

The Soil Geochemical Atlas of Portugal: Overview and applications

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Abstract

The continental area of Portugal is now entirely covered by a soil geochemical survey (1 site/135 km²), taking as the sampling media topsoils (upper mineral horizons, A) and organic horizons (humus, O). Standard methods for sampling, sample preparation and analysis were used in order to achieve high quality and consistent data. Each sample was analyzed for 32 chemical elements, pH, electrical conductivity and organic matter content.

The main purpose of the survey was to obtain baseline levels for various chemical elements. The compilation of all data (nearly 45,000 individual data) in an organised way, led to the production of the first Soil Geochemical Atlas of Portugal. In this Atlas it is possible to find for each chemical element a set of information statistics (basic statistical parameters, boxplots, cumulative frequency curves, etc.), maps of spatial distribution, among other information of geochemical and environmental interest. This paper gives an overview of the Soil Atlas and examples of application. The data were used to calculate reference values for 9 elements of environmental importance and to obtain empirical formulae allowing the estimation of elements in the coarse fraction of soils (<2.00 mm) from known concentration in a finer fraction (<0.18 mm).

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1. Introduction

The idea of low-density/low-cost sampling for geochemical mapping (Nichol et al., 1966; Garrett and Nichol 1967) has gained renewed interest over the past 15 years (Darnley and Garrett, 1990; Darnley et al., 1995; Plant et al., 2001). Initially the geochemical mapping programmes were focused on the obtainment of regional baseline information for mineral exploration but the resulting databases soon proved to be multi-purpose basic tools with application, for example, to environmental studies, mineral exploration, agriculture, geomedicine and many other investigations, well documented in the literature (Appleton and Ridgway 1993; Tarvainen 1996; Xie Xuejing et al., 1997). National geochemical surveys became a priority for many countries.

Portugal has participated in a European ultra low-density geochemical survey (1 site/5 000 km²) carried out in recent years in 26 countries under the auspices of the Forum of European

Geological Surveys (FOREGS). The resulting Geochemical Atlas of Europe and map interpretation are already published (Salminen, 2005; De Vos and Tarvainen, 2006).

The whole continental area of Portugal, which is about 89,000 km², is also covered by a low density geochemical survey (1 site/135 km²) which was carried out at the University of Aveiro, between 1994 and 2000. The sampling and analytical programme was performed according to the standards set by the IGCP Project 259 (Darnley and Garrett, 1990; Darnley et al., 1995).

The resulting multi-element data base shows the present composition of the surface environment. An overview of the data and some examples of applications are given in this paper.

2. The study area

Mainland Portugal is located in the western edge of Europe between latitudes 37° and 42°N. The latitude, together with the orography and the proximity to the Atlantic Ocean are considered to be the key factors conditioning the climate. The northern part of the country is mountainous, with 90% of the land above 400 m,

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whilst rolling plains prevail in the south, where 60% of the land is below 400 m.

The climate is mild Mediterranean. Mean annual precipitation is around 900 mm, with a high degree of spatial variation. The

highest values (3000 mm) are found in the highlands of the northwest and the lowest (500 mm) in the south coast and the inland areas. Mean annual temperature varies between 7 °C in the inner highlands of central Portugal and 18 °C in the south coast.

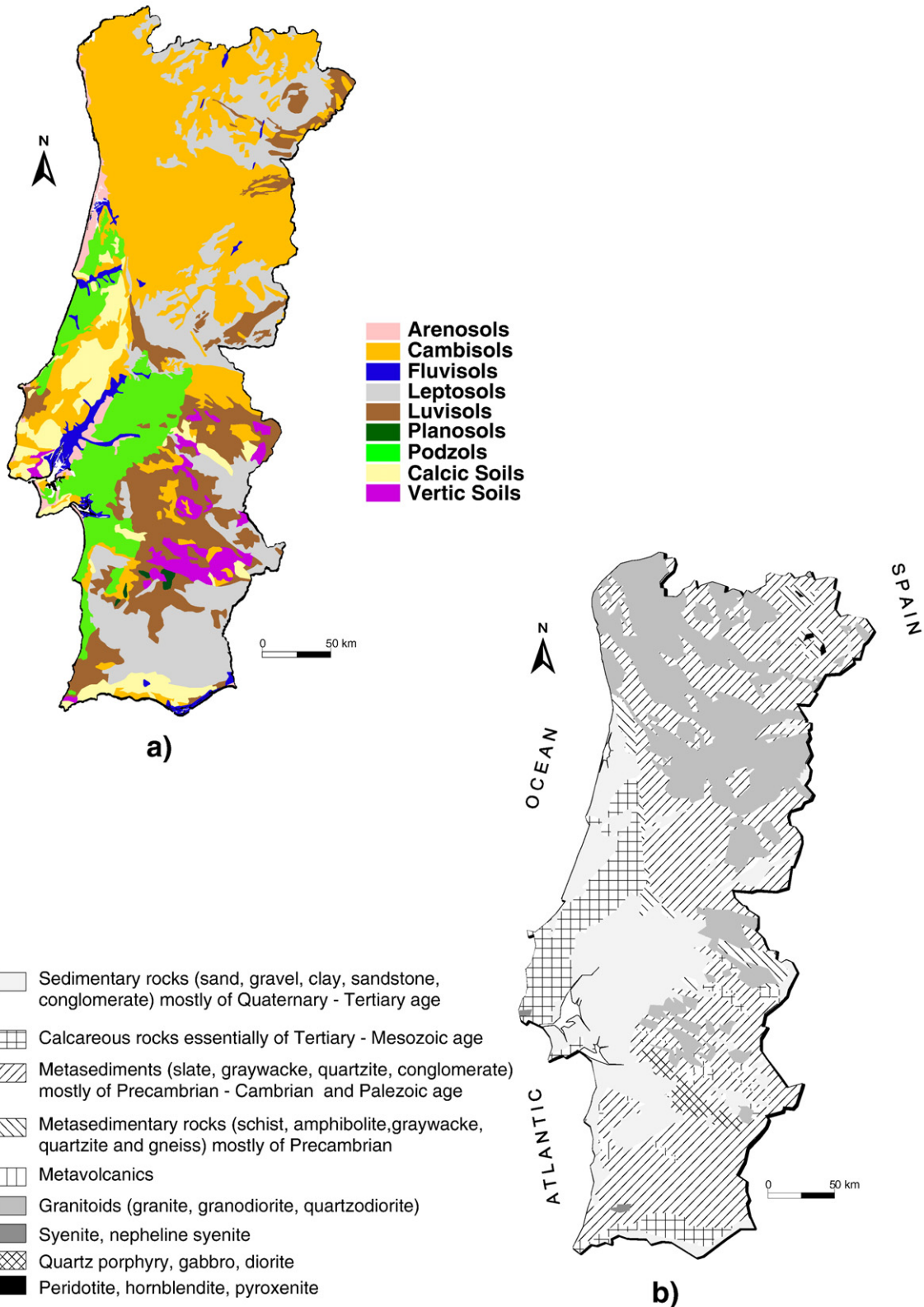


Fig. 1. (a) Major soil types in Portugal (simplified from Cardoso et al., 1973). (b) Lithological map of Portugal (simplified from DGA, 1992).

