.10	−0.19	−0.03	0.31*	0.43*
Zn	−0.08	0.09	0.19	0.17	0.09	0.08	0.16	0.21*
Free soil								
Cd	0.13	0.09	0.18	0.01	0.01	0.01	0.08	0.10
Cr	0.09	0.41*	0.31*	0.40*	0.19	0.30*	0.13	0.12
Cu	0.25*	0.21*	0.48*	0.24*	0.02	0.24*	0.27*	0.33*
Fe	0.01	0.24*	0.25*	0.39*	0.37*	0.29*	0.14	0.04
Mn	0.14	0.20	0.05	0.36*	0.45*	0.15	−0.06	−0.05
Ni	0.17	0.41*	0.29*	0.35*	0.17	0.29*	0.06	0.11
Pb	0.17	0.01	0.19	−0.14	−0.17	−0.07	0.27*	0.41*
Zn	0.14	0.14	0.10	0.07	0.07	−0.01	0.09	0.18

*$P<0.01$.

soil, for both soil types, except for Zn in free soil and Cd in both media. Each of the datasets was submitted to a Principal Component Analysis, and the principal factors obtained were matched by Co-inertia Analysis. The factorial planes produced by Co-inertia Analysis for moss and under-moss soil elements show in general a good agreement between the two sets (Fig. 2). The ordination of the elements along factor 1 follows the same sequence for both media, with some changes for Fe and Pb. The same can be observed for the table relating moss and free soil contents (Fig. 3). The ordination of soil elements along the first axis for each of the soil types shows slight differences, but a major common pattern is easily found. These results show that local soil has an important contribution to the moss contents, or that the atmospheric deposition affects both media in comparable levels. Even elements with sources other than crustal material, identified in the comparison between elements in mosses with environmental factors (see Section 4), such as Cu, show good agreement between both media, indicating equivalent atmospheric contamination of both moss and soil material. The same was observed in other studies that compared moss and humus contents of some elements (Kortesharju et al., 1990; Äyräs et al., 1997). In addition to the contamination from atmospheric deposition, it is possible that the resuspension of soil particles by wind or rain drops contributes to the correspondence of values, in particular in sites of dry climatic conditions and with low plant coverage, which are the bulk of sites in the south part of the country. Another factor that can account for the frequent resuspension of soil particles is the low bryophyte coverage observed in approximately 70% of the sites. This also indicates that the moss layer is not sufficiently continuous to filter the average atmospheric deposition at each site, insofar as to cause differences between element

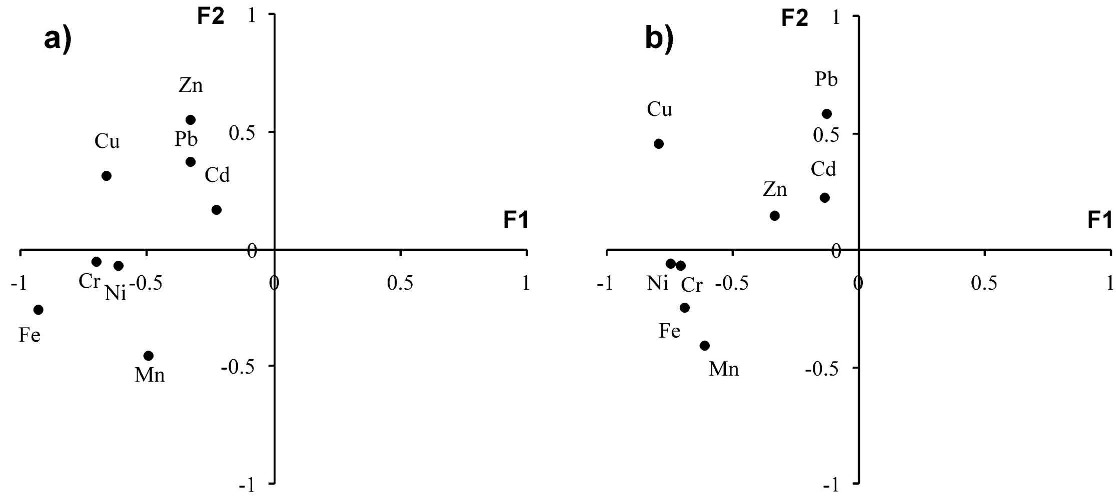

Fig. 2. Results of the Co-inertia analysis of the moss (a) and under-moss soil (b) concentration of elements. F1, factor 1; F2, factor 2.

