Geoderma 193–194 (2013) 265–274

Contents lists available at SciVerse ScienceDirect

Geoderma

journal homepage: www.elsevier.com/locate/geoderma

Sources, background and enrichment of lead and other elements: Lower Guadiana River

Maria J. Batista [a,*], D.P.S. de Oliveira [a,e], Maria M. Abreu [b], J. Locutura [c], T. Shepherd [d], J. Matos [a], A. Bel-Lan [c], L. Martins [a]

[a] LNEG, Unidade de Recursos Minerais e Geofísica, Ap. 7586, 2721-866 Alfragide, Portugal
[b] ISA-Dep. Ciências do Ambiente, Univ. Técnica de Lisboa, Tapada da Ajuda, 1349-017 Lisboa, Portugal
[c] Intituto Geologico e Minero the España, R. Rio Rosas, Madrid, Spain
[d] GEOMEDIC, Nottingham, UK
[e] CREMINER, Universidade de Lisboa, Ed. C6, Piso 3, Campo Grande, 1749-016 Lisboa, Portugal

ARTICLE INFO

Article history:
Received 18 July 2011
Received in revised form 5 July 2012
Accepted 27 August 2012
Available online 20 November 2012

Keywords:
Sources
Enrichment
Lead

ABSTRACT

The lower sector of the Guadiana River Basin, located in southern Portugal and Spain, hosts soils and plants with elevated Pb, Cu and As near former and current mining sites. Two geogenic and two anthropogenic sources of Pb were identified where elevated concentrations are mostly related to the occurrence of sulphide-rich ore deposits, Volcanic Sedimentary formations and mining. These were generally reflected by the multiple regression analysis (MRA) and confirmed by isotope determinations. Nevertheless, caution was needed in interpreting statistical and isotopic results; therefore the combination of both techniques was important. Elements, such as Ca, Na, Cu and As, show enrichment in soil developed on shale, sandstone and conglomerate of Upper Devonian age belonging to the Phyllite-Quartzite Group. Lead exhibits an enrichment in soil developed on felsic volcanic rocks from the Volcanic Sedimentary Complex (VSC) of Upper Devonian-Lower Carboniferous age, which has been identified by the relationship between topsoil median values of different lithologies and grand subsoil median values. In the same soil, Fe, As, Co, Ni and Cr are depleted. Translocation of Pb to the aerial parts of plants is insignificant in all three plant species studied and analysed (*Cistus ladanifer* L., *Thymus vulgaris*, *Lavandula luisieri*). High Pb concentrations in soil, where *Cistus ladanifer* L. developed, the only representative number of species analysed, do not correspond generally to elevated Pb contents in plants, except near mine sites, where lower pH of soil, increases Pb bioavailability. The different statistical methodologies combined with Pb isotopic studies were successfully applied in the identification of Pb sources in soil and *Cistus ladanifer* L. plant of the Lower sector of Guadiana River basin. Therefore, rocks, mineralisations, subsoil, topsoil and plant processes were successfully integrated to understand the migration of Pb into the food chain.

1. Introduction

The Iberian Pyrite Belt (IPB) is one of the most outstanding European ore provinces, hosting one of the largest concentrations of massive sulphides in the Earth's crust and has a long and rich mining history. Due to its richness in base metals, related to the geological environment that hosts the mineralisation, the soil developed in this region contains high concentrations in the same base metals. Background values are in principle associated with the pristine soil concentrations, little affected by human activities (Cheng et al., 1999; Garrett, 2005; Levinson, 1980; Stanley and Noble, 2007; Ziaii et al., 2009). The long period of mining and smelting activities of IPB pose difficulties in identifying the origin of base metals in the soils. The aim of this study is to utilise different methodologies to define the sources of metals in soils and plants, by analysing different sample media ranging from rocks, mineralisations, soils and three species of plants (*ladanifer* L., *Lavandula luisieri* and *Thymus vulgaris*).

Volcanic hosted massive sulphide (VHMS) Cu–Pb–Zn is one typical host deposit for Pb that is common in the IPB (Tornos, 2006). The Lower sector of the Guadiana River basin in southern Portugal and Spain includes the IPB, composed mainly of metasedimentary and volcano-sedimentary rocks that host the orebodies. Lead was exploited, but it was occasionally left in dumps at the mines when market values were low (Batista et al., 2008).

Lead sulphides oxidise relatively slowly, when exposed to the surface environment, during meteoric alteration, resulting in a release of Pb that can then be incorporated and/or adsorbed onto clay-rich

---

* Corresponding author. Fax: +351 214718980.
E-mail address: joao.batista@ineti.pt (M.J. Batista).

0016-7061/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.geoderma.2012.08.033

minerals, iron and manganese oxides, carbonates and arsenates, and soil organic matter becoming insoluble (Alloway, 1995; Callender, 2004; Figueiredo and Silva, 2011; Levinson, 1980; Pereira et al., 2007). According to Adriano (2001), manganese oxides appear to be more efficient absorbers of Pb than iron oxides. However, Johnson (1990) and Rodda et al. (1996) associated Zn and Pb adsorption to goethite, Lai et al. (2006) related Pb adsorption to goethite dependence on temperature and pH, whereas Nelson et al. (1999), Tebo et al. (2004) and Ulrich (2007) reported that Pb, and other metal ions, can be absorbed by biogenic manganese oxides and become immobile. Lead also seems to be found in high concentrations in organic matter rich soils (Kabata-Pendias and Pendias, 2001; Vreca et al., 2001). Lead mobility in near-surface oxidising environments is generally low and null in reducing environments where sulphides, such as galena, form. In acidic environments, exchangeable forms with higher mobility may occur (Sierra et al., 2007; Turpeinen et al., 2000). Laboratory tests carried out on contaminated soil show that available Pb can increase in these situations up to 0.13% (Alloway, 1995; Pereira et al., 2007). Lead in divalent form exhibits isomorphic substitutions with K^+ in the structure of feldspar and micas, with Ca^{2+} in feldspar, pyroxenes and phosphates, and with Fe and Mn in oxides (Sposito, 2008). Lead also substitutes for Ba and Sr in mineral structures or adsorption sites at their surface (Kabata-Pendias and Pendias, 2001).

The mechanisms of accumulation of metals in plants involve extracellular and intracellular chelation, precipitation and translocation and are dependent upon the location, bedrock, climate and most of all upon the plant species (Memon et al., 2001). Of the naturally occurring elements, over 25 are considered essential to plants, whereas elements such as Cd and Pb have not a clear biological benefit and may be considered as contaminants to plants (Kabata-Pendias and Pendias, 2001). However, some plants may adapt to adverse conditions, such as mining sites, and uptake, with no apparent damage, elements such as Pb up to 500 mg kg^{-1} in soil as is the case of *Amaranthus blithoides*, *Cynodon dactylon*, *Cichorium intybus* and *Sylibum marianum* at Aznalcóllar mine (Del Río-Celestino et al., 2006). These plants commonly uptake very little Pb and when it occurs, Pb stays in the roots (Barriquelo et al., 2003; Hagberg and Löfgren, 2007), because very little is, in general, available to uptake from natural concentrations in soil (Sharma and Sahi, 2006).

In this study, sampling and chemical analysis of soils, three species of plants (*Cistus ladanifer* L., *Lavandula luisieri* and *Thymus vulgaris*), rocks and mineralisations were undertaken to quantify Pb distributions. The background, enrichment and depletion of Pb in soils were determined by examining the ratio of median element concentration in topsoils of different lithologies to median values in the subsoil. Multiple Linear Regression was performed to understand element groupings in soil in relation to parent lithologies, mineralisations or other likely sources. To confirm statistical conclusions Pb isotopes were also determined.

Spatial correlation between soil–Pb and plant-Pb enrichment was established to observe the relationship of Pb in soil and plants. This was made by calculating translocation coefficients and relative enrichment in soil, obtained by the ratio between top- and sub-soil. Bi-plot diagrams were plotted to confirm if the Pb concentrations were different in soil and plants in relation with the different parent materials.