A simplified soil map of Portugal based on the 1:1,000,000 map of Cardoso et al. (1973) is presented in Fig. 1a. The major soil groups are listed below, with the equivalent FAO (1988) names in brackets:

Arenosols (Arenosols); Cambisols (Cambisols, except Calcaric or Vertic Cambisols); Fluvisols (Fluvisols, except Calcaric Fluvisols); Leptosols (Leptosols); Luvisols (Luvisols, except Calcaric or Vertic Luvisols); Planosols (Planosols);

Podzols (Podzols); Calcic Soils (Calcaric Cambisols, Calcic Luvisols and Calcaric Fluvisols); Vertic Soils (Vertisols, Vertic Luvisols and Vertic Cambisols).

Cambisols are the most extensive soils, followed by Luvisols and Leptosols.

The geology is considerably diverse and complex. Briefly, the country can be divided into 2 large units: the Hesperian Massif and the Epi-Hercynian cover. The Hesperian Massif,

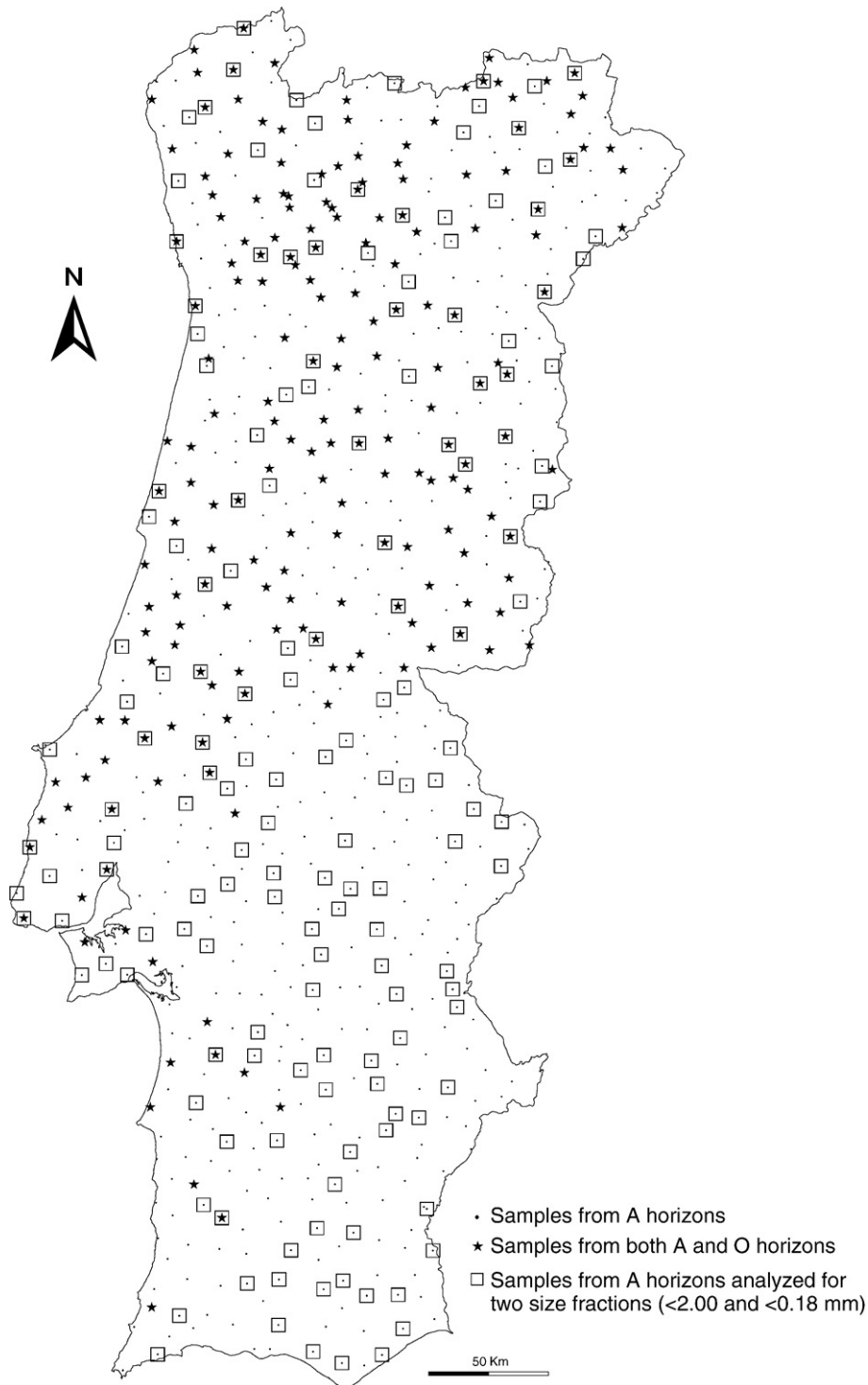


Fig. 2. Map of Portugal showing soil sampling sites.

occupying more than half the country, is of Precambrian and Palaeozoic age. Granitoids and a flysch-type series of schists and graywackes are the dominant lithologies. The Epi-Hercynian cover includes the western and southern Meso-cenozoic margins and the basins of Tejo and Sado rivers. Limestones, marls, shales, sandstones and conglomerates are very common. A lithological map of Portugal is shown in Fig. 1b.

3. Methods

3.1. Sample collection and treatment

Composite samples of the A horizon were collected from 652 sites, at a density of 1 site/135 km². Humus samples (O horizon) were collected where present (195 sites), mostly in forested areas located in the north and centre (Fig. 2). On each site a composite sample made up of five grabs was collected over an area of about 100m².

The sampling sites were selected to represent “natural” soils, therefore locations obviously affected by pollution (near factories, heavy traffic roads, mines) and arable soils were avoided. For both horizons duplicates were taken every 10 sites.

The samples were dried at 35–40 °C. Subsamples were passed through a 180 µm plastic sieve, homogenized and quartered.

At a later stage, a subset of 165 samples, representing the major soil types as well as the major rock types in Portugal, were taken from the total set of 652 stored topsoil samples. They were sieved to minus 2 mm and milled.