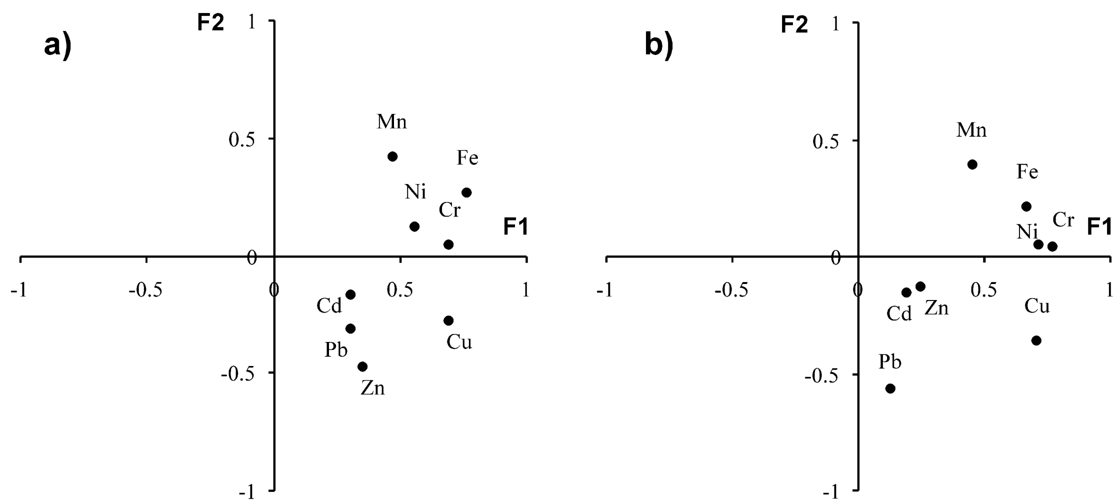

Fig. 3. Results of the Co-inertia analysis of the moss (a) and free soil (b) concentration of elements. F1, factor 1; F2, factor 2.

contents in covered and non-covered soil, and in its relation to moss contents, as revealed by the Co-inertia Analysis.

3.2. *Identification of principal contamination sources*

The relationship between element concentration on mosses and several environmental, geological, pedological and anthropogenic parameters was investigated by Co-inertia Analysis. The parameters that characterize each sampling station are presented in Table 3. All data was coded in categories before Co-inertia Analysis input. The element concentration on mosses was divided in three categories, based on the histogram with three classes of equal frequency, coded from 1 to 3 for low, medium and high concentrations. All quantitative variables of the anthropogenic set were also divided in the same way, while the remaining quantitative variables of the environmental set were divided in categories of equal amplitude. Co-inertia was run by matching two Correspondence Analyses of the moss and environmental data.

The first two Co-inertia components account for 60% of total data variability (Fig. 4). For simplicity of reading, the results are displayed separately in four plots, with moss, environmental, geologic and pedologic, and anthropogenic variables. Factor 1 gives the gradients of Fe and Mn, from low to high concentrations (Fig. 4a). Another element with an important contribution to this axis is Cr, whose high values are associated with high values of Fe and Mn. The second factor represents the gradients of Cu and Zn. Also, high concentrations of Pb and Ni, are associated with the high contents of Cu and Zn, in this second factor. Cd categories are represented near the origin, not following the gradients exhibited by the other elements.

The distribution of the environmental parameters in the first factorial plan gives rise to two main groups that

Table 3
Environmental variables used in Co-inertia analysis for identification of contamination sources in mosses

