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Influence of geological setting on geochemical baselines of trace elements in soils. Application to soils of South–West Spain

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Abstract

A collection of 235 samples were taken from 115 sites (representing a density of 1 sampling site ca. 130 km^2) on rural soils derived from the major rock types in the southern Iberian Massif. The geochemical baselines of selected trace elements (As, Co, Cr, Cu, Ni, Pb and Zn) were determined on the <2 mm soil fraction. The sampling sites were not directly influenced by external pollution. Soil geochemical baseline and threshold values were calculated for each element in two geologically different zones: the Ossa-Morena Zone (OMZ) and the South-Portuguese Zone (SPZ).

All the trace elements showed significantly high median concentrations when compared to reference values for soils of Andalusia, the European Union and the world indicative of regional scale enrichment of topsoils, particularly with respect to As (24.7 mg kg^{-1}), Cu (32 mg kg^{-1}) and Pb (37.9 mg kg^{-1}) in the SPZ, and Zn (78.5 mg kg^{-1}) in the OMZ. The distribution patterns of element concentrations are primarily influenced by the lithology and geochemistry nature of bedrock and the occurrence of metallogenic belts in the survey area, notably the Iberian Pyrite Belt. In the SPZ the highest median values of As (34.4 mg kg^{-1}), Pb (56 mg kg^{-1}) and Cu (57.4 mg kg^{-1}) were found in soils derived from acid igneous rocks of the Iberian Pyrite Belt. By contrast, the soils developed on carbonate rocks of the OMZ recorded the largest median values for As (27.8 mg kg^{-1}), Pb (44 mg kg^{-1}) and Zn (83.1 mg kg^{-1}), probably regarded to base-metal (SEDEX) deposits. These results indicate that regional geology is an important determinant of soil geochemical baselines for soil pollution assessment.

Keywords: Trace elements baselines; Soil geochemical baselines; South–West Spain

1. Introduction

The term "geochemical baseline", officially introduced in 1993 in the context of the International Geological Correlation Program (IGCP Project 360), *Global Geochemical Baselines*, refers to the natural variation in the concentration of an element in the superficial environment (Salminen and Tarvainen, 1997; Salminen and Gregorauskiene, 2000). The term can indicate the actual content of an element in the superficial environment at a given point in time (Salminen and Gregorauskiene, 2000; Frattini et al., 2006; Albanese et al., 2007). It includes the geogenic natural concentrations (natural background) and the diffuse anthropogenic contribution in the soils (Tarvainen and Kallio, 2002; Cicchella et al., 2005; Frattini et al., 2006; Albanese et al., 2007).

Environmental geochemical baselines are needed in order to assess the present state of the surface environment and provide guidelines and quality standards for environmental legislation and political decision-making, especially in the assessment of contaminated soils (Salminen and Tarvainen, 1997; Baize and Sterckeman, 2001). Global geochemical baselines are desirable given that geochemical phenomena extend across political and geographical boundaries (Darnley, 1997). The establishment of

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a global geochemical reference network was recommended by the working group on *Global Geochemical Baselines* (Darnley et al., 1995), but unfortunately many countries do not follow the same protocols for achieving the standardized geochemical data.

Geochemical baseline concentrations depend not only on the dominant soil forming factors (parent rock, climate, topography, biota and time) but also on sample material, grain size and extraction method. Since the parent material strongly influences soil chemical properties (Palumbo et al., 2000; Salminen and Gregorauskiene, 2000; Lasheras et al., 2006), a geochemical baseline must be determined separately for each element in geologically different regions. Otherwise, the limiting values (action limits) for contaminated soil may be lower than the natural concentrations (backgrounds) over wide areas (Salminen and Tarvainen, 1997). A critical comparison of the methods used for background determinations is given by Reimann et al. (2005).

The geochemical database for Spain is presently incomplete and varies amongst different regions and geological areas. This is because the data were collected mainly for mineral prospecting purposes. Being based on rocks and sediments analyses, they do not meet the basic requirements for establishing national environmental baselines. The 1998 mine tailing accident that occurred in Aznalcóllar (e.g. Grimalt et al., 1999) showed the lack of reliable geochemical baseline data to assess the heavy metal pollution of soils affected from mining activities. Subsequently, a geochemical survey was carried out to assess the abundance and distribution of toxic trace elements in the soils of Andalusia, providing information about the present surface environment. The results of this project (electronic version available from http://www.juntadeandalucia.es/medioambiente/site/web/) have contributed to the establishment of guidelines for regional legislation and policy. Likewise, several Spanish regional communities such as Basque Country (IHOBE, 1993), Aragón (Navas and Machín, 2002) and Madrid (De Miguel et al., 2002) have set up their own geochemical baselines.

This study is a part of the above-mentioned survey on the soil trace elements in Andalusia. Here we present the total concentrations of a suite of potentially harmful trace elements in soils of SW Spain, focussing on the abundance and spatial variability of the different elements together with the influence of bedrock and geological setting on soil geochemistry. By establishing geochemical baselines and threshold values for distinctive geotectonic zones, we were able to separate anomalies from background data.

2. Study area

The study area measures approximately 148,00 km^2 of the Andalusian provinces of Huelva, Sevilla and Córdoba, covering a large part of SW Spain (Fig. 1).

The most typical landscape in the area is the so-called Spanish *dehesa* (Joffre et al., 1999), a savannah-like woodland that represents one of the better preserved ecosystems in southern Europe, that has been declared a biosphere reserve by UNESCO. Large areas of the *dehesas* are covered by holm oak (*Quercus ilex*) and cork oak (*Quercus suber*), surrounded by meadows and Mediterranean scrub.

This peculiar agroforestry system is conditioned by the following factors: a) the Mediterranean climate, albeit somewhat

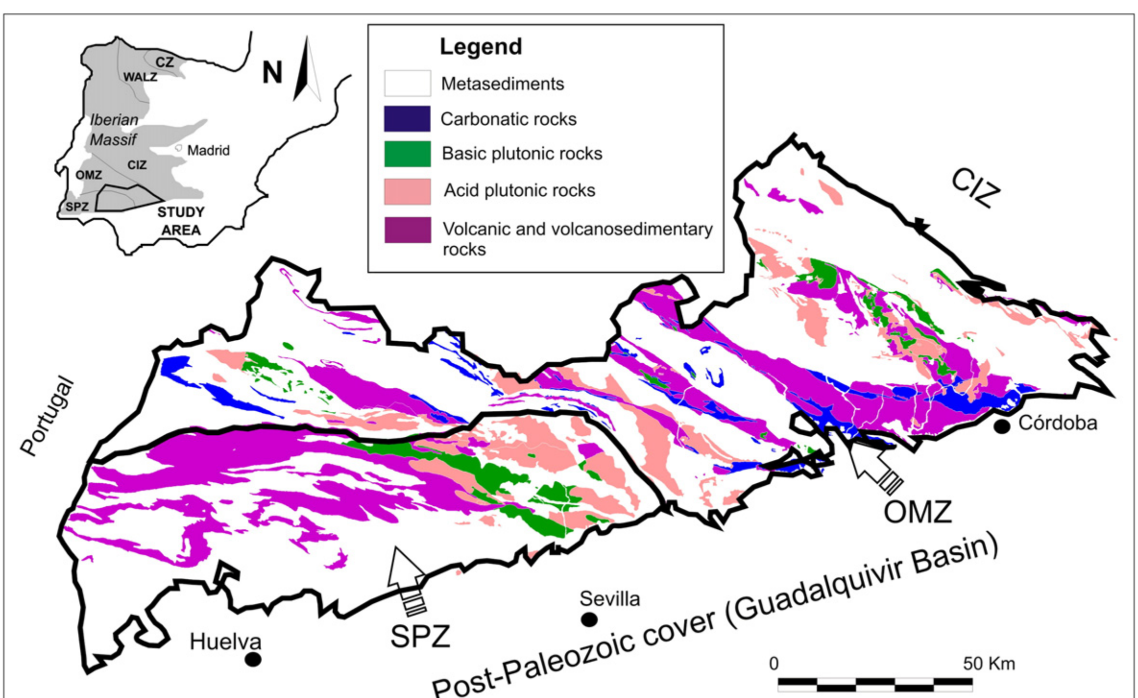

Fig. 1. Location map of the study area showing the main lithological units and geotectonic zones (SPZ: South-Portuguese Zone; OMZ: Ossa-Morena Zone; CIZ: Central Iberian Zone, WALZ: Western Asturian-Leonese Zone; CZ: Cantabrian Zone).

influenced by the Atlantic Ocean; b) the low fertility of the soil, making arable farming unprofitable; and c) the hilly topography of Sierra Morena, an alignment of low-medium altitude mountains (up to 1300 m) that run across the survey area, separating Andalusia from the Castilian plateau.

In general, the soils are poorly developed Regosols, Leptosols and Cambisols that have been affected by human activities over the last two millennia. The relatively well developed soils, such as Luvisols and Acrisols, are relicts from an earlier period (Cano and Recio, 1996). Alluvial soils are also widespread.