2. Geographical, geomorphological and geological setting

The source of the Guadiana River is in the Ruidera lagoons in the Campo de Montiel plain at 1700 m a.m.s.l. and flows along 801 km, where the last 110 km form the border between Portugal and Spain. Within Spain the Guadiana River catchment trends in an E–W direction, whereas in Portugal has a N–S direction. From the morphological point of view the river divides itself in 5 distinct sections: Alto Guadiana or Ruidera lagoons, the Miocene age Mancha plain, "Monte do Toledo", Central Extremadura and finally the Portuguese section (Feio, 1951). The study area is located in the latter section of the catchment basin, which is orientated N–S, until the mouth of the river (Fig. 1.). The Guadiana River Basin occupies a total area of 66,850 km^2 in both Spain and Portugal, of which 8350 km^2 include part of the IPB.

The IPB is characterised by the presence of a relatively simple geological record with a sequence that includes about 1000 to 5000 m of Late Palaeozoic rocks and the study area contains Lower Devonian to Neogene age rocks. The oldest, the Pulo do Lobo Group, is made up of sandstone, schist and turbiditic sequences. Overlying the Pulo do Lobo Group is the Phyllite-Quartzite (PQ) Group (Upper Devonian age), which consists of a monotonous detrital sequence of alternating mudstone and sandstone, with features typical of a stable epicontinental platform (Leistel et al., 1997; Ribeiro et al., 1990; Tornos, 2006). In the Spanish sector of the study area, the Upper Devonian is also represented by the Atalaia and Duque formations. The PQ Group is overlain by the Volcanic Sedimentary Complex (VSC; Upper Devonian to Lower Carboniferous age) that includes a complex mafic–felsic volcanic sequence interbedded with mudstone and sediments, and hosts the massive sulphide deposits. Both Devonian sequences are overlain by non-mineralised Carboniferous shale and sandstone of the Culm Sequence that covers most of the southern part of the Lower Guadiana Basin.

Near the Guadiana River mouth the Palaeozoic formations grade into sediments of the Meso-Caenozoic Algarve basin represented locally by Triassic sandstone and volcanic rocks, Jurassic limestone, Miocene sandstone, dune sands and Holocene beaches and wetlands. From Ayamonte to Huelva the Palaeozoic rocks are covered by detrital sediments of Tertiary-Quaternary age (Leyva and Ramirez, 1979; Salazar Rincón, 2006). Of these detrital sediments, the thin Vermelha formation, consists of low angle alluvial cones trending in a general ENE-WSW orientation. The source of these sediments, which have been deposited along the Cadiz Gulf due to marine currents regime (Leyva and Ramirez, 1979; Salazar Rincón, 2006; Fig. 1), may be from the nearby IPB or further upstream. Soils in this region were classified as Leptosols meaning that they have low organic carbon, small thickness and an important direct relationship with the bedrock, therefore, with little soil-forming processes developed (Carvalho Cardoso, 1965).

3. Methodology

Soil and vegetation sampling was carried out in three areas on the west side of the basin, in Portugal, and in one large area on the east side of the basin, in Spain. To observe if the areas were uniformly sampled in each sub-area a χ^2 test was performed. The test verified that the observed points correspond to the sampling sites. The sub-areas, divided in equal parts, were expected to have the same sampling sites. This calculation is given by Davis (1986):

$$\chi^2 = \sum \frac{(O-E)^2}{E} \tag{1}$$

O Number of observed sites;
E Number of expected sites given by the formula: E = total of sampling sites/number of sub areas

Degrees of freedom is ν

$$\nu = (T-2) \tag{2}$$

For two degrees of freedom, the number of sub-areas were 232 km^2, 97 km^2 and 400 km^2 in Portugal, and 900 km^2 in Spain,

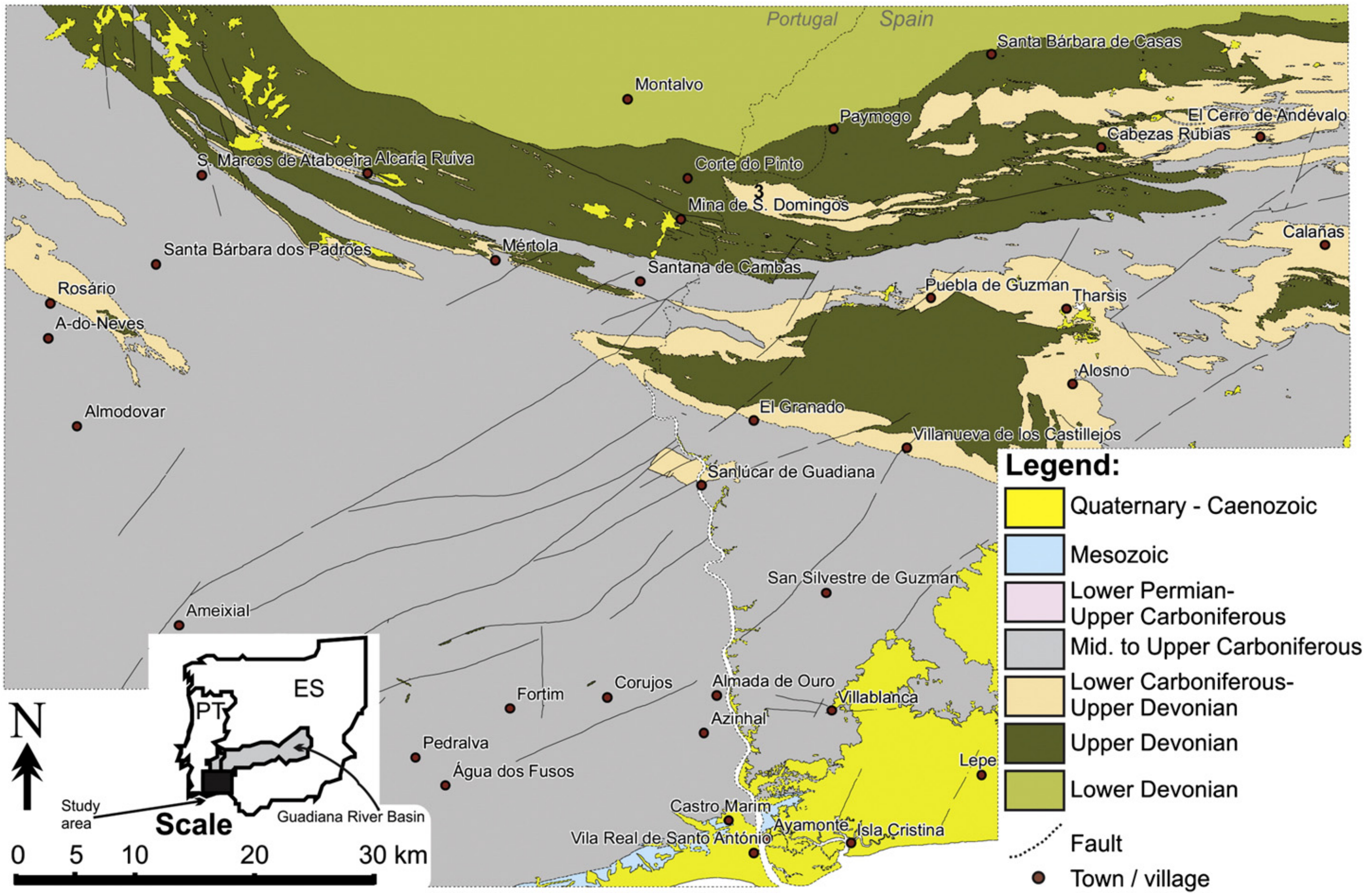


Fig. 1. Geological map of the Lower Sector of Guadiana Basin.

and the critical value is 5.99 at the 95% confidence level. In this case, the soil sampling density was 1 sample per 5 km^2, and covered uniformly all areas, and estimated χ^2-values do not exceed the critical value. Sampling of the topsoil 0–20 cm was carried out at 353 sites, and at 66 of these sites, where the soil profile was deep enough for subsurface sampling, subsoil samples were collected from a depth of 20–40 cm.