Parameter	Units	No. of classes	Abbreviation	Source
Environmental				
Type of plant cover				
Herbaceous			herbc	
Pine/eucaliptus plantation			pinec	
Oak forest			querc	
Cork-oak plantation			qsubc	
Percentage of cover				
Bryophyte	%	5	brio	
Herbaceous	%	4	herb	
Shrub	%	4	shrub	
Tree	%	4	tree	
Amount of humus		3	hm	
Altitude	m	3	alt	DGA, 1998
Insolation	hour	3	ins	DGA, 1998
Precipitation	mm/year	3	prec	DGA, 1998
Relative humidity	%	3	hum	DGA, 1998
Annual temperature	°C	3	temp	DGA, 1998
Substratum				
Earthly			earth	
Mineral			miner	
Organic			org	
Geologic and Pedologic				
Lithology				
Sedimentary			sed	DGA, 1998
Sedimentary and metamorphic			sedmet	DGA, 1998
Eruptive and plutonic			erpl	DGA, 1998
Carbonated			carb	DGA, 1998
Rock outcrops larger than 20 cm		4	rock	
Soil group				
Cambisols			cambs	DGA, 1998
Litosols			litos	DGA, 1998
Luvisols			luvis	DGA, 1998
Podzols			podzs	DGA, 1998
Regosols			regos	DGA, 1998
Anthropogenic				
Population density	inhabitant/km^2	3	dens	INE, 2000
Urban area	%	3	uarea	INE, 2000
Fuel sellings	tons	3	fuel	Anonymous, 1998
Electric power consumption				
Domestic	×1000 kwh/consumer	3	dpc	Anonymous, 1998
Industrial	×1000 kwh/consumer	3	ipc	Anonymous, 1998

allow the identification of relationships with elements in mosses. It can be observed that higher concentrations of Fe, Mn and Cr were found in the driest areas, which are identified by having the lower annual precipitation average, lower relative humidity and higher insolation rates (Fig. 4b). The vegetation in these areas is characterized by lower tree and shrub coverage percentage, high herbaceous coverage, which is the situation verified in *Quercus suber* plantations, where the humus content is low. These conditions facilitate the creation and dispersion of soil dust, contributing to the contamination of mosses by soil rich elements. This observation was already made in other regions where the plant coverage is low, like the artic areas (Steinnes, 1995). In the sites of higher moss concentration of these elements, the soil is of litosols and luvisols type (Fig. 4c). The former soils are characterized by their shallow depth or by their very high gravel content. The limited soil volume makes them subject to drought, but also to waterlogging and run-off. When exploited for agriculture, these soils are highly susceptible to erosion. The luvisols soils are characterized by the presence of a clay horizon at some depth. The lithology of these areas is composed by sedimentary and metamorphic rocks, mainly schists. The second Co-inertia axis explains mainly the variability of Cu and Zn. On the positive part of the axis are projected the categories of high values of these elements, and of Pb and Ni. These elements are associated with anthropogenic variables of the environmental dataset, like total fuel selling, domestic and industrial electric power consumption, and