3.2. Analysis and analytical quality control

The chemical analysis was performed in the ACME Analytical Laboratories, Ltd, Vancouver, Canada. Representative 0.500 g subsamples were extracted for 1h with a mixture of HCl–HNO₃–H₂O (3-2-1) at 95 °C and the extracts were analysed by ICP-AES (cold vapour only for Hg) for 32 elements (9 major — Al, Ca, Fe, K, Mg, Mn, Na, P, Ti — and 23 trace elements — Ag, As, Au, B, Ba, Bi, Cd, Co, Cr, Cu, Hg, La, Mo, Ni, Pb, Sb, Sr, Th, Tl, U, V, W, Zn).

All the subsamples were randomly numbered prior to analysis in order to remove any systematic relationship between order of analysis and geographic location.

Some additional soil analyses were carried out in the Department of Geosciences, University of Aveiro. The pH was determined on duplicate samples in a water suspension, using a soil:water ratio of 1:2.5. Electrical conductivity (EC) was measured on duplicate samples in a soil:water suspension (1:10) after 1hour shaking and standing for 20h. Organic matter content (OM) was estimated gravimetrically by loss-on-ignition; duplicate 5g oven-dried samples were ignited for 16h in a furnace at 450 °C. Particle size analysis was performed by the classical combination of sieving and the pipette method.

The analytical results for Ag, Au, B, Bi, Cd, Mo, Na, Sb, Ti, Tl, U and W may be inadequate for some purposes because more than 25% values were below the limit of detection and should be re analyzed in the future; 15% of the analytical results

for Hg were also disregarded because the limit of detection (1mg/kg) was too high. The accuracy and precision for the remaining 20 elements (Al, As, Ba, Ca, Co, Cr, Cu, Fe, Hg, K, La, Mg, Mn, Ni, P, Pb, Sr, Th, V and Zn), checked by analysis of ACME Analytical Laboratories standard C3, two international standards (US Geological Survey GXR6 and GXR2), duplicates (analytical splits) of randomly selected samples and by field duplicates, was acceptable. Some of these results are shown in Tables 1 and 2.

3.3. Statistical processing and mapping

Basic statistical parameters for each variable, correlation matrices, histograms and boxplots were calculated using Statistica® software. The boxplots were obtained after the method described by Tukey (1977). The first and second order outliers (extremes) correspond to a hinge spread >1.5 or >3 times the interquartile range (75th Percentile–25th percentile), respectively.

The distribution maps were prepared following recommendations in Darnley et al. (1995). The color maps for all elements, as well as for pH, EC and OM in A horizons, based on 652 soil samples, were plotted by kriging using a variogram model adjusted for each variable. The software used was Surfer 7.0 (Keckler, 1999) and the geostatistical analysis was performed by Variowin 2.21 (Pannatier, 1996). Point symbol geochemical maps were preferred for representing the spatial distribution of elements in the organic horizon, because only 195 samples are available. These maps were obtained using the technique described in Björklund and Gustavsson (1987) and Gustavsson et al. (1997) in which the diameter of symbol points is related to metal contents by a continuous function curve. The legends of point symbol and color maps are classified in percentiles.

For the compilation of the maps and other mathematic-statistical calculations, contents below the detection limit were replaced by half that value.

4. Results and discussion

The recognition of high or unusual concentrations of specific elements in soils requires the evaluation of what concentrations should be considered normal or usual. These normal concentrations are referred to in the literature as background or baseline levels, sometimes taken as synonymous. Geochemical background concentrations should represent natural levels of an element in natural media, which ideally exclude human influence. Geochemical baselines represent levels measured in a specific area at some point in time and generally are not true backgrounds (Adriano, 2001). The term geochemical baseline is used in the text according to this definition.

Some basic statistical parameters for 20 selected elements (Al, As, Ba, Ca, Co, Cr, Cu, Fe, Hg, K, La, Mg, Mn, Ni, P, Pb, Sr, Th, V and Zn) and the variables pH, EC and OM in O and A horizons are shown in Table 1. The analytical results for Ag, Au, B, Bi, Cd, Mo, Na, Sb, Ti, Tl, U and W were disregarded for the purpose of statistical data processing because the limit of detection of the analytical method was too high.

Table 1 (continued)

Element	Media	N	>LD	<LD	P	A	Range	P10	P25	Mdn	M	GM	P75	P90	P95	CV
EC (mS/cm)	A (<0.18 mm)	647	–	–	–	–	0.000–4.500	0.037	0.092	0.220	0.393	–	0.500	1.050	1.372	122.1
	O (<0.18 mm)	186	–	–	–	–	0.032–8.920	0.610	0.869	1.221	1.642	1.279	1.980	3.350	3.880	76.9
OM (%)	A (<0.18 mm)	651	–	–	–	–	1.21–41.48	2.82	4.25	6.05	7.78	6.37	9.58	15.46	19.80	70.0
	O (<0.18 mm)	191	–	–	–	–	9.96–80.23	11.44	14.19	20.85	23.73	21.17	28.99	37.11	47.96	53.2

Concentrations are in mg/kg, except for Al, Fe, Ca, Mg and P (in %); >LD, percentage of samples above the limit of detection; <LD, percentage of samples below the limit of detection; A, Accuracy (deviation from certified as %) given by C3 standard of ACME Analytical Laboratories; P, precision (coefficient of variation as %); Range, minimum–maximum; M, arithmetic mean; Mdn, median; GM, geometric mean; CV, coefficient of variation (%); P10–95, percentiles.

Maps showing the spatial distribution of several elements are presented throughout the text.

4.1. General interpretation

Among other findings the soil survey identified: (1) strong regional differences in geochemical baselines, (2) relationships between the geochemical patterns and lithology, soil type and mineral occurrences, (3) areas with low concentration of many elements or where concentrations of potentially harmful elements are high and (4) the influence of anthropogenic factors.

Regional differences in geochemical baselines are illustrated in Fig. 3 for As and Ni. It can be seen that these elements present considerably different average and median concentrations for the same area (approximately 5500 km²) in different places of Portugal. The most significant difference is for As, having in the northern area median and average concentrations nearly 20 times higher than in the south central area.

The geochemical patterns obtained are generally controlled by lithology, soil type and mineral occurrences. For example, high concentrations of Co, Cr, Ni and V are related to Leptosols

and Vertisols developed from metasediments and mafic–ultramafic rocks. These relationships can be observed by comparing the spatial distribution of Ni (Fig. 3) and Co (Fig. 4) with the soil and lithological maps presented in Fig. 1, as well as in the boxplots for V according to soil type and bedrock lithology (Fig. 5). Ca and Sr anomalies develop where Calcic Soils and calcareous rocks occur and high Al, As, K, La, P and Th contents are found in Cambisols of granitic areas. The highest values for As can be related with some important mineralizations normally associated with the contact between the granites and metasediments. The spatial distribution of W and U can also be connected with the presence of ore deposits. Fig. 6 shows the spatial distribution of W in A horizons and the location of major mineral occurrences of W, W–(Sn) and Sn–(W). This element is above the limit of detection only for 45 soil samples (6.9%). The highest concentrations, above 5 mg kg⁻¹ (2.5% of the samples) are all found in the northern area where the ore deposits occur.