Three species of plants (*Cistus ladanifer* L., *Lavandula luisieri* and *Thymus vulgaris*) were chosen for study, because they are common in the field area and are used as animal or human food. The *Cistus ladanifer* L. plants (aerial parts and roots) were sampled at 137 locations in the areas of the Guadiana River basin in Portugal and Spain. Nine *Lavandula luisieri* (Rozeira) Rivas-Martinez plants were sampled in the same areas in Portugal and 3 *Thymus vulgaris* L. plants in Spain. In order to quantify the Pb and other element concentrations, 16 bed rock samples from the main IPB formations, 13 sulphide mineralisation samples were collected from the major ore deposits (São Domingos in Portugal; Cabezas de Pasto, Romanera, Lagunazo, Isabel Mn, Cármen 1 and 2, Herrerias, Sierrencilla Matutera and Vuelta Falsa-Trimpancho in Spain).

Chemical analysis of samples of rock and mineralisation (after milling in a agate ring mill), soil (after drying below 40 °C, sieving to less than 2 mm and milling) and plants (after drying, milling and ashing) was carried out in Activation Laboratory Ltd., Canada, by Instrumental Neutron Activation Analysis (INAA) and quantified in mg kg^{-1} (As, Au, Ba, Br, Ce, Co, Cr, Eu, Fe, Hf, Hg, Ir, La, Lu, Na, Nd, Rb, Sb, Sc, Se, Sm, Sn, Ta, Th, Tb, U, W, Yb), and Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES), following digestion by $HCl + HNO_3 + HF + HClO_4$ acid and quantified in mg kg^{-1} for the elements [Ag, Al(g kg^{-1}), Be, Bi, Ca(g kg^{-1}), Cd, Cu, K(g kg^{-1}), Mg(g kg^{-1}), Mn, Mo, Ni, P(g kg^{-1}), Pb, S(g kg^{-1}) Sr, Ti(g kg^{-1}), V, Y, Zn]. Results from plant analyses were converted back to dry weight. Soil samples were further characterised by the determination of pH in the proportion of 1 part of water per 2.5 potassium chloride. Total organic carbon (TOC) (Póvoas and Barral, 1992), exchange cations (Na, K, Mg, Ca, Mn), cation exchange capacity (CEC) and percentage of saturation of the exchangeable complex (BS%) using ammonium acetate at pH = 7 were also determined.

Lead isotopes were determined on a few samples of both soil and plants. Soil samples were chosen from different lithologies and plants analysed were only *Cistus ladanifer* L., because these plants were the most representative (137 samples in the study area). The isotope compositions were measured on a Finnigan MAT 'Neptune' ICP-multi-collector mass spectrometer and are reported as $^{208}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$, $^{206}Pb/^{204}/Pb$, $^{208}Pb/^{206}Pb$ and $^{207}Pb/^{206}Pb$ ratios. Data were corrected for mass discrimination using Tl as an internal standard (Ketterer et al., 1991). Mean analytical uncertainties (2σ) were 0.015%, 0.015%, 0.016%, 0.004% and 0.003%, respectively. It was necessary to compile information from literature about sulphide mineralisation isotope ratios (Marcoux, 1998) in order to compare with the determinations on soil, rock and plant samples of this study. Lead isotopes were only determined on topsoil samples; it was assumed that the source of Pb in subsoil was the bedrock. Fig. 2A and B show the Pb isotope diagrams of sources in rocks and mineralisations, compiled from Marcoux (1998), with Pb isotope determinations on topsoil and on *Cistus ladanifer* L. plants, respectively.

Quality control for soil chemical analyses consisted of analytical replicates, where there is no significant deviation between original and replicate measurements (ratio between 0.8 and 1.2). Certified Reference Materials (CRMs) were used for INNA analysis (DMMAS),

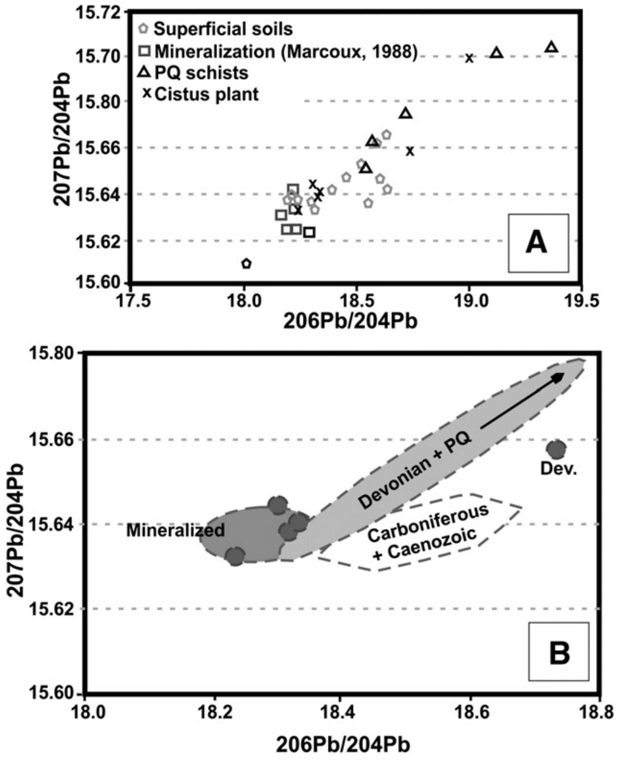


Fig. 2. Isotopic relationship of $^{206}Pb/^{204}Pb$ vs. $^{207}Pb/^{204}Pb$ in (A) samples of superficial soils and *Cistus ladanifer* L. plants in relation to both rocks and mineralisation; (B) Cistus plant samples projected in the geological domains.

where six repetitions were made and the accuracy (1) was higher (R<5%) for Au, As, Co, Cr, Fe, Sc, La, Sm.

$$R_r\% = \left|\frac{\mu-\bar{X}}{\mu}\right| \times 100 \qquad (3)$$

Where:

μ	standard value given by the laboratory,
$\bar{X}$	mean of determinations;

Quality control for ICP-OES analysed elements was determined with several reference materials, each analysed one time. The ratio between certified value and measured value was good (0.85–1.1) for all elements, except Al and P and elements, such as Ag, Cd, Bi, Be and Mo with low concentrations were not considered due to below detection limit values measured in the reference materials. In Method Blank analyses no value was reported equal or above detection limit. Median, minimum and maximum concentrations (Table 1) were examined in all sample media: topsoil, subsoil, shoots and roots of plants of Cistus (136 specimens collected), whereas samples of Lavandula (n = 7) and Thymus (n = 3) plants, respectively, were not summarised due to their small number.

Background element concentrations in topsoil and subsoil (Table 2) were adapted from Van der Veer (2006), using the appropriate lithological median value for each site in case of topsoil, and grand median for subsoil per chemical element. The reason for this distinction was based on the fact that topsoil is more influenced by microbiology, climate, erosion and human influence than subsoil, and differ from lithology to lithology. While subsoil is more directly related to parent material, so the grand median was used. Enrichment and depletion of elements in soil were calculated using the ratio between topsoil median of the different lithologies and grand median of subsoil (Table 3). Soils developed on post-Palaeozoic sediments in the southern part of the basin near the mouth, were excluded from these studies of background and enrichment to avoid other anthropogenic influence.

Multiple Linear Regression was performed to establish the relationship between groups of chemical elements with the soil parent material. The regressors (dependent variables) were the set of elements, described above, except Al, Ba, Fe, K and Mg, considered as predictors (independent variables), due to the fact that they are generally almost constant in lithologies (Grimes and Carvalho, 1994; Grimes and Kropschot, 1998; Richards, 1995; see Fig. 3). The selection of these variables was tested empirically, to avoid multi-collinearity problems and were considered non-redundant. Cross-validation was also tested, because the same variables were used in topsoil and subsoil sets, and the results were consistent. The coefficient of determination (R^2) is below 0.7, indicating a low correlation with the predictors, assuming that the origin may be caused by other than natural variation.