2.1. Geological setting

Two major tectono-stratigraphic units have been distinguished in SW Iberia (Fig. 1), namely the Ossa-Morena Zone (OMZ) and the South-Portuguesa Zone (SPZ). They represent the southernmost geotectonic zones of the Pre-Mesozoic Iberian Massif in the western branch of the European Variscan orogen. The Aracena metamorphic belt forms the contact between the OMZ and the SPZ (Díaz-Azpiroz et al., 2004). The stratigraphy, structure, metamorphism, and magmatism of both zones have been comprehensively reviewed by Dallmeyer and Martinez-García (1990), Gibbons and Moreno (2002), Azor (2004) and Simancas (2004). Here, we give only the salient lithological and metallogenical features in order to clarify the geological setting of the soil parent rocks.

2.1.1. Ossa-Morena Zone (OMZ)

The OMZ is characterized by a complex geological framework resulting from the superimposition of various tectono-metamorphic and magmatic events dating from the Upper Riphean to the late Carboniferous (Eguiluz et al., 2000).

The Precambrian succession is made up of two formations: "Serie Negra" and "Malcocinado" Formation. In its lower part, the "Serie Negra" consists of black schists and metagreywackes with abundant amphibolites, while the upper sequence is composed of interlayered volcanogenic greywackes and slates. The Malcocinado Formation includes a volcano-sedimentary complex mostly consisting of interbedded tuffs, rhyolitic lavas and abundant conglomerates.

The Paleozoic series comprises a pre-orogenic succession (Cambrian–Lower Devonian) and a syn-orogenic succession of Devonian–Carboniferous age. The Cambrian rocks are represented by conglomerates and sandstones with interbedded shales that lie unconformably over the Precambrian basement, and are overlain by several sequences of carbonatic and siliciclastic materials. The Ordovician–Silurian–Devonian sucessions consist predominantly of terrigenous sediments such as green siltstones and shales, sandstones, ampelitic black shales and lydites. Finally, the Paleozoic syn-orogenic deposits are dominated by turbidites (flysch facies) and minor volcanic and conglomeratic intercalations, while continental detrital sediments occur in the upper successions.

The large-scale and most penetrative structures in the OMZ follow the Variscan trend (NW–SE) and dip to the north. Regional metamorphism is of low-grade in most of the zone, with the exception of several medium to high-grade metamorphic massifs (Aracena metamorphic belt and Sierra Albarrana domain, among others). The general features of the OMZ magmatism are small size of plutonic bodies, common occurrence of basic rocks, frequent time-space association of

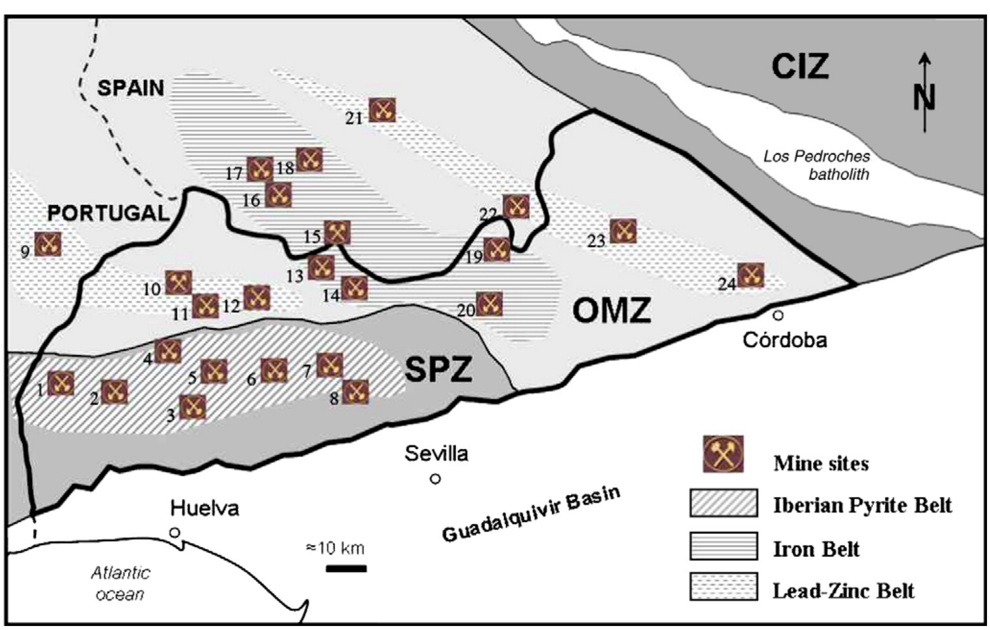

Fig. 2. Major metallogenic belts in the southern Iberian massif and some representative mines: 1. Herrerías; 2. Tharsis; 3. Sotiel-Migollas; 4. Aguas Teñidas; 5. La Zarza-Perrunal; 6. Riotinto; 7. Castillo de las Guardas; 8. Aználcollar; 9. Algares-Portel; 10. María Luisa; 11. Fuenteheridos; 12. Los Marines; 13. Cala; 14. Teuler; 15. Aguablanca; 16. La Berrona; 17. San Guillermo; 18. Monchi; 19. Cerro del Hierro; 20. El Pedroso; 21. Puebla de la Reina; 22. Azuaga-Berlanga; 23. Nava-Paredón; 24. Cerro Muriano-Los Arenales.

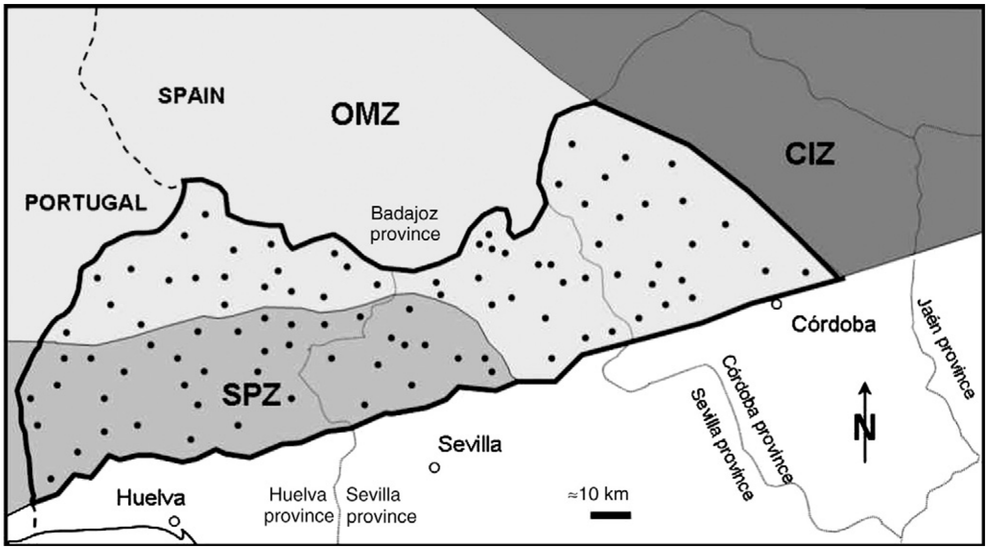

Fig. 3. Sampling sites location map.

acid and basic rocks, and significant volcanic and subvolcanic events.

The complex tectono-metamorphic evolution of the OMZ has produced many types of mineralization (Fig. 2) as well as the largest number of ore deposits in the Iberian Massif (Tornos et al., 2004). The OMZ contains more than 650 mineral occurrences formed during the Cadomian and Variscan orogenic cycles in distinct geological setting, including volcanic-hosted massive sulphides (VHMS), Pb–Zn sedimentary exhalative (SEDEX) deposits, Fe-(Cu) skarns and replacements, Ni-(Cu) orthomagmatic ore bodies, and a variety of metal-bearing hydrothermal veins.

2.1.2. South-Portuguese Zone (SPZ)

The SPZ represents the continental crust of the tectonic plate whose oceanic crust was subducted under the continental crust of the OMZ. Structurally, the SPZ constitutes a south-facing skinned fold and thrust arcuate belt. All the materials appear penetratively deformed and regionally metamorphosed under low-grade conditions, from anchimetamorphic regime in the south to the greenschist facies in the north. Intrusive bodies of granitoid rocks belonging to the Seville Range batholith (De la Rosa, 1992) are exposed in the north-eastern part of the SPZ.

By far, the most conspicuous feature of the SPZ is the occurrence of large and abundant VHMS deposits forming a pyrite belt that extends from Portugal to Spain in the SW corner of the Iberian Peninsula (Fig. 2). The Iberian Pyrite Belt (IPB) is one of the world's largest reservoirs of VHMS deposits, with total reserves in excess of 1400 million tons that are mainly concentrated at seven localities: Riotinto, Tharsis, La Zarza, Aznalcóllar and Sotiel in Spain, and Aljustrel and Neves-Corvo in Portugal (Leistel et al., 1998). About 60 mines were operative during the last century, mainly for S and Cu although the orebodies also contain appreciable amounts of Zn and Pb, precious metals (Au, Ag), and a variety of other trace elements such as Sn, Cd, As, Co, Hg, Bi and Se. Besides the massive sulfide deposits, the IPB contains a large number of manganese mineralizations.

From bottom to top the stratigraphic sequence of the IPB consists of the following formations (Schermerhörn, 1971), from bottom to top: a) Phyllite–Quartzite Group, a monotonous detritic sequence with lenses of limestones of Upper Devonian age; b) Volcanic–Sedimentary Complex (VSC), a heterogeneous lithological unit comprising mafic, intermediate and felsic volcanic rocks within a sedimentary framework; and c) Culm Group, an Upper Carboniferous turbiditic sucession of slates and greywackes.