Extensive areas of naturally low concentrations of many elements, namely plant and animal nutrients, could be delineated. The western region underlain by sedimentary detritic rocks, where Podzols and Arenosols develop, is impoverished in all of the elements studied. Low concentrations of Ca, Co, Cr, Cu and Ni were also recorded in Cambisols of granitic areas. These data could be of use in further investigations concerning animal deficiency diseases in these areas. One extensive area where As concentrations are clearly above all international guidelines was identified in the northern part of the country.

The contribution of anthropogenic factors like industry and urban development can be seen in the spatial distribution of Pb (Fig. 4). The high values located around two large cities, Lisboa and Setúbal, and in the littoral region south of Setúbal, where ore deposits are not known, can be related with traffic and industrial emissions.

4.2. Evaluation of quality standards for soils

Portugal lacks its own regulation to assess soil quality and at present the “Interim Canadian Environmental Quality Criteria for Contaminated Sites” are recommended by the governmental Portuguese authorities.

Trace element contents in soils are strongly related to soil properties, particularly organic matter and clay contents, and increase almost linearly as a function of them (Adriano, 2001). Some authors use the term “soil resistance to heavy metal contamination” in relation to the critical levels of metals that exhibit toxic effects on plants and environments. Usually, the resistance of a non-acid heavy soil with a higher content of

Table 2

Quality control based on 85 field duplicates and 45 analytical splits

	σ_D^2	σ_{sa}^2	F1	σ_a^2	F2	R1	R2
Al	1.11	0.024	54.0	0.006	4.4	0.98	0.99
As	0.220	0.013	17.3	0.008	1.5	0.97	0.95
Ba	0.076	0.003	23.4	0.001	3.6	0.95	0.99
Ca	0.572	0.009	63.2	0.002	4.4	0.98	1.00
Co	0.118	0.005	24.4	0.001	4.1	0.99	0.99
Cr	0.115	0.004	28.8	0.001	5.7	0.98	0.99
Cu	0.084	0.002	35.0	0.002	1.0	0.99	0.99
Fe	1.468	0.026	55.8	0.015	1.7	0.99	0.99
K	0.124	0.001	95.5	0.001	2.5	0.99	0.99
La	0.069	0.002	35.7	0.001	2.3	0.99	0.99
Mg	0.145	0.002	61.7	0.001	2.7	0.99	0.99
Mn	0.176	0.002	71.7	0.001	1.7	0.99	1.00
Ni	0.143	0.005	31.8	0.002	1.8	0.99	0.99
P	0.095	0.002	41.5	0.001	2.0	0.97	0.98
Pb	0.065	0.016	4.1	0.005	2.9	0.87	0.88
Sr	0.126	0.003	45.7	0.001	2.4	0.97	0.99
Th	0.151	0.007	23.3	0.004	1.7	0.96	0.94
V	0.077	0.002	50.0	0.000	4.0	0.98	0.99
Zn	0.080	0.005	15.5	0.001	7.9	0.98	0.98

σ_D^2 Regional variance; σ_{sa}^2 Sampling and analytical variance; σ_a^2 Analytical variance (Garrett 1969, 1973). Critical values for the F1-ratio (84 and 85 degrees of freedom) and F2-ratio (85 and degrees of freedom) and at 95% are, respectively, 1.48 and 1.56. R1 and R2 — Spearman correlation coefficients between samples and field duplicates and between samples and analytical splits, respectively (significant for $P < 0.001$). Data were log-transformed for this analysis of variance, excepted for Al and Fe.