Translocation of Pb in different plant species was estimated as the translocation factor (TF): TF = [Me] outer part/[Me] root (Kovalevskii, 1979), and it is shown in Fig. 4. On the same figure, it is possible to observe the relative enrichment between topsoil and subsoil.

Biplots were used to determine the relationship between topsoil Pb concentrations and the aerial parts and roots of the Cistus plants. Only Cistus plants were used once again, due to their representative number (Fig. 5).

4. Results and discussion

4.1. Quantification of Pb and other chemical elements in lithologies, mineralisations, soils, and in the native plant species

The mineralisations that occur in S. Domingos, Cabezas de Pasto, Romanera, Lagunazo, Cármen 1 and 2, Herrerias, Sierrencilla Matutera e Vuelta Falsa-Trimpancho had high concentrations of S (between 15% and more than 20%), Cu (between 336 mg kg^{-1} and more than 10,000 mg kg^{-1}), Pb (between 1078 mg kg^{-1} and more than 5000 mg kg^{-1}), Zn (between 1886 mg kg^{-1} and more than 10,000 mg kg^{-1}) and Au was also present. High concentrations of Pb were detected in the purple and black shales of the VSC, 96 mg kg^{-1} and 52 mg kg^{-1}, respectively. These values exceed, in general, the accepted values corresponding to the average abundance of Pb in the crust (12.5 mg kg^{-1}) and metasediments (20 mg kg^{-1}) (Levinson, 1980). Also the PQ group and Mn formation in the Spanish sector of the study area had high concentrations of Pb (63 mg kg^{-1}), suggesting a radiogenic origin (Ketterer et al., 2010). The PQ group, represented by the schist-rich Puebla de Gusman antiform, outcrops more in the Spanish than in the Portuguese sector. These formations, according to the radiometric surveys, carried out in the IPB (Sociedade Mineira Rio Artézia, 1992), show a more important radiogenic signature.

The highest concentrations of Pb, higher than 5000 mg kg^{-1}, were reported for the Cu–Pb–Zn massive sulphide ore samples from the abandoned mines of Cabezas del Pasto, Romanera and Serrencillas. In the stockwork mineralisation at S. Domingos the concentration of Pb reaches 862 mg kg^{-1}. However, the scarcity of samples analysed precludes a thorough characterisation of the sulphide mineralisations of the IPB. Although massive sulphide concentrations of Pb are highly variable within the IPB, as stated in Tornos et al. (2005), they are nevertheless coincident with the results presented here.

The highest concentrations of Pb in plants were found in the roots of the three studied species, a finding that is in accordance with previous studies (Adriano, 2001; Barriquelo et al., 2003). Lavandula plants were found to contain the highest Pb concentrations, whereas Thymus plants the lowest. The concentrations of Pb in the aerial parts (stems and leaves) were 25 to above 5000 mg kg^{-1} and 11 to 15 mg kg^{-1} in *Lavandula luisieri* (Rozeira) Rivas-Martinez roots and

Table 1
Median, minimum, and maximum element concentrations in topsoil, subsoil and aerial and root parts of *Cistus ladanifer* L. plant (concentrations in mg kg^{-1}, except where otherwise indicated).

Parameter	Topsoil			Par.	Subsoil			Par.	Cistus plant aerial parts			Cistus plant roots		
	Median	Min.	Max.		Median	Min.	Max.		Median	Min.	Max.	Median	Min.	Max
Au (μg kg^{-1})	2.00	2.00	763.00	Au	2.00	2.00	1060.00	Au	17.00	1.00	97.00	1.00	1.00	109.00
Ag	0.40	0.30	16.40	Ag	0.30	0.30	33.00	Ag	0.40	0.30	0.90	0.30	0.30	1.10
Cu	28.00	3.00	1190.00	Cu	27.00	3.00	1050.00	Cu	90.00	48.00	432.00	74.00	42.00	332.00
Cd	0.30	0.30	8.10	Cd	0.30	0.30	0.90	Cd	3.40	0.40	23.20	2.50	0.15	15.90
Mo	1.00	1.00	9.00	Mo	1.00	1.00	6.00	Mo	2.00	0.50	5.00	0.50	0.50	9.00
Pb	25.00	5.00	25700.00	Pb	23.00	9.00	5000.00	Pb	12.00	3.00	308.00	28.00	3.00	982.00
Ni	40.00	2.00	450.00	Ni	36.50	2.00	116.00	Ni	61.00	11.00	270.00	25.00	4.00	94.00
Zn	66.00	9.00	2940.00	Zn	63.00	11.00	622.00	Zn	729.00	321.00	2230.00	309.00	165.00	1210.00
S (%)	0.01	0.01	3.30	S	0.01	0.01	3.48	S	0.54	0.32	1.22	0.17	0.09	0.50
Al(%)	2.91	0.71	7.66	Al	3.60	0.85	15.00	Al	0.79	0.24	2.68	1.20	0.27	4.18
As	17.80	1.60	2570.00	As	15.15	4.20	2820.00	As	3.20	0.50	56.80	4.90	0.50	70.60
Ba	500.00	<50.00	1310.00	Ba	400.00	50.00	950.00	Ba	290.00	25.00	1760.00	280.00	50.00	1700.00
Be	2.00	1.00	5.00	Be	2.00	1.00	3.00	Be	0.50	0.50	4.00	0.50	0.50	2.00
Bi	2.00	2.00	98.00	Bi	2.00	2.00	181.00	Bi	1.00	1.00	5.00	1.00	1.00	4.00
Br	3.30	0.50	12.80	Br	2.95	0.50	14.40	Br	45.30	7.10	174.00	8.00	2.80	21.60
Ca(%)	0.12	0.02	4.57	Ca	0.10	0.02	2.63	Ca	19.00	7.83	30.00	26.90	4.73	34.10
Co	17.00	<1.00	68.00	Co	13.50	3.00	36.00	Co	19.00	5.00	210.00	9.00	1.00	49.00
Cr	79.00	2.00	661.00	Cr	65.50	19.00	408.00	Cr	18.00	2.00	47.00	23.00	2.00	223.00
Cs	5.00	<1.00	11.00	Cs	4.00	1.00	10.00	Cs	2.00	0.50	7.00	2.00	0.50	7.00
Eu	1.30	0.20	2.50	Eu	1.00	0.20	2.40	Eu	0.10	0.10	0.90	0.40	0.20	1.80
Fe(%)	3.92	0.72	12.20	Fe	3.43	0.81	11.10	Fe	0.70	0.17	4.34	0.86	0.14	10.70
Hf	5.00	3.00	15.00	Hf	5.00	2.00	12.00	Hf	0.50	0.50	6.00	2.00	0.50	9.00
				Hg	1.00	1.00	95.00	Hg	0.50	0.50	0.50	0.50	0.50	2.00
								Ir	2.50	2.50	2.50	2.50	2.50	2.50
K	1.84	0.07	3.64	K	1.58	0.43	4.23	K	5.41	2.95	12.60	2.23	1.07	8.43
Mg	0.49	0.05	5.99	Mg	0.39	0.04	1.67	Mg	3.59	1.33	6.32	1.17	0.62	3.15
Mn	767.00	24.00	44400.00	Mn	668.00	51.00	7920.00	Mn	6570.00	1000.00	22700.00	3630.00	666.00	14000.00
Na(%)	0.63	0.06	3.06	Na	0.54	0.07	1.96	Na	0.44	0.16	2.24	0.32	0.13	1.03
P(%)	0.04	0.01	0.30	P	0.03	0.01	0.07	P	1.59	0.69	3.12	0.40	0.19	0.92
Rb	93.00	<15.00	222.00	Rb	84.00	15.00	213.00	Rb	51.00	7.50	200.00	37.00	7.50	164.00
Sb	2.00	0.60	485.00	Sb	1.70	0.60	693.00	Sb	0.70	0.10	8.60	0.60	0.10	11.80
Sc	13.40	1.60	45.30	Sc	12.30	2.10	37.30	Sc	2.40	0.70	7.90	3.80	0.70	10.80
								Se	1.50	1.50	1.50	1.50	1.50	1.50
Sr	81.00	17.00	1370.00	Sr	73.00	18.00	192.00	Sr	583.00	238.00	2150.00	872.00	243.00	3320.00
Ta	0.50	0.50	3.10	Ta	0.50	0.50	2.30	Ta	0.25	0.25	1.60	0.25	0.25	1.50
Ti(%)	0.51	0.09	1.24	Ti	0.48	0.11	0.76	Ti	0.02	0.01	0.18	0.07	0.01	0.19
Th	10.40	2.00	20.20	Th	8.60	3.00	17.30	Th	1.50	0.30	6.10	2.90	0.60	9.20
U	3.30	0.50	8.50	U	2.80	0.50	6.70	U	0.25	0.25	2.00	0.25	0.25	2.50
V	117.00	11.00	331.00	V	102.00	10.00	224.00	V	17.00	6.00	62.00	23.00	3.00	63.00
				W	1.00	1.00	7.00	W	0.50	0.50	2.00	0.50	0.50	10.00
Y	11.00	4.00	46.00	Y	9.00	4.00	76.00	Y	4.00	1.00	15.00	6.00	2.00	28.00
La	33.20	6.80	79.70	La	29.85	8.10	62.00	La	7.80	2.80	48.50	13.00	2.10	70.70
Ce	71.00	16.00	172.00	Ce	53.00	16.00	128.00	Ce	16.00	5.00	77.00	24.00	4.00	117.00
Nd	21.00	<5.00	63.00	Nd	17.50	5.00	43.00	Nd	2.50	2.50	32.00	10.00	5.00	37.00
Sm	4.80	0.90	10.40	Sm	3.80	1.00	8.50	Sm	1.20	0.30	5.00	2.20	0.80	7.70
								Sn	0.01	0.01	0.02	0.01	0.01	0.03
Tb	0.50	0.50	2.10	Tb	0.50	0.50	1.20	Tb	0.25	0.25	0.90	0.25	0.25	1.30
Yb	3.10	0.90	9.90	Yb	2.60	0.90	6.20	Yb	0.50	0.10	1.90	0.80	0.30	3.20
Lu	0.51	0.14	1.57	Lu	0.38	0.13	0.92	Lu	0.08	0.03	0.32	0.14	0.03	0.37
Ca (cmolc kg^{-1})	3.60	0.21	17.97											
Mg(cmolc kg^{-1})	1.53	0.16	13.59											
K(cmolc kg^{-1})	0.19	<0.03	1.54											
Na(cmolc kg^{-1})	0.09	0.00	7.99											
Mn(cmolc kg^{-1})	0.00	0.00	0.00											
S(cmolc kg^{-1})	5.61	0.70	22.11											
CEC(cmolc kg^{-1})	9.52	1.77	21.78											
V%	63.11	14.20	265.78											
pH (H_2O)	5.54	5.52	2.22											
TOC (g kg^{-1})	13.37	12.17	1.24											