The VSC is the only host for all the VHMS deposits and manganese mineralizations. The volcanism is considered bimodal (Munhá, 1983) with a predominance of basaltic rocks of tholeiitic affinity and calc-alkaline silicic rocks, largely pyroclastic, that were emplaced into wet turbiditic siliciclastic deposits (Mitjavila et al., 1997).

3. Sampling and analytical methods

A strategy of stratified sampling was devised in order to reduce the variability of the sample (EPA, 1992). This strategy is the most appropriate for heterogeneous areas (Boulding,

Table 1
General information on soil sampling and sample collection

Geotectonic zone	Ossa-Morena Zone	South-Portuguese Zone	Total
Surface (km^2)	9 120	5 670	14 790
Sampling sites	72	43	115
Sampling density	127	132	129
Topsoil samples	72	43	115
Subsoil samples	32	15	47
Parent rock samples	43	30	73
Total samples	147	88	235

1994). The area is divided in relatively homogenous units called strata. In this case sample locations were selected according to lithological criteria, i.e. on the basis of the type of parent rock from which the soil derived, in an attempt to stratify the area into homogeneous soil types. Thus, a total of 235 samples were collected at 115 sampling sites over the zones under investigation, with a density of approximately 1 sampling point per 130 Km^2 (Fig. 3, Table 1). In order to reduce variability, a composite sample was obtained at each site from five soil cores collected in crossing directions, and spaced approximately 1.5 m around the central point. The samples were taken at two different depths (0–20 cm and 20–40 cm) using a bucket auger, and represent rural soils with no direct source of pollution other than atmospheric deposition. The subsoil sample is representative of the underlying bedrock in most places, since Leptosols with a shallow profile depth are the most extensive group of soils throughout the region.

The soil samples were air-dried, crushed with a wooden roller, passed through a 10 mesh (<2 mm) sieve, and then ground in an agate mortar. The recovered <63 µm particles were separated for chemical analysis. The bulk rock samples were crushed and pulverised in a mechanical agate mill into particle of <63 µm, and thoroughly homogenised prior to analyses.

Chemical analyses of selected trace elements, including priority pollutant metals, were performed at Activation Laboratories Ltd. (Ontario, Canada). Total concentrations (detection limits between brackets) of Cu (1 mg kg^{-1}), Ni (1.0), Pb (3.0) and Zn (1.0) were determined after 4-acid digestion (HF, $HClO_4$, HNO_3 and HCl) by inductively coupled plasma-optical emission spectrometry (ICP-OES), whereas As (0.5), Cr (2.0) and Co (1.0) determinations were conducted by instrumental neutron activation analysis (INAA). The validity of the analytical procedure was assessed by comparison of measurements versus reference certified values. The reproducibility was found to be smaller than 10% for all trace elements.

A statistical evaluation of the analytical data was accomplished to ascertain baselines and threshold values separating anomalies from background data, including the determination of significant descriptive parameters such as mean, median, range, standard deviation, lower and upper quartiles and 95th percentile. Because of the lognormal distribution of elements in geological materials (e.g. Salminen and Tarvainen, 1997; Reimann et al., 2005), we assume the median (value at the 50th percentile of the background data) as soil geochemical baseline for each element, reflecting natural processes unaffected or diffusely affected by human activities. Box and whisker plots were constructed to identify outliers and

Table 2
Descriptive basic statistics of trace element concentrations in the Ossa-Morena Zone

Element (mg kg^{-1})	N	Mean	Median	95th percentile	Minimum	Maximum	Std. deviation	Std. mean error
As								
Topsoil	72	26.42	18.5	96.1	1.1	198	30.19	3.56
Subsoil	32	15.76	11	56	1	62.1	16.21	2.87
Parent rock	42	12.59	8.9	45.9	1.3	66.4	13.72	2.11
Co								
Topsoil	72	21.65	19	49	2	62	11.36	1.34
Subsoil	32	18.69	17.5	41	2	48	10.54	1.86
Parent rock	43	18.84	16	49	2	64	13.15	2.01
Cr								
Topsoil	72	87.78	82.5	182	<2	237	45.82	5.4
Subsoil	32	86.44	84.5	221	6	308	61.30	10.84
Parent rock	43	73.88	79	148	<2	347	66.43	10.13
Cu								
Topsoil	72	49.54	27.5	142.8	7	728	88.73	10.46
Subsoil	32	72.23	26	123	5	1270	219.84	39.86
Parent rock	43	39.56	25.1	96.22	2	509	76.93	11.73
Ni								
Topsoil	72	39.83	37	73.24	2.6	175	23.64	2.79
Subsoil	32	47.09	38.5	98.04	11	217	38.32	6.77
Parent rock	43	39.54	36	77.11	2.9	233	36	5.49
Pb								
Topsoil	72	53.6	32	200	<3	568	79.89	9.42
Subsoil	32	39.45	21.5	109	<3	328	59.54	10.53
Parent rock	41	29.48	15	65	<3	428	66.51	10.39
Zn								
Topsoil	72	103.57	78.5	327	<1	327	93.39	11.01
Subsoil	32	68.3	59	149	7	164	35.09	6.2
Parent rock	43	80.36	67	201.26	1.1	257	53	8.08

extreme values that lie outside the expected distribution range. According to Tidball and Ebens (1976) the 95th percentile was used as threshold value above which metal concentrations are likely to be of human rather than natural origin. The term threshold was introduced to differenciate between background and anomaly (Reimann and Garrett, 2005; Reimann et al., 2005). Threshold is the outer limit of background variation (Garrett, 1991).

4. Results

Descriptive statistical parameters for trace elements, categorised by topsoil (0–20 cm), subsoil (20–40 cm) and parent rock, are summarised in Table 2 (Ossa-Morena Zone) and Table 3 (South-Portuguese Zone). In Fig. 4, box and whisker plots for trace element concentrations are shown depicting: a) the median value within a box defined by the interquartile range; b) the outliers and extreme values that exceed the expected distribution range; and c) the whiskers representing the non-outlier range. On the other hand the concentration of the trace elements in the topsoils is represented in the histograms of Fig. 5, which show the inhomogeneous distribution of the values. The standard deviation and standard mean error values are relatively high, because of that inhomogeneous distribution of trace elements for both geotectonic zones.

4.1. Abundance and distribution of trace elements in topsoil

The abundance and distribution of trace elements is shown in Fig. 6 for topsoil samples. The Pearson linear correlation matrix (Table 4) is used to evaluate the interrelationships among trace elements in topsoil samples of Ossa Morena and South Portuguese zones.

4.1.1. Ossa-Morena Zone (OMZ)

The total As content ranges between 1 and 198 mg kg^{-1}, although the median value is relatively low (18.5 mg kg^{-1}); arsenic concentrations well above the average occur in the southern margin of the OMZ, linked to Cambisols developed on the Aracena metamorphic belt.

The median Co content is 19 mg kg^{-1}, with a range from 2 to 62 mg kg^{-1}; the total Cr concentration shows a greater variability, from less than 2 mg kg^{-1} up to 237 mg kg^{-1} (median value 82.5 mg kg^{-1}), whereas the total Ni concentration varies between 2.6 and 175 mg kg^{-1}, with a median of 37 mg kg^{-1}. The spatial distribution pattern of these metals is relatively

Table 3
Descriptive basic statistics of trace element concentrations in the South-Portuguese Zone

Element (mg kg^{-1})	N	Mean	Median	95th percentile	Minimum	Maximum	Std. deviation	Std. mean error
As								
Topsoil	43	47.52	24.7	179	3.1	262	60.23	9.19
Subsoil	15	28.41	16.6	168	1.7	168	41.05	10.6
Parent rock	29	31.63	21	129	<0.5	177	38.49	7.15
Co								
Topsoil	43	19.19	19	36	2	43	9.33	1.42
Subsoil	15	22.73	16	66	9	66	16.02	4.14
Parent rock	30	17.2	15.5	42	<1	52	12.76	2.33
Cr								
Topsoil	43	101.95	95	248	7	299	66.48	10.14
Subsoil	15	109.33	104	364	<2	364	84.15	21.73
Parent rock	30	88.7	100	176	<2	246	60.85	11.11
Cu								
Topsoil	43	46.38	32	147	10.3	191	39.4	6.01
Subsoil	15	37.85	26	156.8	8.4	156.8	38.36	9.91
Parent rock	30	52.74	32.2	186	2.2	429	79.63	14.54
Ni								
Topsoil	43	35.08	35	63.1	2	75	19.11	2.91
Subsoil	15	42.36	38	87	10.5	87	24.68	6.37
Parent rock	30	40.73	35	88.3	1.1	231	42.47	7.75
Pb								
Topsoil	43	142.88	37.9	205	9.3	3 449	531.06	80.99
Subsoil	14	41.93	32.2	142	12	142	38.18	10.21
Parent rock	28	29.26	17.3	85.6	<3	143	31.37	5.93
Zn								
Topsoil	43	88.54	75.8	173	28	347	55.84	8.52
Subsoil	15	84.41	65.4	295	27	295	61.97	16
Parent rock	30	71.62	65	160.1	23	193	40.96	7.48