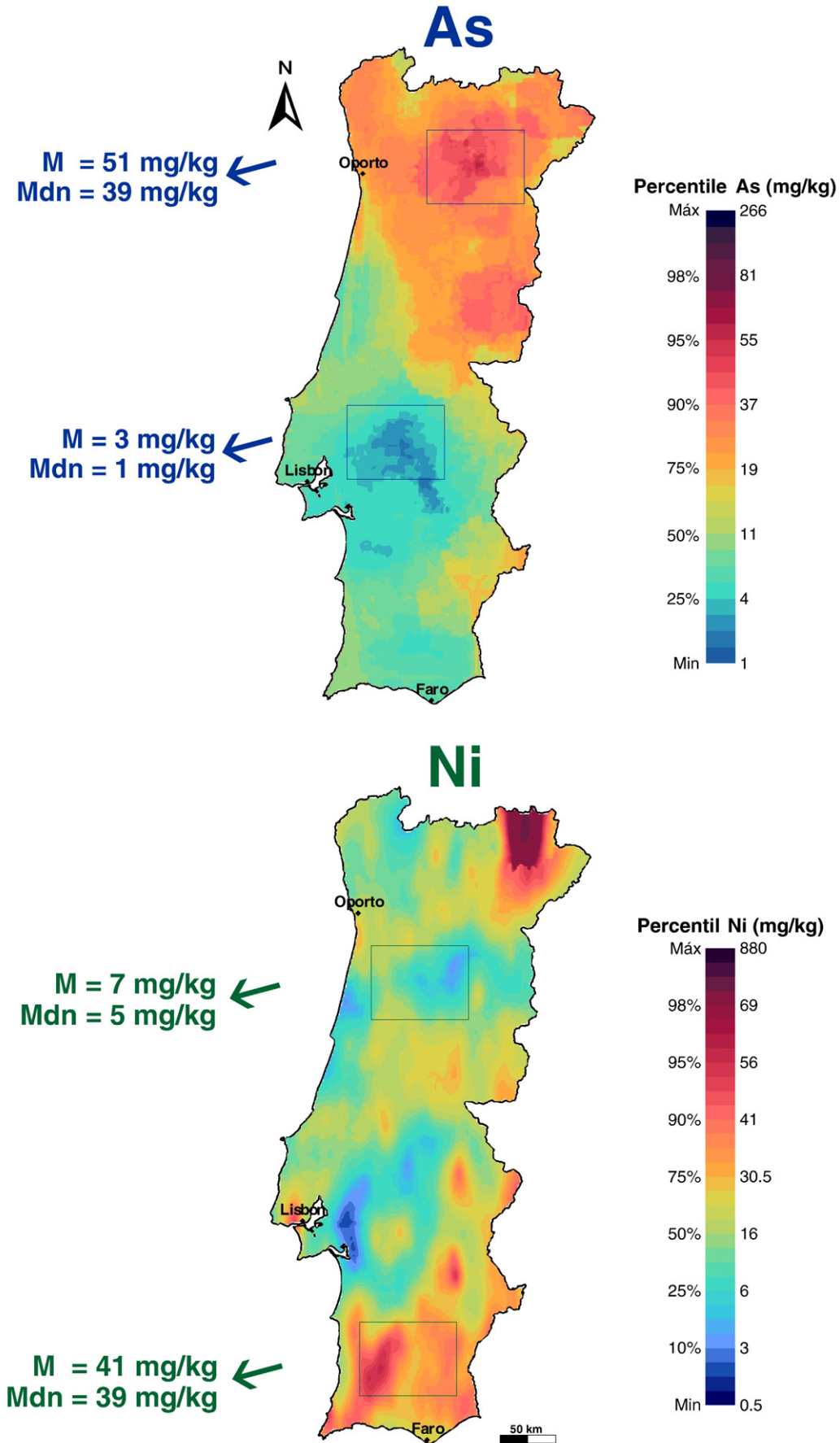


Fig. 3. Median (Mdn) and arithmetic mean (M) of As and Ni, for the same area in different places of Portugal. Spatial distribution maps were plotted by kriging with variogram information.

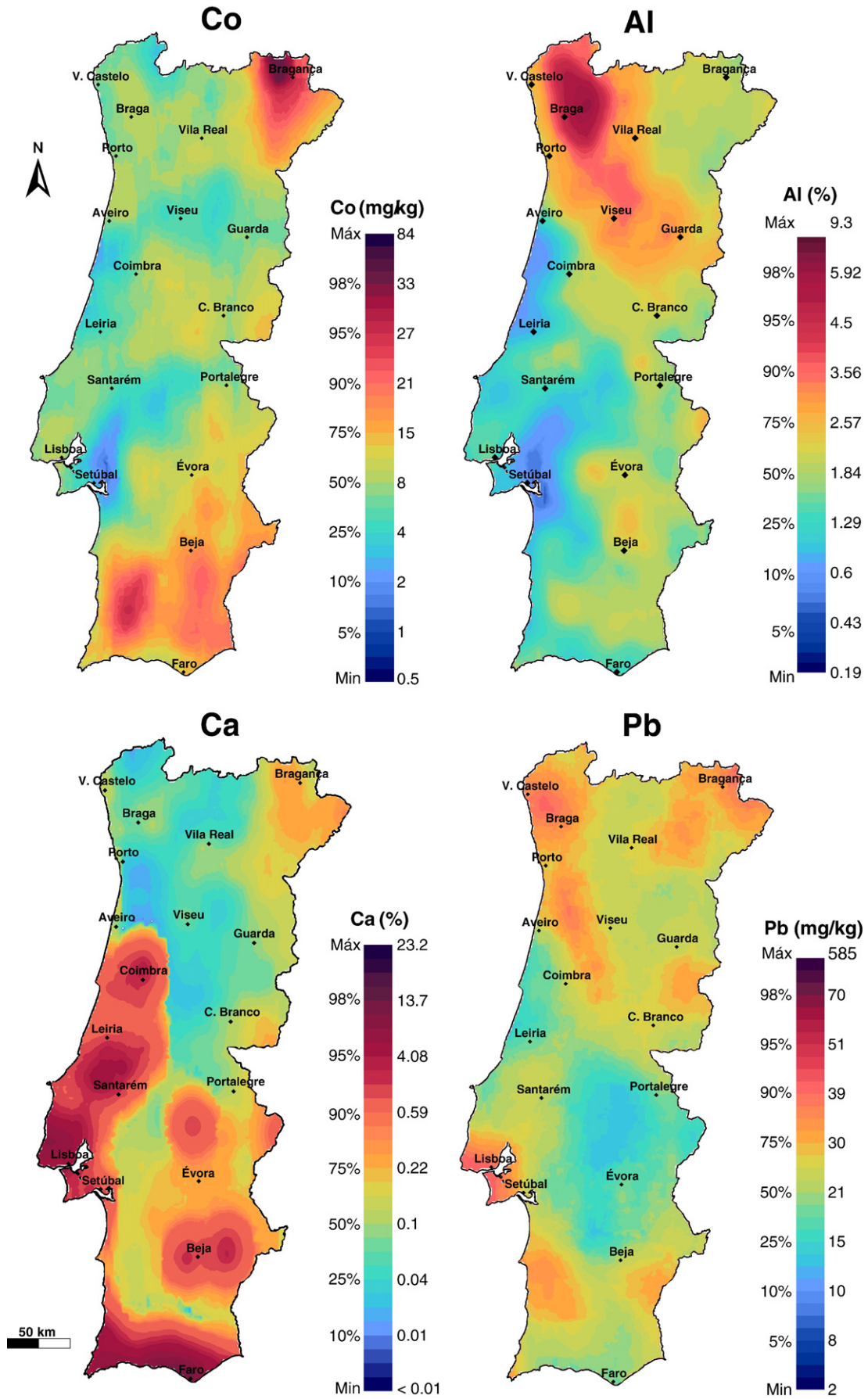


Fig. 4. Spatial distribution of Co, Al, Ca and Pb in the A horizons plotted by kriging using a variographic model.

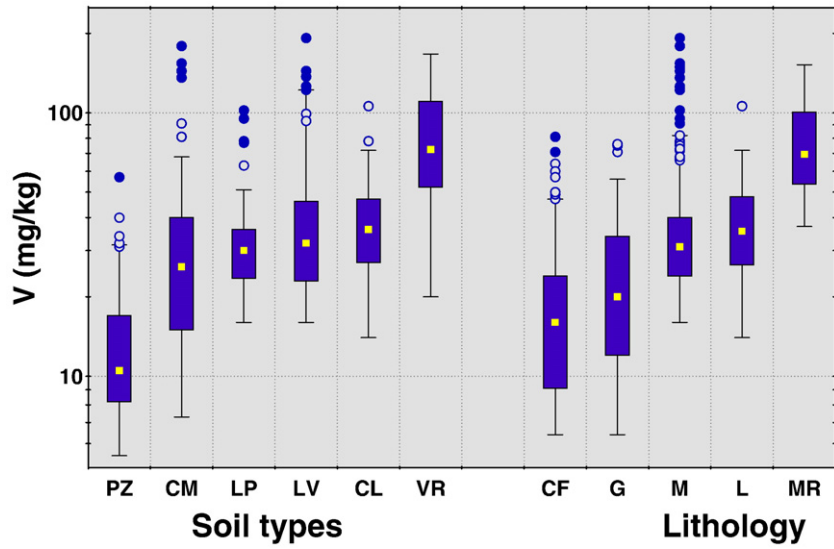


Fig. 5. Boxplots for V according to major soil groups (PZ — Podzols; CM — Cambisols; LP — Leptosols; LV — Luvisols; CL — Calcic Soils; VR — Vertic Soils) and bedrock lithology (CF — Clastic Formations; G — granitoids; M — Metasediments; L — Limestones; MR — Mafic Rocks). Median; Box: 25%, 75%; Whisker: Non-Outlier Min, Non-Outlier Max; Outliers, Extremes. Concentrations in mg/kg.

organic matter exceeds several times the resistance of a light sandy acid soil (Kabata-Pendias, 2001). Soil quality reference values are being developed in different countries for legislation

purposes. A number of these generic soil quality standards were developed as a function of clay and organic matter (VROM, 2000; IHOBE, 1998).