Element concentrations in subsoil, aerial parts and roots of cistus plants across the table have the same units as the first column.

aerial parts, respectively; 3 to 982 mg kg^{-1} and 3 to 308 mg kg^{-1}, in *Cistus ladanifer* L. roots and aerial parts, respectively; and 35 to 70 mg kg^{-1} and 8 to 29 mg kg^{-1} in *Thymus vulgaris* L. roots and aerial parts, respectively. Aerial parts of the plants are those usually consumed by animals in pasture, and in this case Pb seems to be of no threat, because its highest concentrations were in the roots.

In general, Pb concentrations were found to be higher in plants than in soil, although harmful elements, such as Pb, As and Cr, have overall lower concentrations in plants than in soil. Manganese concentrations were elevated in soil, but are also very high in plants in accordance with other studies, such as Li et al. (2007), where Mn shows a high uptake and translocation in plants. Very high concentrations of Br and Ca in Cistus plants were detected compared to soil. Distribution of chemical element concentrations in soil and in *Cistus ladanifer* L. of the Lower Guadiana basin sector is presented in Table 1.

Table 2
Median element concentrations in topsoil by lithology. Topsoil concentrations were used as baseline conditions and subsoil contents as background values.

	Median values of topsoil per lithology					
	S	Al	Ba	Br	Ca	Na
Flys ($n=54$)	0.010	2.760	510	2.800	0.110	1.000
Plobo ($n=16$)	0.010	3.815	685	2.250	0.055	0.395
PQ ($n=29$)	0.015	3.445	520	1.600	0.245	0.590
XB ($n=22$)	0.010	2.995	470	6.100	0.060	0.325
VA ($n=3$)	0.010	2.610	530	2.300	0.130	1.100
ME ($n=7$)	0.010	3.270	590	2.900	0.120	0.320
Standard deviation	0.002	0.4985	82.583	1.779	0.077	0.352
Coefficient of variation	0.188	0.143	0.139	0.532	0.573	0.559
Grand median value for subsoil ($n=66$)	0.01	3.55	400	3	0.1	0.55

Lithology	Cu	Pb	Ni	Zn	As	Co
Flys ($n=54$)	29.000	29.000	39.000	76.000	16.300	18.000
Plobo ($n=16$)	31.500	33.000	63.500	101.000	23.000	19.000
PQ ($n=29$)	131.500	45.000	48.500	74.500	36.800	19.500
XB ($n=22$)	20.000	25.500	37.500	59.000	21.750	14.000
VA ($n=3$)	27.000	54.000	12.000	50.000	11.800	9.000
ME ($n=7$)	53.000	36.000	61.000	67.000	26.600	24.000
Standard deviation	46.985	11.883	18.813	19.469	9.442	5.155
Coefficient of variation	0.865	0.287	0.433	0.246	0.381	0.299
Grand median value for subsoil ($n=66$)	27	23	37	65	15	14

Lithology	Cr	Fe	K	Mg	Mn	P
Flys ($n=54$)	81.000	3.780	1.730	0.480	863.000	0.033
Plobo ($n=16$)	116.000	4.740	2.540	0.320	478.500	0.041
PQ ($n=29$)	96.500	4.520	2.495	0.420	925.500	0.037
XB ($n=22$)	88.500	4.310	2.020	0.245	441.500	0.037
VA ($n=3$)	20.000	2.580	2.230	0.510	1190.000	0.027
ME ($n=7$)	89.000	4.460	2.000	0.450	1660.000	0.042
Standard deviation	32.565	0.796	0.313	0.102	457.694	0.005
Coefficient of variation	0.398	0.196	0.145	0.252	0.494	0.151
Median values for subsoil ($n=66$)	66	3.46	1.58	0.41	673	0.032

Lithology	Rb	Sr	V
Flys ($n=54$)	93.000	88.000	121.000
Plobo ($n=16$)	142.500	68.500	175.500
PQ ($n=29$)	125.500	121.000	144.000
XB ($n=22$)	116.000	74.000	122.500
VA ($n=3$)	122.000	91.000	54.000
ME ($n=7$)	119.000	79.000	132.000
Standard deviation	17.926	20.451	44.614
Coefficient of variation	0.134	0.215	0.321
Grand median values for subsoil ($n=66$)	84.000	73.000	102.000

Flys — Mid-Upper Carboniferous meta-sediments, turbidite formations; Plobo — Lower Devonian tectonised phyllite inter-bedded with metabasic rocks; PQ — Upper Devonian Phyllite–Quartzite group with shale, sandstone and conglomerate; XB — Upper Devonian–Lower Carbonifeous Purple shale; VA — Upper Devonian–Lower Carbonifeous felsic volcanic rocks; ME — Upper Devonian–Lower Carbonifeous epiclastic meta-sediments; number of samples in brackets.

Table 3
Element enrichment or depletion in topsoil based on the ratio of lithological median values in topsoil to grand median values of subsoil.