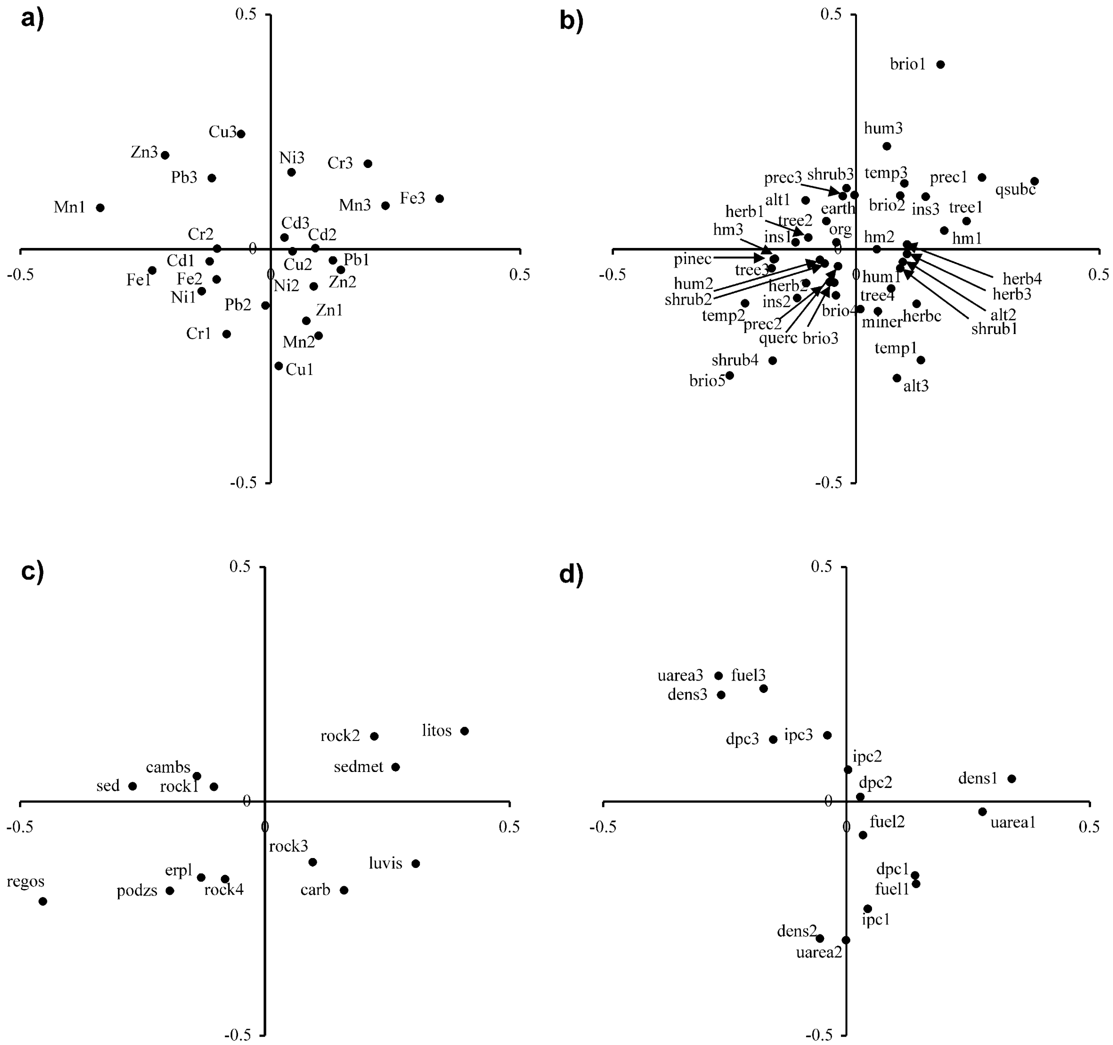

Fig. 4. Co-inertia ordination of element concentration in mosses (a) and of environmental variables, divided in three groups of variables for readability: (b) environmental; (c) geological and pedological; and (d) anthropogenic parameters. See text and Table 3 for explanation of codes.

medium and high categories of population density and percentage of urban area (Fig. 4d).

The interpretation of these results allows the identification of the main contamination sources of the elements under scrutiny, except for Cd, which could not be related with any of the environmental variables used. Two main groups of elements were identified, with the associated environmental factors. Fe is normally considered a lithophilic element, while Cr and Mn are mainly of soil origin, and are related to parameters describing the soil typology and site conditions. Cu, Zn, Pb and Ni are related mainly to anthropogenic contamination sources. The environmental variables related to the later elements are indirect measurements of contamination caused by human activity. Parameters like population density, electric power consumption or percentage of urban area do not directly drive contamination of trace elements to the environment. They can be, nevertheless, related to other contaminating sources like traffic exhausts (in this case also indirectly assessed by fuel selling) or industrial areas. Other studies have reported significant positive correlation between population density and the concentration of these elements in mosses (Pott and Turpin, 1998).

The results of Co-inertia allow the identification of general patterns in contamination sources. However, the identification of punctual sources, like power plants, waste incinerators, and other large industrial equipments, are beyond the goals of this analysis, because its identification in the environmental data set would result in outlier samples, and would not be reflected on the results. These instances can only be discussed case by case, when interpreting the distribution of elements on mosses.

The main sources identified by the Co-inertia Analysis for the metals measured in Portuguese mosses are in agreement with results obtained in several other studies. In those, the trace elements are associated to factors determined by factorial analysis, and the identification of sources is obtained from interpretation of the groups of elements assembled. One of the factors normally identify is a soil dust source, which includes Fe and Cr (Schaug et al., 1990; Kuik and Wolterbeek, 1995; Berg and Steinnes, 1997a; Gerdol et al., 2000; Riget et al., 2000). In most cases, this is the factor that accounts for the main data set variability (it is the first factor to be extracted), which shows the importance of soil contamination on element contents in mosses. Even with epiphytic lichens, sampled from tree stems or branches (thus not in direct contact with the soil), the same result was obtained in factorial analysis (Kuik et al., 1993; Freitas et al., 1997). Results also show an association of high values of Mn with Fe and Cr, which may indicate a common source for the elements. Although Mn is not normally indicated in a soil component, it was referred for leaching from living and dead plant material, after root uptake from soil. Hence, it is comprehensible that it appears associated with the other elements (Berg and Steinnes, 1997b).