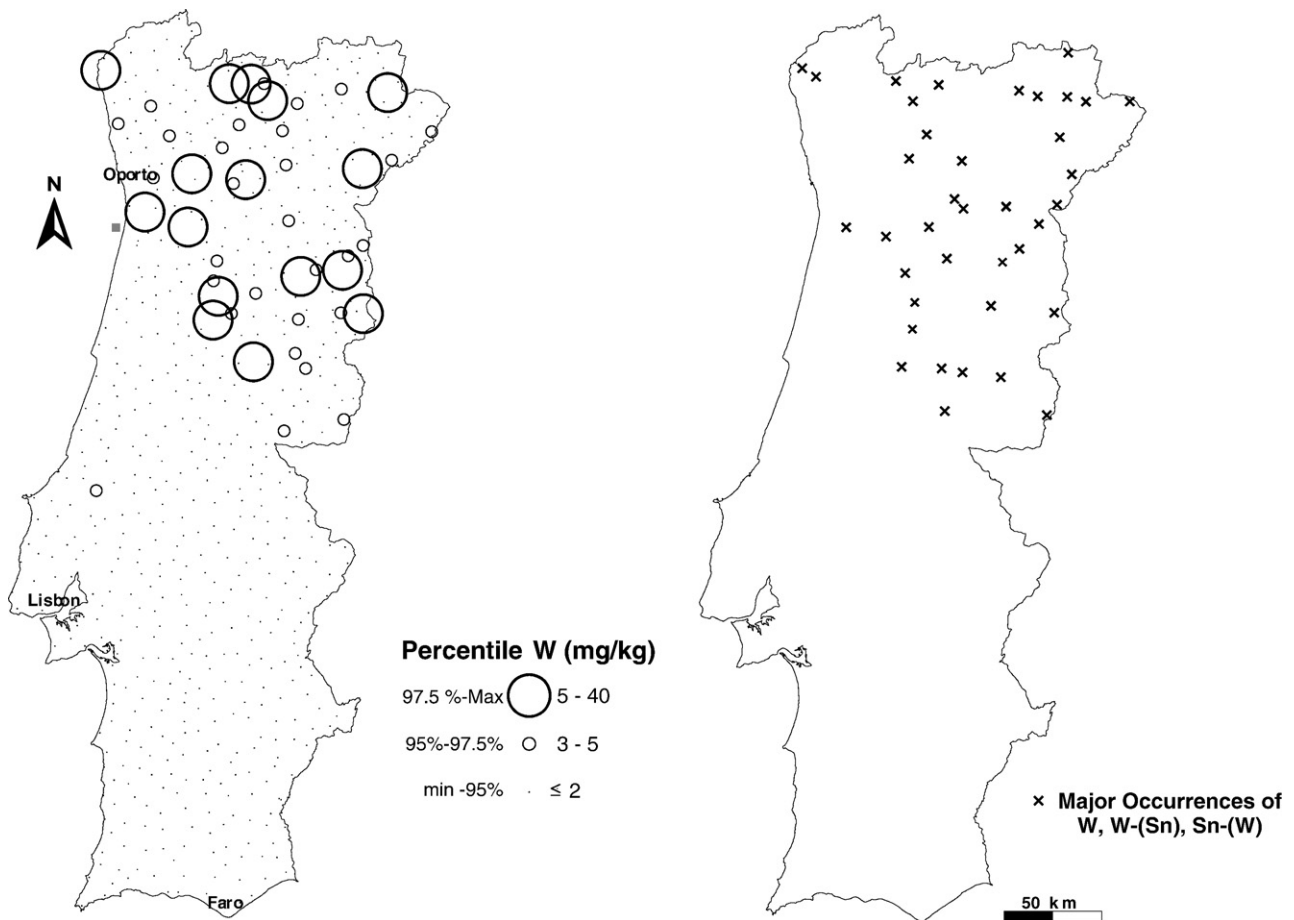


Fig. 6. Dot map showing the spatial distribution of W in A horizons and the location of major mineral occurrences of W, W-(Sn) and Sn-(W).

The database presented was used to evaluate quality standards, namely, reference values, for nine potentially harmful elements in soils: As, Ba, Co, Cr, Cu, Ni, Pb, V and Zn.

A reference value (RV) for a given element represents its maximum concentration in a “clean” soil and should correspond to the upper limit of the geochemical baseline. Soil protection or reference values have been called “preventive values”, “reference values” “target values” or “A-values”, generally with the same meaning: below these levels the soil is considered multifunctional, i.e. fit for any land use, bearing in mind any limitations due to the natural composition of the soil.

In the present study reference values were calculated after the procedure used in The Netherlands (Vegter, 1995, RIVM, 2001) and described in IHOBE (1998), based on empirical relationships between element concentration and the percentage of clay and organic matter in soils, as follows

$$RV = B + a*C + b*OM \quad (1)$$

where

- B* upper limit of baseline (75th percentile)
C clay content;
 OM organic matter content;
a, b constants obtained from regression equations.

The reference values presented in Table 3 were computed for the “average” or standard Portuguese soil, which contains 14% clay and 6% organic matter in the fine (<0.18 mm) fraction (Inácio Ferreira, 2004). Adjustments for different soil types are possible using the formulae in the same table.

The proposed standards for As, Ba, Co, Cr, Cu, Ni, Pb, V and Zn in Portuguese soils are compared to Dutch (VROM, 2000) and Basque Country in Spain (IHOBE, 1998) reference values in Table 3.

Action values (AV), also called intervention values, indicate concentrations above which there is an unacceptable risk to man

or environment due to soil contamination. The action values in Table 3 were selected from directives or recommendations from other countries in the light of toxicological and ecotoxicological information (IHOBE, 1998; RIVM, 2001; VROM, 2000).