Lithology	S	Al	Ba	Br	Ca	Na
Flys ($n=54$)	1.000	0.777	1.275	*0.933	*1.100	1.818
Plobo ($n=16$)	1.000	1.075	1.713	*0.750	*0.550	*0.718
PQ ($n=29$)	1.500	0.970	1.300	*0.533	2.450	1.073
XB ($n=22$)	1.000	0.844	1.175	2.033	*0.600	*0.591
VA ($n=3$)	1.000	0.735	1.325	*0.767	1.300	2.000
ME ($n=7$)	1.000	0.921	1.475	*0.967	*1.200	*0.582
Standard deviation	0.224	0.140	0.206	0.593	0.769	0.639
Coefficient of variation	0.188	0.143	0.139	0.532	0.573	0.559

Lithology	Cu	Pb	Ni	Zn	As	Co
Flys ($n=54$)	*1.074	1.261	1.054	1.169	1.072	1.286
Plobo ($n=16$)	*1.167	1.435	1.716	1.554	1.513	1.357
PQ ($n=29$)	4.870	1.957	1.311	1.146	2.421	1.393
XB ($n=22$)	*0.741	1.109	*1.014	0.908	1.431	1.000
VA ($n=3$)	*1.000	2.348	*0.324	0.769	0.776	0.643
ME ($n=7$)	*1.963	1.565	1.649	1.031	1.756	1.714
Standard deviation	1.740	0.517	0.508	0.300	0.621	0.316
Coefficient of variation	0.965	0.320	0.432	0.273	0.416	0.256

Lithology	Cr	Fe	K	Mg	Mn	P
Flys ($n=54$)	1.227	1.092	1.095	1.171	1.282	1.031
Plobo ($n=16$)	1.758	1.370	1.608	0.780	*0.711	1.266
PQ ($n=29$)	1.462	1.306	1.579	1.024	1.375	1.156
XB ($n=22$)	1.341	1.246	1.278	0.598	*0.656	1.141
VA ($n=3$)	*0.303	0.746	1.411	1.244	1.768	0.844
ME ($n=7$)	1.348	1.289	1.266	1.098	2.467	1.313
Standard deviation	0.548	0.249	0.214	0.271	0.471	0.160
Coefficient of variation	0.442	0.212	0.156	0.274	0.342	0.142

Lithology	Rb	Sr	V
Flys ($n=54$)	1.107	1.205	1.163
Plobo ($n=16$)	1.696	0.938	1.688
PQ ($n=29$)	1.494	1.658	1.385
XB ($n=22$)	1.381	1.014	1.178
VA ($n=3$)	1.452	1.247	*0.519
ME ($n=7$)	1.417	1.082	1.269
Standard deviation	0.213	0.280	0.429
Coefficient of variation	0.150	0.235	0.357

Flys — Mid-Upper Carboniferous meta-sediments, turbidite formations; Plobo — Lower Devonian tectonised phyllite inter-bedded with metabasic rocks; PQ — Upper Devonian Phyllite-Quartzite group with shale, sandstone and conglomerate; XB — Upper Devonian-Lower Carbonifeous Purple shale; VA — Upper Devonian-Lower Carbonifeous felsic volcanic rocks; ME — Upper Devonian-Lower Carbonifeous epiclastic meta-sediments; * standard deviation above half of the median values; number of samples in brackets.

4.2. Background versus enrichment or depletion in soil

Background, enrichment or depletion of element concentrations in soil are presented in Tables 2 and 3. Elements, such as Ca, Na, Cu and As, show enrichment in soil developed on shale of the PQ group, sandstone and conglomerate, which are marine sediments with carbonates at the top of the stratigraphical sequence. Copper showed the greatest enrichment in the PQ group-derived soil, but was depleted in soil developed on the purple (Upper Devonian-Lower Carboniferous) shale. This behaviour of Cu may be explained by the mixture of mine wastes in topsoil that were present in formations of the former, and by leaching of acid soil (between pH = 4 and pH = 5) in the latter, and in the majority of soil types (Bengtsson et al., 2006; Tack et al., 1999). Lead shows an enrichment in soil developed on the Upper Devonian-Lower Carboniferous formations of felsic volcanic rocks of the VSC and in the PQ group shale, sandstone and conglomerate, whereas Fe, As, Co, Ni and Cr show a depletion in soil developed on these rocks. Elements, such as Al, Ba, Fe, K, Mg, P and Sr, exhibit no significant coefficient of variation across the individual lithologies, suggesting that the elements in these soil types are derived from the bedrock (Table 2, see Fig. 1). The depletion of elements, such as Fe and As, which are also constituents of these formations, may be caused by mobilisation, possibly related with the general acidity of soil or natural vertical mobility, as reported by Adriano (2001). Lead shows an enrichment, associated with atmospheric deposition, as suggested by Manjunatha et al. (1996) and Blaser et al. (2000), but in the present study the enrichment may be associated also to the reduced vertical mobility of the element according to Kabata-Pendias and Pendias (2001).

Bromine is enriched in the soil developed on the Upper Devonian–Lower Carboniferous formations of purple-coloured shale of the VSC, and its fixation in topsoil is probably associated with the climatic and drainage conditions (Plano de Bacia Hidrográfica do Rio Guadiana, 2001). Climatic conditions, topography, especially the lack of a good drainage system, may contribute to increase Br concentration in the surface of soil, first leached to water, and after, concentrated in soils, due to poor draining and high evaporation rate (Gerritse and George, 1988). In the surroundings of São Domingos mine, the

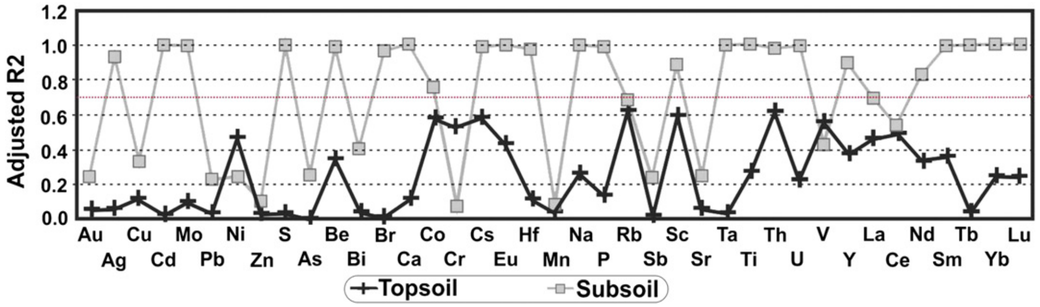


Fig. 3. Multiple Linear Regression (adjusted R^2) results with Al, Ba, Fe, K, Mg as independent predictors and Ag, As, Au, Be, Bi, Br, Ca, Cd, Ce, Co, Cr, Cs, Eu, Hf, La, Lu, Mn, Mo, Na, Nd Ni, P, Pb, Rb, S, Sb, Sc, Sm, Sr, Ta, Tb, Ti, Th, U, V, Y, Yb and Zn as regressors. Topsoil and subsoils are compared.

enrichment of Pb in soil was significant, probably due to wind dispersion from the mine wastes, and scarce vegetation cover (Batista, 2000). This feature also occurred at other abandoned mine sites, e.g., at a Pb mine in West Wales, U.K. (Davies and White, 1981) and the Witwatersrand goldfield of South Africa (Chevrel et al., 2005). Lead concentration was also high in the Huelva region, due proximity to a Pb mineralisation or related with the smelting activity (Querol et al., 2004). Huelva has one of the largest smelters in Europe, and studies by Chopin and Alloway (2007) have shown that the elevated concentrations of trace metals, usually present in the massive sulphide ores, are only restricted very near to the smelter area, and there is only some minor dispersion at the Guadiana River mouth.

The MRA statistics show consistence about the Pb associations and its origin in soil, whereas the most important source was the VSC formations and the characteristic IPB sulphide mineralisations.

Considering the predictors (Al, Ba, Fe, K and Mg), previously described for MRA, all chemical elements have $R^2<0.7$ in topsoil, probably resulting from a mixture with a non-topsoil origin, such as mineralisation, whereas dump material from the mine sites could be transported to significant distances by the wind (Davies and White, 1981). The results are in agreement with a study undertaken in SW Spain that demonstrated a general enrichment in topsoil related to lithologies and mineralisations of the IPB (Galán et al., 2008). Long range diffuse pollution can justify the overall slight enrichment in topsoil, even at some distance from mine sites (Blaser et al., 2000; Manjunatha et al., 1996).