The main sources for the group of elements including Pb, Cu and Zn measured in mosses are non-ferrous metallurgical industries, coal combustion and oil combustion (Kuik and Wolterbeek, 1995; Berlekamp et al., 1998). Road traffic should also be considered as source for all three metals (Monaci et al., 2000), despite the decrease of use of leaded gasoline (in Portugal the leaded gasoline was still used at the time of the moss sampling campaign). The results showing higher values for these elements were found in most populated areas, with larger fuel consumption. This corroborates the theory that these sources are the main contamination factors of atmospheric deposition on mosses.

3.3. *Spatial distribution of atmospheric contaminants in Portugal*

In order to identify the principal contaminated areas by the elements studied, maps of their distribution on mosses were drawn after geostatistical interpolation of values (Figs. 5 and 6). The interpolation of metal values on mosses was made after verifying the existence of spatial structure of all variables, by calculation of experimental variograms in four main directions (N–S, E–W, NE–SW and NW–SE). It was observed a stationary variogram in all variables, with high nugget effects, showing high variability at low scale. A global spherical model was fitted to all variables, which coefficients are presented in Table 4.

The interpretation of the metal patterns is based mainly on the identification of local contamination sources, despite the possibility of pollution produced along the Portuguese coast by the intense maritime traffic of freight ships crossing the area, or long range transport of elements from other parts of the European continent. The lack of concrete information on these factors prevents any consideration about them as sources.

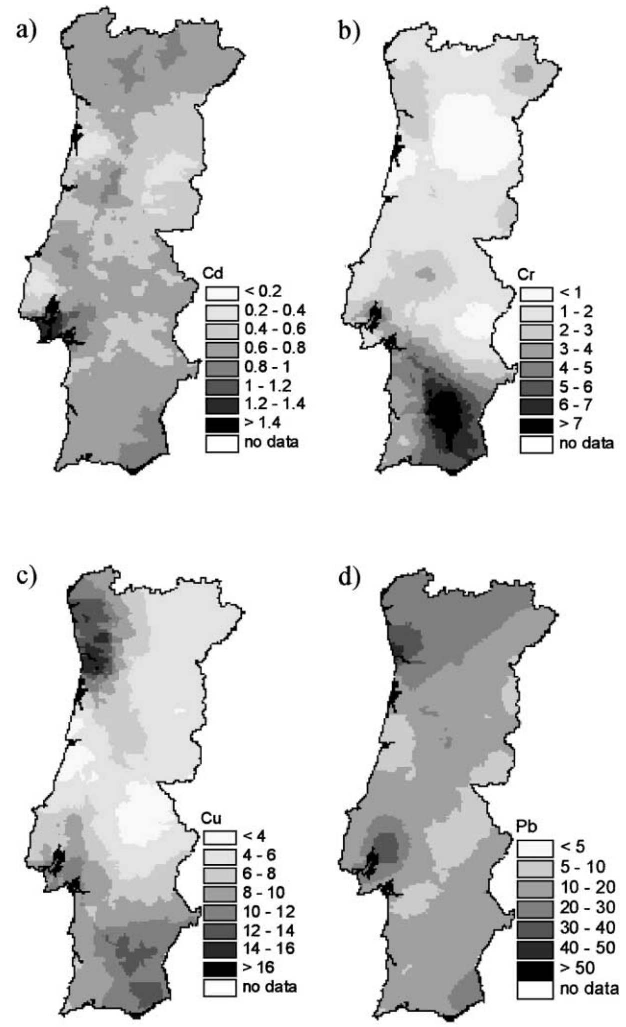

Fig. 5. Spatial patterns of moss concentrations (μg/g dry wt. moss) of four elements: (a) cadmium; (b) chromium; (c) copper; (d) lead.

3.3.1. *Cadmium*

The distribution pattern of this element is not restricted to urban or industrialized areas (Fig. 5a). High values were found in areas where strong action on the environment took place for construction of new roads, and due to the extraction of inert materials. Areas where these interventions took place are localized south of Lisbon and in the central north part of the country. Other source for this element in the southern area is the use of fertilizers in rice agriculture. To the west area of Lisbon, the soil contents are also high, as observed on geochemical analysis (Ferreira, 1997), which may indicate that dust can be also another contamination source for this element on mosses.