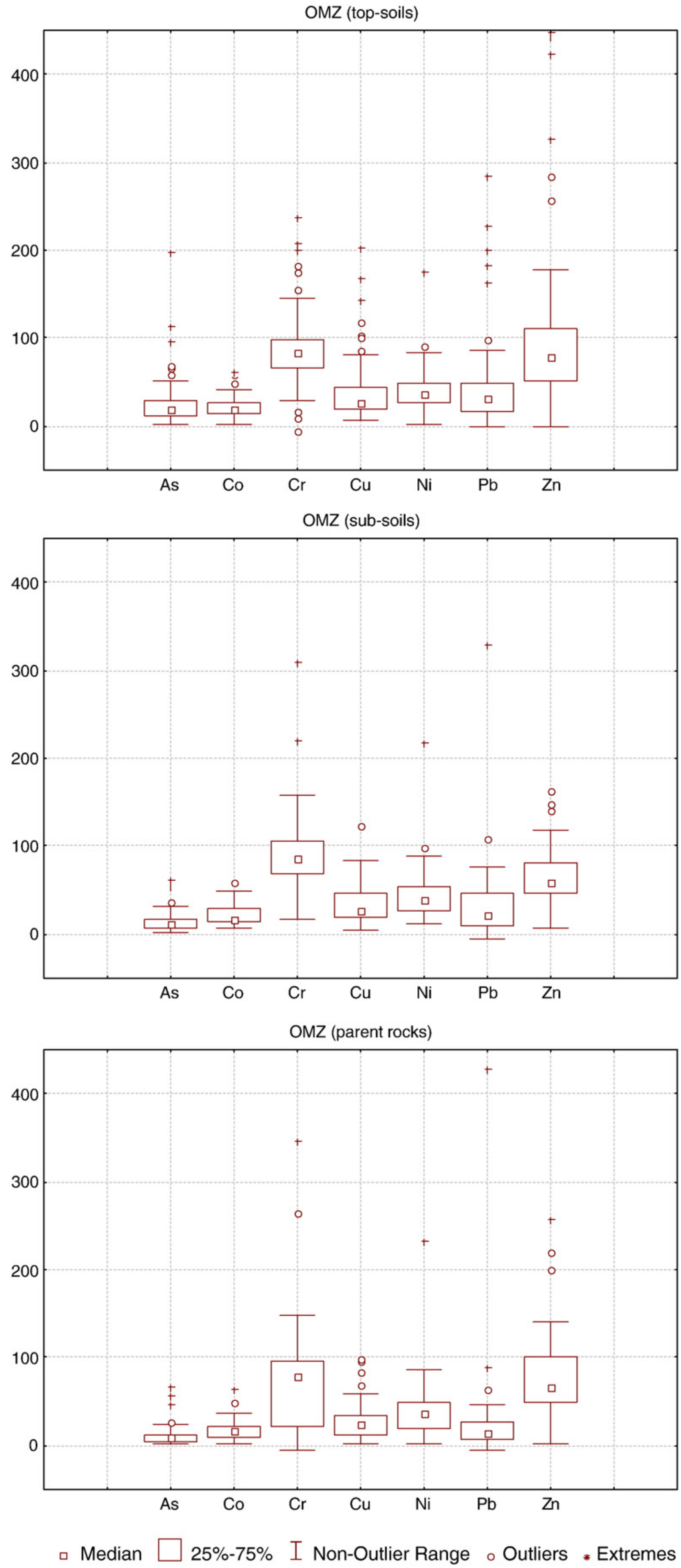

Fig. 4. Box and whisker diagram of topsoils, subsoils and parent rock samples of the Ossa-Morena and South-Portuguese zones.

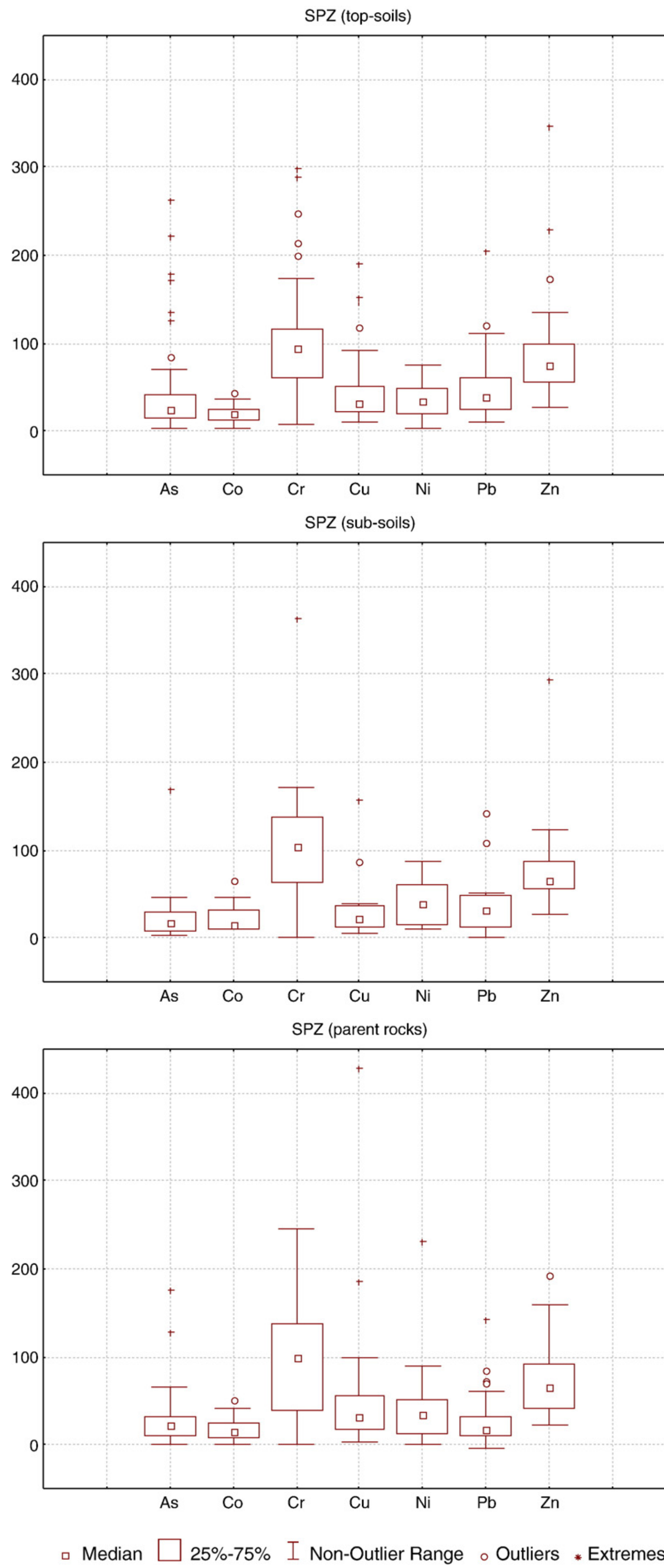

Fig. 4. (*continued*).

Ossa Morena Zone

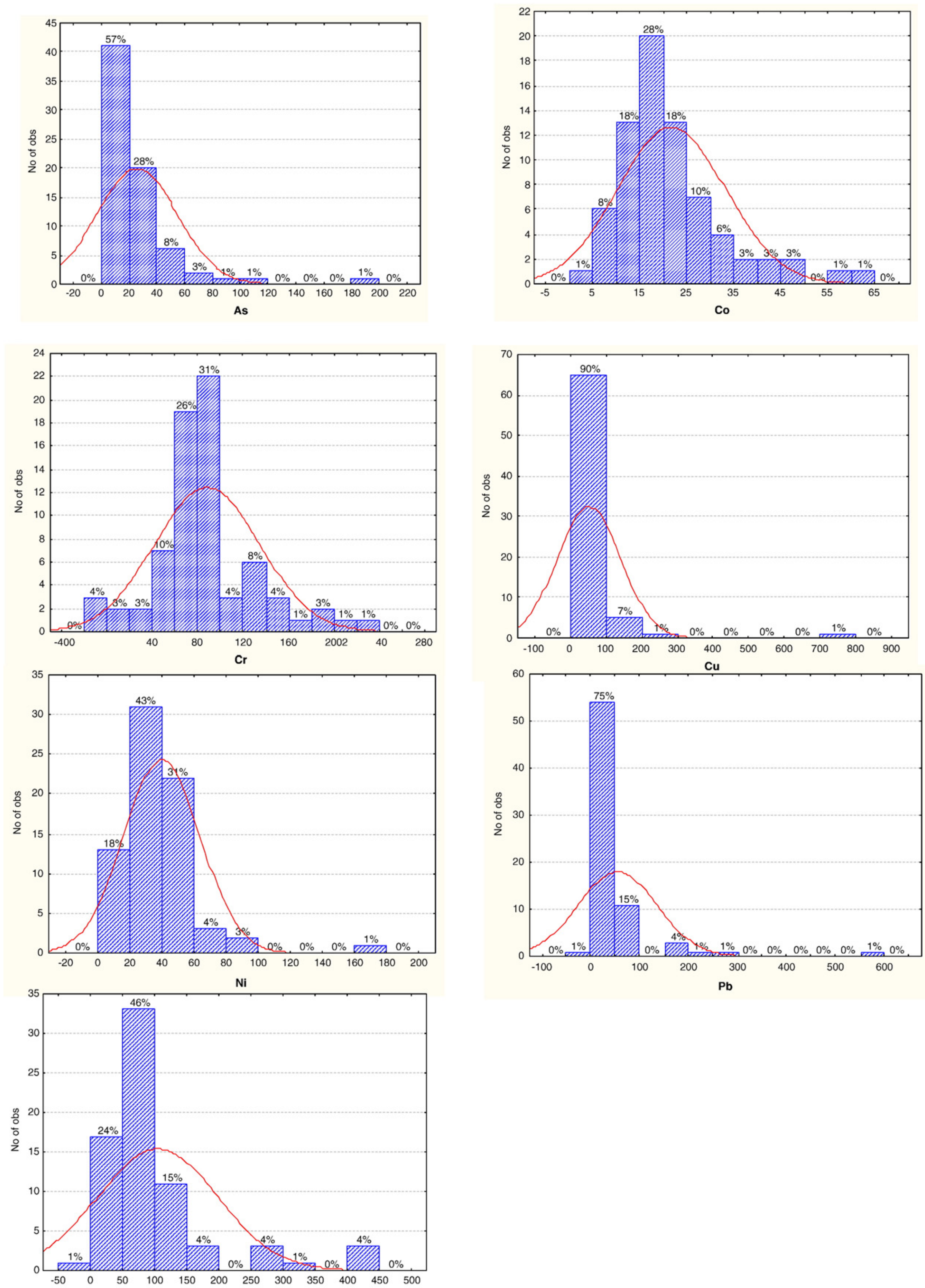

Fig. 5. Histograms of trace elements concentracions of topsoils of the Ossa-Morena and South-Portuguese zones.