On the other hand, subsoil samples have an $R^2>0.7$ (Van der Veer, 2006) for a larger number of chemical elements, and in particular Ag, Cd, Mo, S, Br, Ca, Cs, Eu, Hf, Na, P, Ta, Ti, U, Sm, Tb, Yb and Lu have in fact $R^2>0.90$ (Fig. 3). This suggests that elements in subsoil are

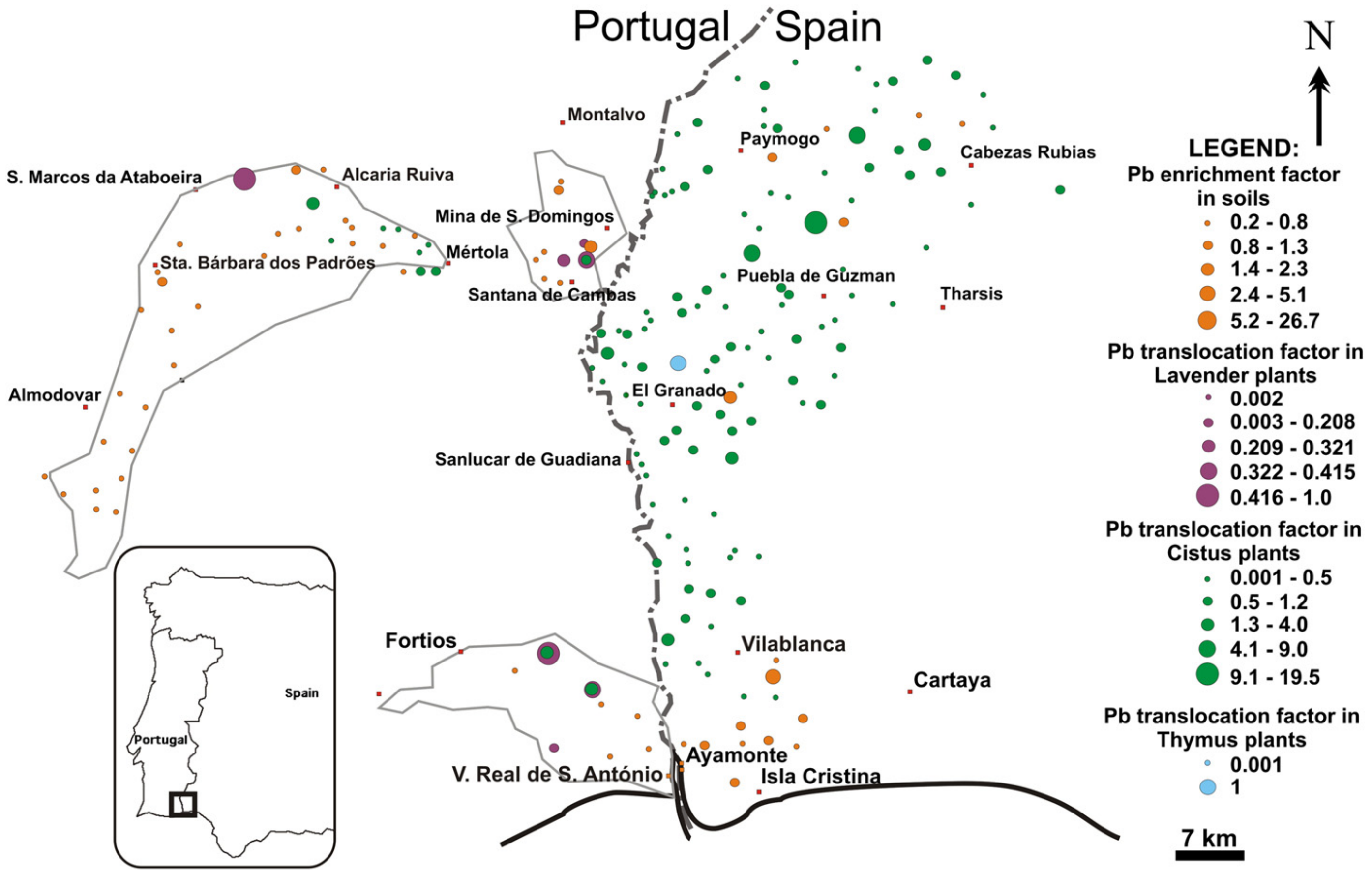
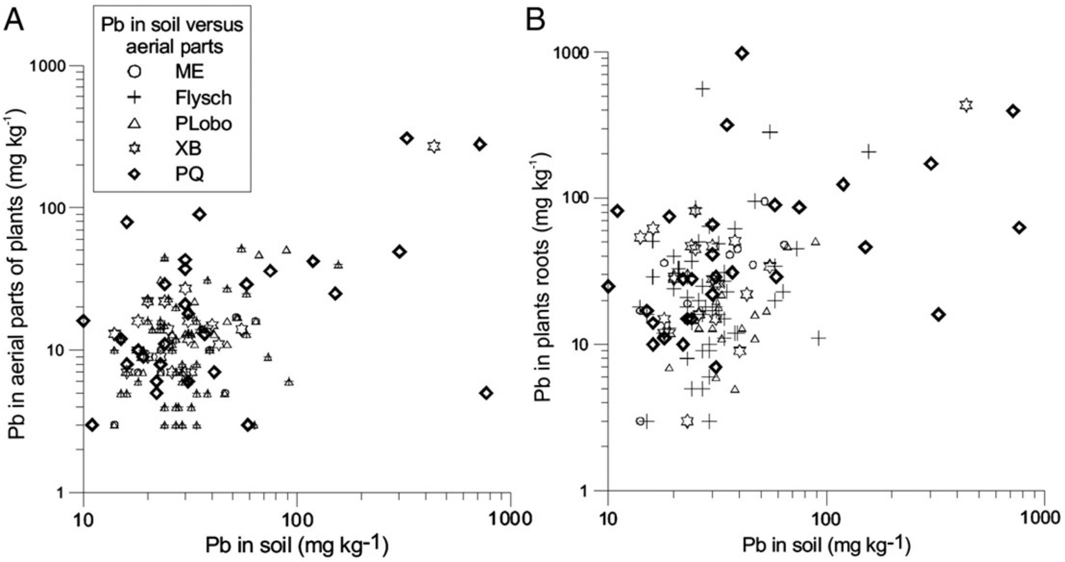


Fig. 4. Translocation factors (transfer inside the plant) in Cistus plant, Lavandula plant and Thymus plant related with the topsoil Pb enrichment.



ME – Mesozoic formations; Flysch- Flysch formations; PLobo-Pulo do Lobo formations; XB – Purple shale formation; PQ- Phylito-Quartzitic group

Fig. 5. Bi-plot diagrams of Pb concentrations in (A) soil lead versus aerial parts, and (B) soil lead versus roots of the Cistus plants in Lower Guadiana river basin.

directly related to bedrock lithology. However, in the same subsoil samples Pb, Ni, Zn, As, Bi, Cr, Mn, Sb, Sr and V do not show a clear relationship with the predictors ($R^2<0.7$; see Fig. 3). The reason for this dubious statistical result is the fact that lithologies, such as those of the VSC formations, are also enriched in the same elements as the mineralisations, which can also occur locally with other formations, such as PQ group lithologies. Due to the ore formation, these host rocks are in fact, at least in part, the source of these metals that may be concentrated in certain areas due to leaching by hydrothermal fluids (Relvas et al., 2006). This situation reduced the effectiveness of the statistical method.

4.3. Sources of Pb occurring in soil and in plants

Fig. 2A shows the isotopic ratios of $^{206}Pb/^{204}Pb$ versus $^{207}Pb/^{204}Pb$ of samples of soil, Cistus plants, shale lithology (PQ group), and the sulphide mineralisations compiled by Marcoux (1998). Fig. 2B presents the geological and mineralogical domains of plant samples.