The spatial distribution of concentrations above the action value was plotted for each element. It was found that As levels in Portuguese soils are clearly above the concentrations usually given in the literature (see Table 1 and Fig. 3). If the Canadian Guidelines are taken for total As (20 mg/kg) nearly 25% of Portuguese “natural” soils will be above the remediation criteria. The proposed Action Value (AV) for As (55 mg/kg), leaving 5% of soils above this value, seems more adequate to the Portuguese reality.

The present database allows the calculation of different regional baselines which should be considered for the purpose of legislative decision making.

4.3. Comparative analysis of data based on different size fractions

This geochemical database was obtained from the analysis of a finer fraction (<180 µm) than the usually preferred by soil scientists and environmental researchers (<2 mm).

The main purpose of the present analysis was to compare the concentrations of selected elements in both size fractions and to develop functional relationships to estimate the concentration of the elements in the coarse fraction from known concentrations in the fine fraction, thus allowing the use of the present geochemical database for environmental purposes.

The elements having, for both size fractions, less than 90% analytical results above the limit of detection were disregarded for this study. The following 18 elements were selected: Al, Ba, Ca, Co, Cr, Cu, Fe, K, La, Mg, Mn, Ni, P, Pb, Sr, Th, V and Zn.

Concentrations are generally higher in the fine fraction. There is a good correlation between element concentrations in the two size fractions as shown in Table 4. The lowest concentrations for all elements are found in Arenosols and Podzols.

Table 3

Proposed standards for As, Ba, Co, Cr, Cu, Ni, Pb, V and Zn in Portuguese soils compared to Dutch (VROM, 2000) and Basque Country in Spain (IHOBE, 1998) reference values

	As	Ba	Co	Cr	Cu	Ni	Pb	V	Zn
Regression clay (C)	n.s.	n.s.	4.36+0.32*C	11.21+0.76*C	7.99+0.63*C	4.79+0.90*C	n.s.	15.70+0.91*C	36.27+0.86*C
Regression organic matter(OM)	8.49+0.54*OM	n.s.	n.s.	n.s.	n.s.	n.s.	17.32+0.62*OM	n.s.	n.s.
Final equation	B+0.5OM	–	B+0.3C	B+0.8C	B+0.6C	B+0.9C	B+0.6OM	B+0.9C	B+0.8C
<i>B</i>	19	81	15	32	27	30	30	38	74
Reference value (RV)	22	163	19	43	35	43	34	51	85
No. of samples exceeding RV	132	27	84	66	87	55	109	81	99
Action value (AV)	55	750	50	300	200	100	500	–	500
No. of samples exceeding AV	32	0	2	1	1	4	1	0	2
Dutch RV	29	160	9	100	36	35	85	–	140
Basque Country RV	23	–	20	–	24	40	44	–	106

Concentrations in mg/kg.

(n.s. — non significant correlation, $P < 0.001$).

Table 4
Spearman's rank order and Pearson correlation coefficients between element concentrations in fine and coarse fractions ($n=165$ samples)

	Al	Ba	Ca	Co	Cr	Cu	Fe	K	La	Mg	Mn	Ni	P	Pb	Sr	Th	V	Zn
c. (Pearson)	0.86	0.91	0.98	0.97	0.96	0.89	0.93	0.93	0.83	0.93	0.96	0.98	0.65	0.71	0.98	0.93	0.96	0.97
c. (Spearman)	0.89	0.90	0.94	0.98	0.95	0.93	0.94	0.88	0.83	0.94	0.93	0.97	0.86	0.73	0.86	0.83	0.93	0.89

These correlation coefficients are significant at $p < 0.001$.

In addition, all elements concentrate in the fine fraction of these soils, being at least twice higher. This is likely to be related to the nature of the soil parent material, consisting of sands with a coarse fraction dominated by quartz.

Table 5
Parameters for linear functional relationships

Type of soil	r (Pearson)	Regression equation	No. of pairs
Al Arenosols + Podzols	0.57*	Al (C)=0.311* Al (F)−0.036%	23
Other soils	0.81	Al (C)=0.670 * Al (F)+0.423%	139
Ba Arenosols + Podzols	0.42**	Ba (C)=0.303*Ba (F)+7.398 mg/kg	25
Other soils	0.91	Ba (C)=0.882*Ba (F)+7.779 mg/kg	140
Ca Arenosols + Podzols	0.50**	Ca(C)=0.193*Ca (F)+0.023%	23
Other soils	0.97	Ca(C)=0.840*Ca (F)+0.006%	121
Co Arenosols + Podzols	0.68	Co (C)=0.172*Co (F)+0.409 mg/kg	21
Other soils	0.97	Co (C)=1.176*Co (F)−2.100 mg/kg	140
Cr Arenosols + Podzols	0.69	Cr (C)=0.265*Cr (F)+0.958 mg/kg	22
Other soils	0.94	Cr (C)=1.003*Cr (F)−0.516 mg/kg	134
Cu Arenosols + Podzols	0.49**	Cu (C)=0.303*Cu (F)+0.262 mg/kg	22
Other Soils	0.95	Cu (C)=0.986*Cu (F)−1.285 mg/kg	137
Fe Arenosols + Podzols	0.83	Fe (C)=0.410*Fe (F)−0.115%	23
Other soils	0.91	Fe (C)=1.145*Fe (F)−0.515%	140
K Arenosols + Podzols	0.34***	K (C)=0.214*K (F)+0.027%	23
Other soils	0.91	K (C)=0.833 * K (F)+0.061%	138
Mg Arenosols + Podzols	0.74	Mg (C)=0.220*Mg (F)+0.007%	22
Other soils	0.94	Mg (C)=0.868 *Mg (F)+0.051%	136
Ni Arenosols + Podzols	0.60*	Ni (C)=0.205*Ni (F)+0.389 mg/kg	22
Other soils	0.97	Ni (C)=1.067*Ni (F)−3.151 mg/kg	140
P Arenosols + Podzols	0.47**	P (C)=0.212*P (F)+0.004%	22
Other soils	0.89	P (C)=0.772*P (F)+0.010%	136
Pb Arenosols + Podzols	0.35***	Pb (C)=0.173*Pb (F)+2.780 mg/kg	23
Other Soils	0.84	Pb (C)=0.790*Pb (F)+1.260 mg/kg	136
V Arenosols + Podzols	0.67	V (C)=0.238*V (F)+0.432 mg/kg	23
Other soils	0.93	V (C)=1.002*V (F)−0.865 mg/kg	134
Zn Arenosols + Podzols	0.50**	Zn (C)=0.098*Zn (F)+2.616 mg/kg	22
Other soils	0.89	Zn(C)=Zn (F)−5.865 mg/kg	136

Pearson's correlation coefficients between element concentration in two fractions: fine fraction, F (<0.18 mm) and coarse fraction, C (<2.00 mm). Correlation coefficients are significant at $P < 0.001$, except (*) $P < 0.01$; (**) $P < 0.05$ (***) $P < 0.1$.