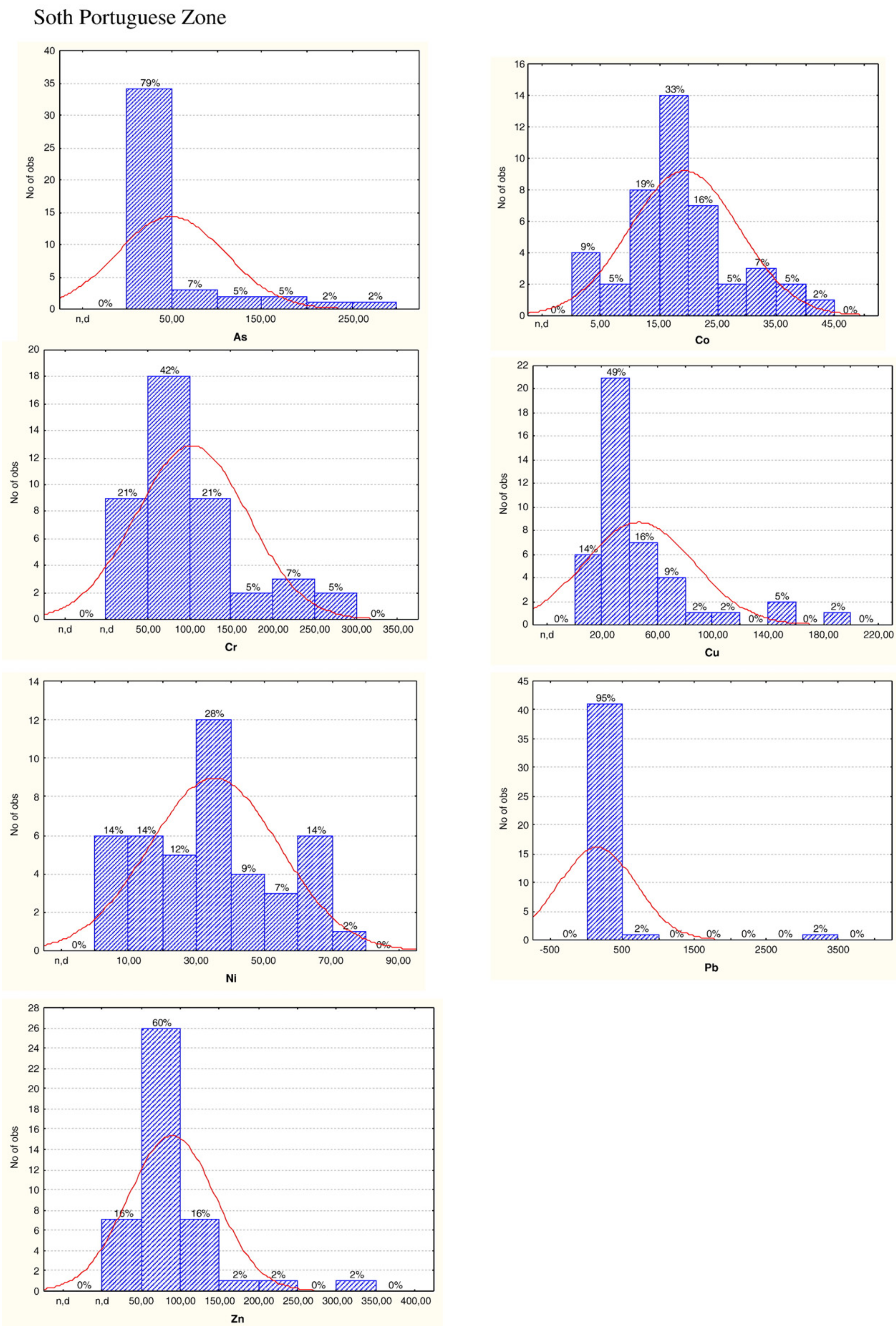

Fig. 5. (*continued*).

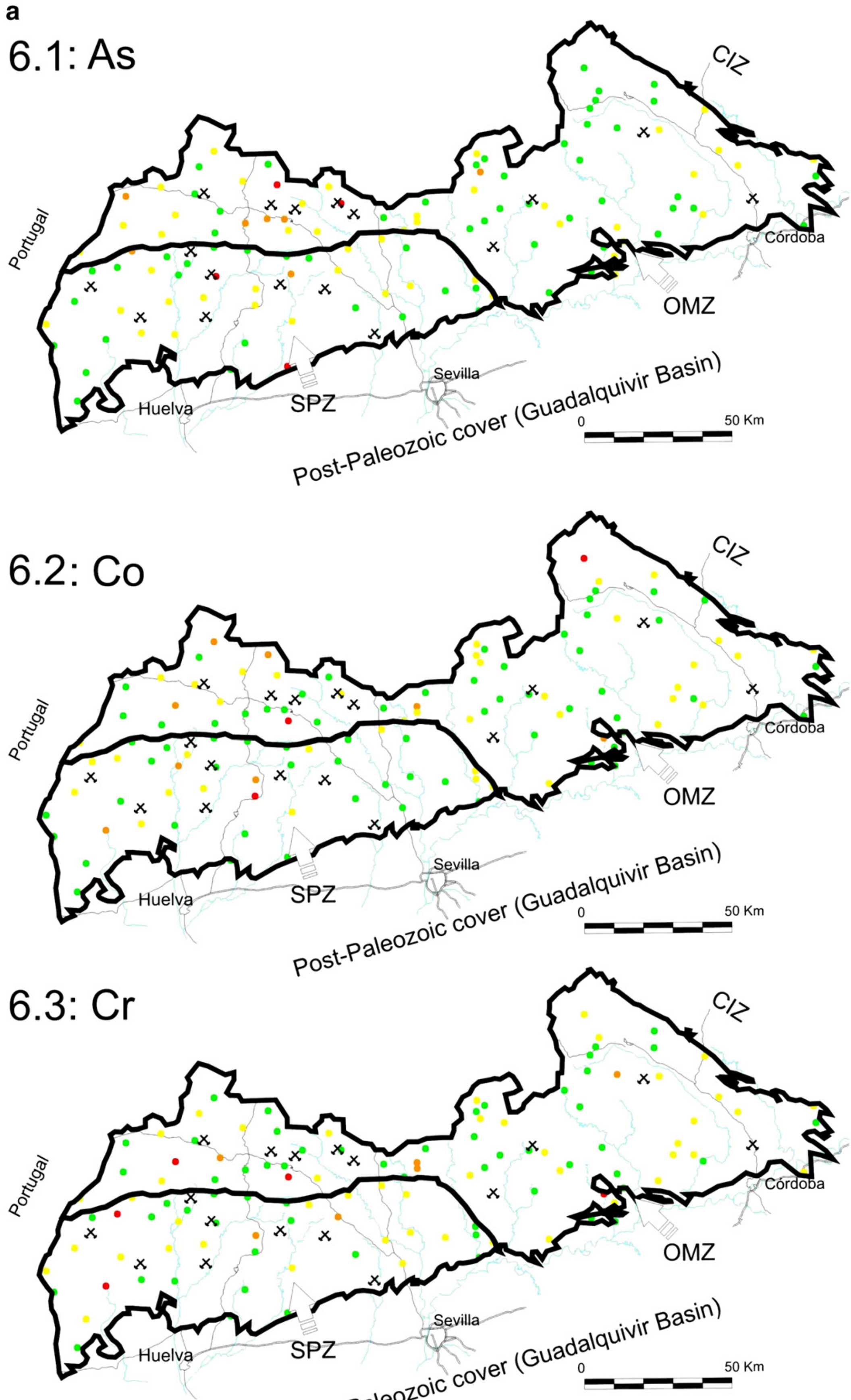

Fig. 6. Regional distribution of trace elements in topsoil. 6.1: As; 6.2: Co; 6.3: Cr; 6.4: Cu; 6.5: Ni; 6.6: Pb; 6.7: Zn.