3.3.2. *Chromium*

The presence of this element is mainly associated with lithology, and observed in dry areas with low plant coverage, in the southern part of the country (Fig. 5b). In the north, the high values can be related to the

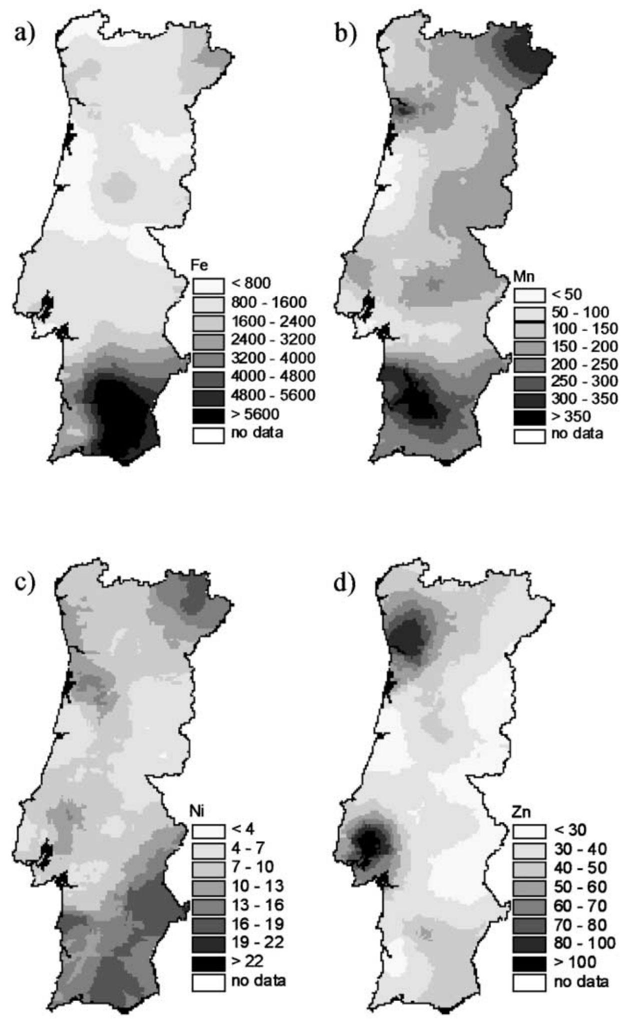

Fig. 6. Spatial patterns of moss concentrations (μg/g dry wt. moss) of four elements: (a) iron; (b) manganese; (c) nickel; (d) zinc.

presence of serpentine rock formations observed in the area. In the south-western Atlantic coast, an anthropogenic source can be identified, as a result of coal burning for power production.

3.3.3. Copper

The highest values of this element were obtained in samples from the northern region, including the Oporto urban area (Fig. 5c). Contamination sources in the region are likely to be the petrochemical industries that are settled in the area. Another important source in this area may be the use of pesticides to control vine downy mildew, used for more than 50 years, which is likely to also cause soil contamination (Brun et al., 1998). In the southern most part of the country, the presence of this metal can be related to the mineral extraction in mines located in the region. Other sources could be the shipment of copper concentrate in the Setúbal harbour, south from Lisbon, and road traffic, in major urban areas.

3.3.4. Lead

The more densely populated areas in the country show the higher contamination by this element (Fig. 5d). In these areas, the intense road traffic may still have represented the main source, because only in early 1999, was leaded gasoline totally substituted by lead-free gasoline. In the Lisbon region, the area extends to the northeast through the Tagus valley, showing the influence of metallurgical industries operating there. Some spots with elevated values were found in more inland areas in the north, which correspond to new motorway junctions. The overall concentration of this element in the urban areas has shown some reduction in comparison with previous campaigns (Sérgio et al., 1993), as a result of the successive substitution of leaded by unleaded gasoline, a trend also observed in other countries (Rühling and Steinnes, 1998). The northern part of the country generally shows higher concentration of lead. Although this may reflect, to some extend, higher emissions in the strongly industrialized Oporto region, the influence of precipitation in the retention efficiency of lead by mosses should not be excluded, in particular, because the affected areas extend far inland to some rural areas. It was observed in our data (Fig. 4) and in other studies (Pott and Turpin, 1998) that there is a general trend to increased metal contents in mosses collected from sites with higher precipitation. It may be explained by the high affinity of lead to exchange sites, when present in ionic form on wet deposition, that in mosses is higher than the majority of metals (Tyler, 1990), leading to the fixation of the element. In relation to this, the percentage of dissolved lead in rainwater is of great importance, and it depends on pH of precipitation, which is normally lower on urban environments (Chester et al., 2000).