In Vertisols, which are mature (well developed) soils, most metals are slightly higher in the fine fraction and this can be linked to pedogenesis. On the other hand, the contents of many elements are higher in the coarse fraction of Leptosols. This can be explained again by soil genesis since many elements in poorly developed soils are left in partially weathered minerals in the coarse fraction.

4.3.1. Regression models

The development of functional relationships that could be used to estimate element concentrations in the coarse fraction of soils from known concentrations in the fine fraction was attempted. After analysing the scatter diagrams it was found that the regression equations obtained for Arenosols and Podzols are very similar, the same applying for those concerning the remaining soil types.

Table 5 presents the regression models for 6 major elements and 8 trace elements of environmental concern. The second order outliers (extremes) were rejected before estimation of regression models. Pearson's correlation coefficients (square root of coefficient of determination) are given in Table 5 as indicators of fitness.

These regression equations allow the use of the present geochemical database for environmental purposes and this could be extended to many soil surveys which are sparse all over the country.

5. Conclusions

Baselines for 20 elements and threshold concentrations for 9 elements are now defined for the soils of mainland Portugal. Maps of spatial distribution were used to investigate provenance and to identify areas with unusually high or low element concentrations. Empirical formulae for the calculation of elements in the coarse fraction of soils (<2.00 mm) from known concentration in a finer fraction (<0.18 mm) widen the usefulness of the database.

The soil samples collected in the course of this survey are stored at the University of Aveiro and therefore many further analyses are possible. The re-analysis of Cd, Hg, Mo, Sb, U and the determination of F, I and Se are planned for the near future in order to establish natural background and threshold concentrations for these elements often investigated in animal and human health research.

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References

- Adriano, D.C., 2001. Trace Elements in Terrestrial Environments: Biogeochemistry, Bioavailability and Risk of Metals. Springer, New York. 866 pp.
- Appleton, J.D., Ridgway, J., 1993. Regional geochemical mapping in developing countries and its application to environmental studies. *Applied Geochemistry* 2 (Suppl.), 103–110.
- Björklund, A., Gustavsson, N., 1987. Visualization of geochemical data on maps: new options. *Journal of Geochemical Exploration* 29, 89–103.
- Cardoso, J.C., Bessa, M.T. and Marado, M.B., 1973. Carta dos solos de Portugal na escala 1:1 000 000. *Agronomia Lusitana* 33, 481–602.
- Darnley, A.G., Garrett, R.G., 1990. International geochemical mapping. *Journal of Geochemical Exploration* 49, 1–250.
- Darnley, A.G., Björklund, A., Bölviken, B., Gustavsson, N., Koval, P.V., Plant, J.A., Steinfeld, A., Tauchid, M., Xie Xuejing, X., 1995. A global geochemical database for environmental and resource management. Recommendations for international geochemical mapping. Final report of IGCP project 259. UNESCO Publishing.
- De Vos, W., Tarvainen, T. (Eds.), 2006. Geochemical atlas of Europe. Part 2 Interpretation of Geochemical Maps, Additional Tables, Figures, Maps, and Related Publications. Geological Survey of Finland, Espoo (Electronic version <http://www.gtk.fi/publ/foregsatlas/>).
- DGA, 1992. Atlas Digital do Ambiente. (Electronic version <http://www.iambiente.pt/atlas/>).
- FAO, 1988. FAO–UNESCO soil map of the world, revised legend. World Soil Resources Report 60. FAO, Rome.
- Garrett, R.G., 1969. The determination of sampling and analytical errors in exploration geochemistry. *Economic Geology* 64, 568–574.
- Garrett, R.G., 1973. The determination of sampling and analytical errors in exploration geochemistry. *Economic Geology* 68, 282–283.
- Garrett, R.G., Nichol, I., 1967. Regional geochemical reconnaissance in eastern Sierra Leone. *Transactions of the Institution of Mining and Metallurgy* B76, 97–112.
- Gustavsson, N., Lampio, E., Tarvainen, T., 1997. Visualization of geochemical data on maps at the Geological Survey of Finland. *Journal of Geochemical Exploration* 59, 197–207.
- IHOBE, S.A., 1998. Valores Indicativos de Evaluación (VIE-A, VIE-B, VIE-C) para la Protección de los Ecosistemas.
- Inácio Ferreira, M.M., 2004. Dados geoquímicos de base de solos de Portugal Continental, utilizando amostragem de baixa densidade. Ph.D. Thesis, University of Aveiro, Portugal.
- Kabata-Pendias, A., 2001. Trace Elements in Soils and Plants, 3rd ed. CRC Press, Boca Raton, FL. 413 pp.
- Keckler, D., 1999. Surfer for Windows Version 7, User's Guide. Golden Software, Inc., USA.
- Nichol, I., Garrett, R.G., Webb, J.S., 1966. Studies in regional geochemistry. *Transactions of the Institute of Mining and Metallurgy* B75, 106–107.
- Pannatier, Y., 1996. Variowin — Software for Spatial Statistics. Analysis in 2D. Springer-Verlag, New York 0-387-94679-9.
- Plant, J.A., Smith, D., Smith, B., Williams, L., 2001. Environmental geochemistry at the global scale. *Applied Geochemistry* 16, 1291–1308.
- RIVM, 2001. Technical evaluation of the Intervention Values for Soil/Sediment and Groundwater. Human and Ecotoxicological Risk Assessment and Derivation of Risk Limits for Soil, Aquatic Sediment and Groundwater. Report 711701023. 147 pp.
- Salminen, R. (Ed.), 2005. Geochemical Atlas of Europe. Part 1. Background Information, Methodology and Maps. Geological Survey of Finland, Espoo (Electronic version <http://www.gtk.fi/publ/foregsatlas/>).
- Tarvainen, T., 1996. Environmental Applications of Geochemical Databases in Finland. Synopsis. Geological Survey of Finland, Espoo.
- Tukey, J.W., 1977. Exploratory Data Analysis. Addison-Wesley.
- VROM, 2000. Circular on Target Values and Intervention Values for Soil Remediation, DBO/1999226863.
- Vegter, J.J., 1995. Soil protection in The Netherlands. In: Salomons, W., Förstner, U. (Eds.), Heavy metals: Problems and solutions. Springer-Verlag, Berlin, pp. 79–100.
- Xie Xuejing, X., Xuzhan, M., Tianxiang, R., 1997. Geochemical mapping in China. *Journal of Geochemical Exploration* 60 (3), 99–113.