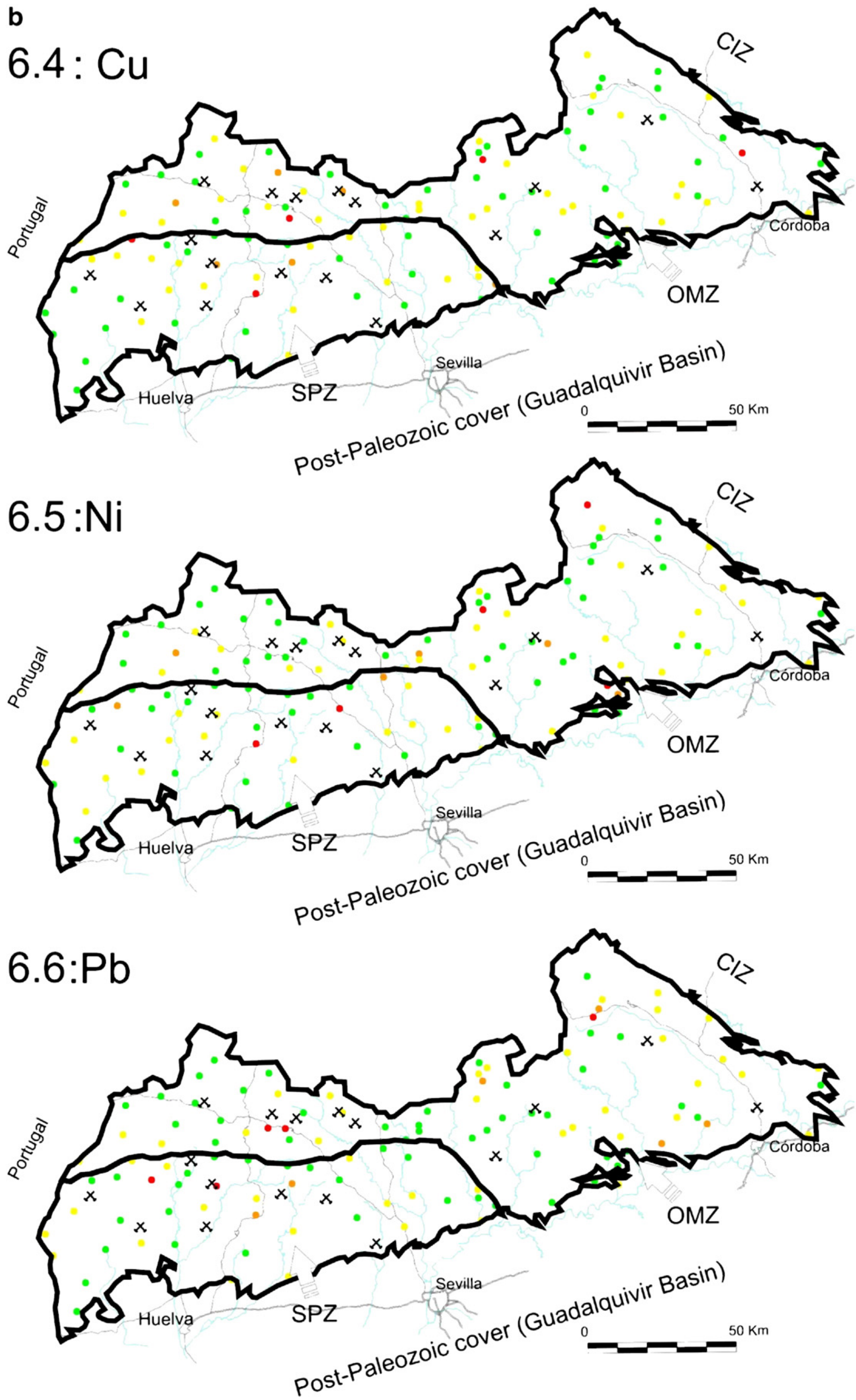

Fig. 6. (*continued*).

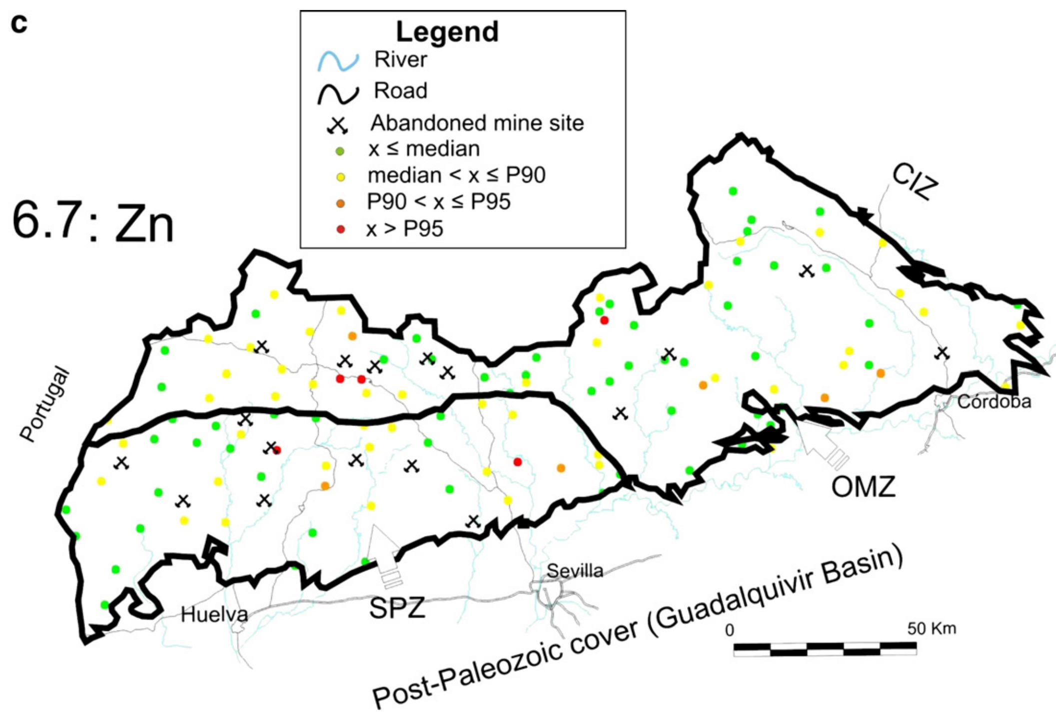

Fig. 6. (*continued*).

similar because they appear strongly correlated, with linear correlation coefficients as high as 0.77. On the other hand, the total Cu abundance varies within two orders of magnitude (from 7 to 728 mg kg^{-1}), with a median value of 27.5 mg kg^{-1}.

Finally, the total Pb content ranges from less than 3 mg kg^{-1} up to 284 (median value 32 mg kg^{-1}), while Zn also varies largely from less than 1 mg kg^{-1} up to 327 with a median of 78.5 mg kg^{-1}. Both elements are well correlated (r=0.60). The outliers and extreme values of such heavy metals are found over the lead–zinc metallogenic belts of the OMZ.

4.1.2. South-Portuguese Zone (SPZ)

The total As content varies from about 3 mg kg^{-1} to 262 mg kg^{-1}, with a mean value markedly higher (47.5 mg kg^{-1}) than that found in the OMZ (26.4 mg kg^{-1}). The highest As concentrations are recorded in the Leptosols of the Iberian Pyrite Belt, and they can be attributed not only to geogenic origin but probably also to diffuse mining activities.

In this zone, the medians for Co (19 mg kg^{-1}), Cr (95 mg kg^{-1}) and Ni (35 mg kg^{-1}) are similar to the corresponding values in the OMZ, and likewise they are well correlated with linear correlation coefficients up to 0.68. The total Cu concentration ranges between 10 to 191 mg kg^{-1}, with a median of 32 mg kg^{-1}. There is a strong positive correlation between Cu and As (r=0.63) reflecting the association of both elements in topsoil of the Iberian Pyrite Belt.

The median Pb content is about 38 mg kg^{-1}, although an extreme value as high as 3449 mg kg^{-1} was recorded for one sampling site, while the median Zn concentration is 76 mg kg^{-1}, with a range from 28 to 347. Unlike the situation in the OMZ, the abundances of Pb and Zn are not correlated in the topsoils of the SPZ.