3.3.5. Iron

The origin of this element is normally referred to be of soil material, which is also the case for sites with highest values observed in Portugal (Fig. 6a). The southern part of the country, with lower plant coverage and drier climate, is more exposed to erosion factors, and the suspension of soil material is likely to occur. In the northeastern area, some medium values are likely to have the same source, because the environment there is also characterized by dry climate and low plant coverage.

3.3.6. Manganese

The distribution pattern of this element does not indicate any localised sources (Fig. 6b). The soil contamination might be an important source, because the distribution patterns resembles that of iron, showing higher values in the driest areas with reduced plant coverage. Dust particles are not normally referred as source for this metal, but uptake from soil by vascular plants and subsequent release, reaching the moss by

Table 4
Coefficients of the fitted spherical variogram model for each element

Structure	Range (km)	Anisotropy	Sill							
			Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn
Nugget			0.102	0.150	0.069	0.057	0.087	0.095	0.076	0.038
C_1	80	1.00	0.004	0.057	0.007	0.030	0.033	0.010	0.039	0.017
C_2	170	1.47	0.016	0.027	0.022	0.089	0.027	0.022	0.012	0.018

throughfall was identified as contamination source (Steinnes, 1995; Berg and Steinnes, 1997b). The lowest values of this element were found in sites close to the sea, showing in some areas a gradient inverse to the distance from the coast. This pattern was also observed in other studies, and may indicate the replacement of Mn ions by other cations, e.g. sodium and magnesium, transported inland by marine aerosols (Schaug et al., 1990). This effect is not observed for other elements, like Pb, Cu and Zn, because the affinity of these to the exchange sites of the moss cell walls is stronger than that of the marine cations (Nieboer and Richardson, 1980).

3.3.7. *Nickel*

Local sources for atmospheric contamination by this element are both natural and anthropogenic (Fig. 6c). Near the eastern border of the country, both northern and southern sites with high values correspond to areas with serpentine rocks, known to have high contents of this element (Andrade, 1985; Sequeira and Pinto da Silva, 1992). Other high values in the south may result from moss contamination by soil particles, which is known to have significant nickel contents, as concluded for geochemical studies (Ferreira, 1997). The highest value found for this element was found in samples in the vicinity of the most important power station, which is coal-fired, in Portugal, located on the southwest coast. In this area, other industrial facilities are also in operation, like a petrochemical plant and a refinery, which are likely to also contribute to the contamination by this element. Another area showing some high values is in the northwest region, where emission by local industries is also to be expected to affect moss contents.

3.3.8. *Zinc*

The higher values were found in the larger urban and industrial areas in Portugal, around Lisbon and Oporto cities (Fig. 6d). One major causes of contamination in these areas may be the road traffic, that was shown to be a source for this element (Monaci et al., 2000). The highest value was found in the northern Lisbon area, where several chemical and metallurgical industries, and a battery industry are located in the southern region, a local contamination was identified near a recently closed zinc and lead mine extraction industry. The distribution pattern of zinc is similar to the one of lead, showing that these elements are often associated when released to the environment.

4. Conclusions

Moss analysis is shown to be a valuable method for monitoring atmospheric deposition of trace elements in Portugal. The higher concentrations of Cu, Ni, Pb and Zn were found in more densely populated regions, where emissions by fuel burning by cars and industries occur. The principal areas affected are Lisbon and Oporto urban/industrial areas. The spatial patterns of these elements allow the identification of other local sources, like coal burning power plants and mine exploitation facilities. For Fe, Cr and Mn, the soil dust seems to be the principal contamination source. The higher concentrations of these elements were found in the driest areas of the country, located in the south of the country. In these areas, the plant coverage is low, and some soil erosion occurs, which may contribute to the resuspension of soil particles by wind and rain drops.

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