4.2. Vertical distribution and relationship with parent rocks

Fig. 7 shows and compares the medians of trace elements concentrations in topsoil, subsoil and parent rocks. The differences between the median values for the topsoil and subsoil are generally small for Co, Cr, Ni and Cu, the average topsoil/subsoil ratio being close to unity. However, the

Table 4
Pearson's correlation matrix of trace elements content of top soils

		Ossa-Morena Zone						
		As	Co	Cr	Cu	Ni	Pb	Zn
South−Portuguese Zone	**As**		0.03	−0.01	0.26	−0.02	0.16	0.48
	Co	−0.23		**0.62**	0.21	0.58	−0.07	0.13
	Cr	0.02	0.55		0.17	**0.77**	−0.08	−0.04
	Cu	**0.63**	0.20	0.04		0.19	0.06	0.16
	Ni	−0.02	**0.68**	0.52	0.12		−0.03	0.07
	Pb	0.21	−0.12	−0.19	0.22	−0.18		**0.60**
	Zn	0.34	0.19	0.00	0.33	0.34	0.03	

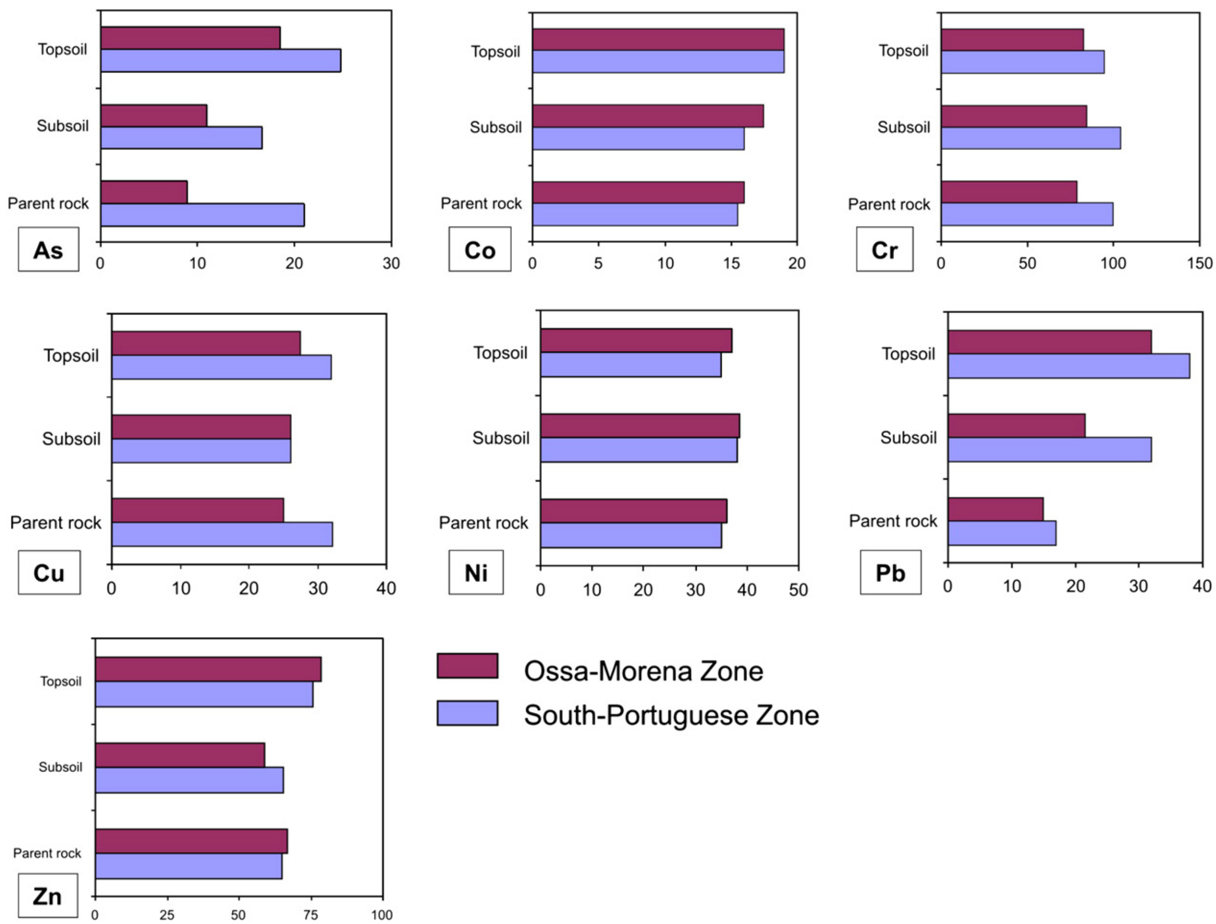

Fig. 7. Trace element distribution in topsoil, subsoil and parent rock of the Ossa-Morena Zone (OMZ) and South-Portuguese Zone (SPZ). The values correspond to median concentrations and are expressed in mg kg^{-1}.

concentrations of As and certain heavy metals like Pb and Zn show systematic enrichment in the topsoil as compared with the subsoil. In fact, As, Pb and Zn accumulate in the surface horizons, giving a topsoil/subsoil ratio of 1.68, 1.49 and 1.33, respectively, in the OMZ, while the respective values for the SPZ are 1.49, 1.18 and 1.16.

Table 5 lists the mean, median and standard deviation values for trace elements in the topsoils for the difference types of parent rock, while Fig. 8 compares the median concentrations according to the dominant rock type from which the soil derived. In both the OMZ and SPZ, the spatial distribution of Co, Ni, and specially Cr is clearly related to the occurrence of basic and ultrabasic rocks, although the soils derived from metasediments of the SPZ also show significant Ni concentrations. Similarly, the Cu content in the soils of the OMZ seems to be related to basic igneous rocks. On the other hand, the high Cu concentrations in topsoils of the SPZ are linked to the acid volcanic and volcano–sedimentary parent rocks, which gave rise to the massive sulphide deposits of the Iberian Pyrite Belt. The soils that derive from these acid igneous materials also show the highest abundances of As and Pb. However, in the OMZ the great abundance of As, Pb and Zn is shown by topsoils formed from weathering of carbonate rocks rather than igneous rocks or metasediments. There is a good spatial correspondence between the high concentrations of Pb, Zn and As in topsoils and the location of the lead–zinc metallogenic belts of the OMZ.

4.3. Threshold values and baseline levels

Table 6 shows for each trace element the number of anomalous samples detected in the topsoil of both zones which exceed the 95th percentile threshold values, the outliers and extreme values. Soil geochemical baselines (median values) of the background data set are given in Table 7, together with the corresponding values from Andalusia (Junta de Andalucía, 2004), the European Union (Salminen, 2005) and the world (Reimann and De Caritat, 1998).

4.3.1. Arsenic

In the OMZ, the threshold value (96 mg kg^{-1}) indicates a couple of anomalous samples of Leptosols derived from slates and metavolcanic rocks near ancient mining districts. The As threshold value of the SPZ (179 mg kg^{-1}) is almost twice that of the OMZ. The threshold is also exceeded in two sampling locations in the Iberian Pyrite Belt. The distribution of high values is related to sulphide ore occurrence and mining

Table 5
Mean, median and standard deviation values in topsoil according to parent rock lithology

Element (mg kg^{-1})	As	Co	Cr	Cu	Ni	Pb	Zn
Ossa-Morena Zone							
Metasediments (N=38)							
Mean	23.36	20.11	91.29	52.30	42.75	45.66	87.49
Median	18.45	18.50	84.00	29.00	38.50	34.51	77.00
Std. deviation	20.00	7.69	40.65	114.58	25.48	34.70	62.44
Carbonate rocks (N=11)							
Mean	34.00	15.91	71.64	48.63	40.06	74.87	144.80
Median	27.80	15.00	71.00	25.00	38.27	44.00	83.11
Std. deviation	26.73	8.15	34.64	55.77	23.62	77.41	162.53
Acid igneous rocks (N=11)							
Mean	16.45	16.18	63.18	18.55	24.36	94.09	107.55
Median	10.00	17.00	57.00	17.00	20.00	22.00	71.00
Std. deviation	19.21	6.94	36.30	8.81	13.58	176.13	115.71
Basic igneous rocks (N=12)							
Mean	31.83	36.83	112.75	70.03	44.51	22.13	113.01
Median	18.00	34.00	130.50	59.50	47.11	20.50	90.10
Std. deviation	53.17	14.39	66.05	48.09	21.34	10.14	65.47
South-Portuguese Zone							
Metasediments (N=24)							
Mean	45.15	17.96	97.75	38.10	38.19	46.24	85.41
Median	26.15	18.50	97.00	30.74	38.00	37.09	76.00
Std. deviation	52.12	7.39	29.99	26.90	15.33	39.49	44.32
Acid igneous rocks (N=12)							
Mean	64.66	17.29	65.23	69.35	24.73	416.26	94.23
Median	34.40	16.00	50.00	57.40	20.00	56.00	75.81
Std. deviation	78.67	11.99	56.23	57.40	20.38	986.82	85.44
Basic igneous rocks (N=7)							
Mean	30.28	23.37	167.55	29.55	38.02	34.74	78.30
Median	16.80	21.50	163.66	25.25	31.00	29.03	78.00
Std. deviation	47.38	8.79	113.32	16.93	25.12	34.30	27.18

activities. The high topsoil/subsoil ratio (up to 8.0) indicates that the anomalous concentrations are anthropogenic in origin. The topsoil baseline for As is 19 mg kg^{-1} in the OMZ and 25 mg kg^{-1} in the SPZ. These values clearly exceed the median As concentrations for soils of Andalusia (10 mg kg^{-1}), the European Union (7 mg kg^{-1}), and the world (5 mg kg^{-1}).

4.3.2. Cobalt

The threshold value for Co in the OMZ (49 mg kg^{-1}) is surpassed at two sampling sites, while only one is above the threshold in the SPZ (36 mg kg^{-1}). In all cases, the extreme values may have a geologic origin because they apply to soils developed on basic igneous rocks and metabasites with Co contents as high as 37 mg kg^{-1}. High Co concentrations in soil may also be due to adsorption and coprecipitation involving Fe and/or Mn from parent rocks rich in these metals or from mineralisation (Salminen and Tarvainen, 1997). The baseline value for Co is the same in both zones (19 mg kg^{-1}), but is also higher than that for Andalusia (12 mg kg^{-1}), the European Union (8 mg kg^{-1}) and the world (10 mg kg^{-1}).

4.3.3. Chromium

Three samples from the OMZ have Cr contents above the threshold value (182 mg kg^{-1}), while two anomalous samples from the SPZ have Cr contents greater than the threshold value (248 mg kg^{-1}). In both zones, the outlier values are related to basic intrusive and volcanic rocks, and other Cr-rich parent rocks, such as metabasites. Based on this geochemical relationship between Cr content in topsoil and specific lithology of the bedrock, it is likely that the Cr outliers have a geologic origin. The baseline level for Cr (83 mg kg^{-1} in the OMZ and 95 mg kg^{-1} in the SPZ) is slightly above that measured for the world soils (80 mg kg^{-1}), but greatly exceeds the values for soils of the European Union (60 mg kg^{-1}) and Andalusia (70 mg kg^{-1}).

4.3.4. Copper

The threshold value for Cu in the OMZ (143 mg kg^{-1}) is similar to that in the SPZ (147 mg kg^{-1}). In the OMZ, three anomalous samples have been identified in sites with different types of soil (Cambisols and Leptosols) and parent rocks (slates, limestones and amphibolites). In the SPZ, however, the high Cu contents of both topsoil and subsoil appear to be associated with acid volcano–sedimentary rocks. The Cu content of two anomalous samples of leptosols developed on acid tuffs and rhyolites of the Iberian Pyrite Belt surpasses the threshold values of the SPZ for topsoil and subsoil, indicating a probable relation with regional and local mineralisation. The median value of Cu in topsoil is 28 mg kg^{-1} in the OMZ and 32 mg kg^{-1} in the SPZ. These baseline levels are also above the median of the Cu concentrations in soils of Andalusia (24 mg kg^{-1}), the European Union (13 mg kg^{-1}) and the world (25 mg kg^{-1}).

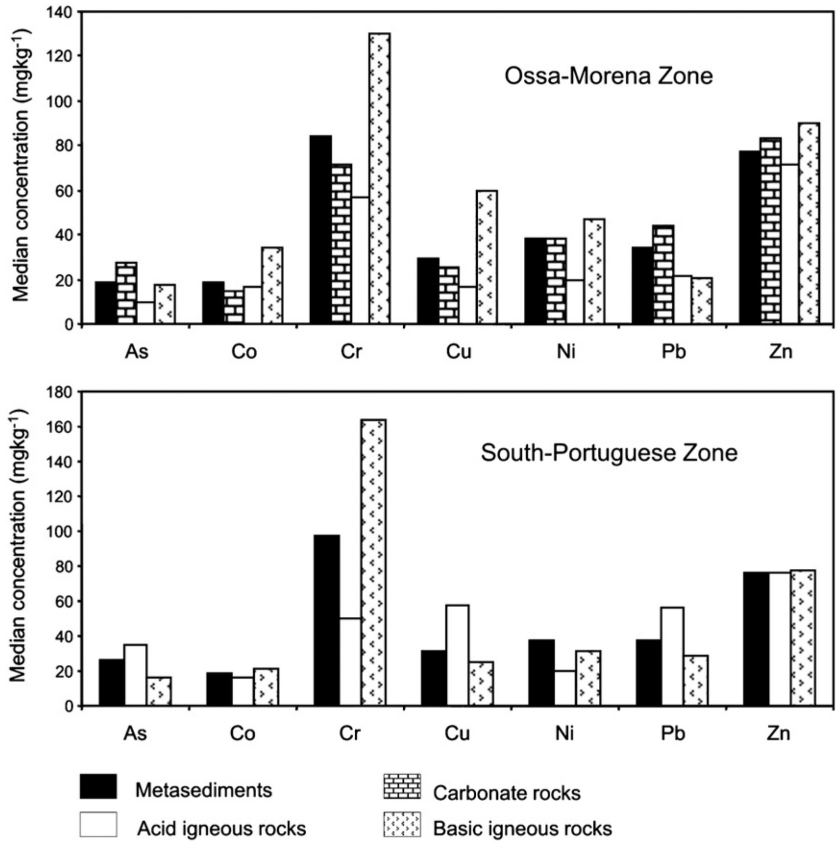

Fig. 8. Trace element distribution in topsoil according to lithology of the rock from soil derived.

4.3.5. Nickel

The threshold values for Ni in the OMZ (73 mg kg^{-1}) and SPZ (63 mg kg^{-1}), exceed those found in three and two sampling sites, respectively. In both zones, the anomalous samples came from different soil groups (Cambisols, Leptosols and Luvisols) derived from basalts, gabbros, metasediments and carbonate rocks. In most of these sampling sites, the topsoil/subsoil ratio is low (<1), indicative of a lithological origin. The baseline levels for Ni (35 mg kg^{-1} in the OMZ and 37 mg kg^{-1} in the SPZ) are well above those for soils of the world (20 mg kg^{-1}) and the European Union (18 mg kg^{-1}), and slightly exceed the regional "background" value for the Andalusian soils (29 mg kg^{-1}).

4.3.6. Lead

The study area records similar threshold values for Pb in the OMZ (200 mg kg^{-1}) and the SPZ (205 mg kg^{-1}). The extreme values (in excess of the thresholds) are given by three topsoil samples from the OMZ and two samples from the SPZ. The OMZ samples are Cambisols developed on carbonate and metavolcanic rocks hosting Pb–Zn-(Ag) stratabound mineralisations, while the SPZ samples are Leptosols derived from acid volcano–sedimentary materials of the Iberian Pyrite Belt. The maximum Pb concentration (3449 mg kg^{-1}) was observed for a SPZ sample. The topsoil/subsoil ratio of about 300 is indicative of pollution from mining operations. By excluding these from validated data set, a baseline level of 32 mg kg^{-1} was derived for

Table 6
Threshold values and number of anomalous samples

Element (mg kg^{-1})	Ossa-Morena Zone (OMZ)	South-Portuguese Zone (SPZ)	Anomalous samples	
			OMZ	SPZ
As	96	179	2	2
Co	49	36	2	1
Cr	182	248	3	2
Cu	143	147	3	2
Ni	73	63	3	2
Pb	200	205	3	2
Zn	327	173	3	2

Table 7
Geochemical baselines of trace elements in the study area and some reference median values reported for Andalusia, European Union and worldwide soils

Element (mg kg^{-1})	As	Co	Cr	Cu	Ni	Pb	Zn
This study							
South-Portuguese Zone	25	19	95	32	35	38	76
Ossa-Morena Zone	19	19	83	28	37	32	79
Andalusian soils[1]	10	12	70	24	29	24	56
European Union soils[2]	7	8	60	13	18	23	52
World soils[3]	5	10	80	25	20	17	70

1. Junta de Andalucía (2004); 2. Salminen (2005); 3. Reimann and De Caritat (1998).

the OMZ, and 38 mg kg^{-1} for the SPZ. These values exceed the "backgrounds" estimated for soils of Andalusia (56 mg kg^{-1}), the European Union (52 mg kg^{-1}), and the world (70 mg kg^{-1}).

4.3.7. Zinc

The threshold value for Zn in the OMZ (327 mg kg^{-1}) is quite distinct from that in the SPZ (173 mg kg^{-1}). The extreme Zn concentrations in the OMZ (up to 448 mg kg^{-1}) occur at the top of the soils developed on limestones and metavulcanites, while in the SPZ (up to 347 mg kg^{-1}) they are recorded in topsoil derived from parent materials belonging to the volcano–sedimentary complex of the Iberian Pyrite Belt. The topsoil/subsoil ratio varies widely between 3.6 and 9.4 in the OMZ, and from 0.8 to 2.7 in the SPZ. The origin of this Zn enrichment seems to result from sulphide mineralisation and anthropogenic pollution due to mining. The baseline levels are similar (79 mg kg^{-1} in the OMZ and 76 mg kg^{-1} in the SPZ), and exceed the median Zn concentrations in soils of Andalusia (56 mg kg^{-1}), the European Union (52 mg kg^{-1}) and the world (70 mg kg^{-1}) soils.

5. Conclusions

The soils developed on crystalline rocks of the southern Iberian Massif are characterized by geochemical baselines with high concentrations of potentially toxic trace elements. The median concentrations of some elements are well above those of the regional baseline for soils of Andalusia, the European Union and the world, particularly for As (25 mg kg^{-1}), Cu (32 mg kg^{-1}) and Pb (38 mg kg^{-1}) in the SPZ, and for Zn (79 mg kg^{-1}) in the OMZ.

Parent rock lithology and mineralisation seem to be the main factors influencing the abundance and distribution of trace elements. Significant enrichments of Co, Cr and Ni are observed in soils derived from basic and ultrabasic rock throughout the survey area. The highest concentrations of the remaining elements are found in soils derived from acid igneous rocks of the SPZ (median values: 34 mg kg^{-1} of As, 56 mg kg^{-1} of Pb and 57 mg kg^{-1} of Cu) and those developed on carbonate rocks of the OMZ (median values: 28 mg kg^{-1} of As, 44 mg kg^{-1} of Pb and 83 mg kg^{-1} of Zn). These parent materials are regarded as a metallotect for the volcanic-hosted massive sulphide (VHMS) deposits of the Iberian Pyrite Belt and for some base-metal, Pb–Zn sedimentary exhalative (SEDEX) deposits of the OMZ, respectively. In some sites the concentrations of trace elements are significantly greater than the calculated threshold values. This may be ascribed to anthropogenic pollution, especially in old mining areas where it is difficult to distinguish human-induced pollution from natural mineralisation.

Soil baseline values not only depend on the geochemical nature of the parent rocks, but also reflect the existence of well-known metallogenic belts. This research illustrates the importance of regional geology with regard to sampling design for purposes of determining soil geochemical baselines.

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