In general, the isotopic compositions of Pb in uncontaminated soil samples are more radiogenic ($^{206}Pb/^{204}Pb \approx 18.5–19.5$), as the greater part of Pb is derived from the alteration of rocks that contributed to the Pb content initially. Furthermore, the isotopic composition of Pb is mostly influenced by the decay of ^{234}U into ^{206}Pb. Soil samples from this study were within the interval corresponding to unpolluted soil, whereas the isotopic composition of mineralisation, where the Pb/U ratio was high, due to the separation of Pb from U, reflects a lower radiogenic composition ($^{206}Pb/^{204}Pb \approx 16.0–18.5$) (Hansmann and Köppel, 2000; Komárek et al., 2007; Fig. 2A). Plants growing on mineralised soil (>100 mg kg^{-1} Pb) fall in the “mineralised” domain on Fig. 2B. However, plants growing in unmineralised soil show greater isotopic variability and may possibly indicate differential absorption related to specific mineral phases (Fig. 2A). Studies by Reimann et al. (2008) in Norway examined relationships of Pb across 11 different types of materials from several species of trees, mineralisations, and soil types (C and O horizons) in close proximity to probable Pb sources, including large industries and major highways, and found considerable Pb isotopic variation. Contamination that had previously been attributed to aerial transport on a continental scale, actually resulted from the dispersion and erosion of local soil (Reimann et al., 2008). Reimann's study shows that fractionation does occur, and in many cases it is associated with microorganisms. Studies such as these may constrain the conclusions drawn from Fig. 2A. Therefore, although plants may have Pb sources largely related to their proximity to mineralisation (Fig. 2B) biological fractionation may also explain some variation.

4.4. Soil–plant Pb relationship

The correlation between Pb and the chemical and physical properties, such as pH, exchange cations in topsoil, the cation exchange capacity (CEC), organic carbon, the percentage of saturation of the exchangeable complex (BS%) in topsoil, is insignificant ($r<0.36$). Only pH has a negative ($r=-0.5$) correlation with the Pb content. Calcium and Mg have good to poor correlation with CEC ($r=0.51$ and $r=0.36$) and good with BS% ($r=0.63$ and $r=0.61$).

The relationship of Pb with other chemical and physical properties, such as grain size (clay content), total organic carbon and CEC is very low ($r<-0.1$). Soil with a higher percentage of clay minerals can, in principle, have a higher reaction surface and, thus, be capable of retaining Pb on their surface and be available in the short and medium term (Carrol, 1959). The present study shows that cations occupying the majority of exchange sites were Ca and Mg, favourable cations, especially Ca in the presence of phosphates, to exchange position with Pb (Cotter-Howell, 1996), but only pH exhibits a weak negative correlation with Pb ($r=-0.24$). This negative correlation corresponds to high concentrations of Pb and low pH in soil. A good correlation is also found between K and CEC with organic carbon suggesting that organic carbon is also related to exchange sites.

The translocation coefficient of the three plant species is insignificant (<0.5). Spatial relationship between relative enrichment of Pb in soil and translocation of Pb in the different plant species is presented in Fig. 4. The highest rates of Pb translocation were not related to topsoil enrichment or to lithological variation. This conclusion is in accordance with studies showing that only in areas closely related with mine sites is translocation more effective (Jung, 2008). In this study, samples reflect a wider area where atmospheric deposition, as well as mining dust dispersion and other reasons, contribute to the relative enrichment of Pb in topsoil. Toxic concentrations of Pb in soil for plants can be above 100 mg kg^{-1} and, depending on soil or plant properties, can reach values above 500 mg kg^{-1} (Del Río-Celestino et al., 2006), showing that plants, such as Cistus, may also adapt to these toxic conditions (Abreu et al., 2008; Abreu et al., 2009).

Biplots of the relationship of Pb in soil and aerial parts and roots of the *Cistus ladanifer* L. plants are presented in Fig. 5, where soils are referred to according to parent material. The biplots show that most individuals plot within a cloud near the origin. Therefore, there is no clear correlation between Pb in aerial parts and roots of the Cistus plants and Pb concentrations in soil. The points that plot outside the cloud are samples collected near to roads or old mines. These isolated samples indicate that the significant elevation of Pb concentration in plants can only be related to the proximity of Pb sources, such as mines or roads where bioavailability of the element is higher.

5. Conclusions

Two geogenic and two anthropogenic sources of Pb were identified using isotopic methods and confirmed by a statistical approach. The VSC is seen as the main geogenic source of Pb. The sulphide mineralisation within the Iberian Pyrite Belt was identified as the main non-geogenic source of Pb, considering that these are areas where sulphides were exploited. As plants derive nutrients from soil, and were collected in mineralised areas, their isotopic signature on the few samples analysed are similar to the mineralisation source, which is also confirmed by the soil–plant relationship study. Whereas, in unmineralised soil they showed a greater isotopic variation, probably because they correspond to specific mineral phases. This suggests that the separate study of these species may produce refined results relative to the bioavailability of Pb in certain mineral phases, within soil, of which the source could be clearly identified by its isotopic ratio. Therefore, the main sources of Pb, both geogenic and anthropogenic, within the lower stretch of the Guadiana River was successfully identified.

Moreover, the utilisation of isotope studies combined with the establishment of background and baseline concentrations in soil, and enrichment and depletion of naturally occurring potentially toxic elements, was useful to the understanding the sources Pb and the processes by which Pb is redistributed in soil and in plants.

In general, base metals, such as Pb, commonly present in mineralisation of the Iberian Pyrite Belt, have a local dispersion associated with the mining areas. The soil samples with the highest concentrations of Pb within the superficial horizon may indicate the effect of diffuse pollution, as a result of the aerial transport of particulate material from local Pb-enriched mine dumps. These soil types also present low mobility of Pb down the soil profile. Furthermore, translocation of Pb within the studied plants (*Cistus ladanifer L., Thymus vulgaris*, *Lavandula luisieri* (Rozeira) Rivas-Martinez) is limited to roots, and especially near to the mining sites. The Lavandula plant, although not representatively sampled, showed the greatest concentrations of Pb.

Rocks, mineralisations, subsoil, topsoil and plant processes were successfully integrated to understand the migration of Pb into the food chain.

Acknowledgements

This study was part of a larger multi-disciplinary environmental project carried out in the framework of an INTERREG IIIA (*Utilização do chumbo como indicador de vulnerabilidade ambiental na Faixa Piritosa Ibérica* — UTPIA — SP5.P9/02) Programme of the European Community between Portugal and Spain. The authors would like to thank an anonymous reviewer, Sarah Fortner, LeeAnn Munk and Alecos Demetriades for constructive criticism of the manuscript.

References

Abreu, M.M., Tavares, M.T., Batista, M.J., 2008. Potencial use of *Erica andevalensis* and *Erica australis* in phytoremediation of sulphide mine environments: S. Domingos, Portugal. Journal of Geochemical Exploration 96, 210–222.

Abreu, M.M., Santos, E.S., Anjos, C., Magalhães, M.C., Nabais, F., 2009. Capacidade de absorção do chumbo por plantas do género *Cistus* espontâneas em ambientes mineiros. Revista de Ciências Agrárias 32 (1), 170–181.

Adriano, D.C., 2001. Trace Elements in Terrestrial Environments: Biogeochemistry, Bioavailability and Risk of Metals. Springer-Verlag, New York. 879 pp.

Alloway, B.J., 1995. Heavy Metals in Soils. Blackie Academic & Professional, London. 368 pp.

Barriquelo, M.F., Juliatti, M.A., da Silva, M.S., Lenzi, E., 2003. Lead behavior in soil treated with contaminated sewage sludge and cultivated with maize. Brazilian Archives of Biology and Technology 46 (4), 499–505.

Batista, M.J., 2000. Environmental State of the Portuguese Test Site. S. Domingos Mine: Past and Present. Report for European Commission. http://www.brgm.fr/mineo/IGM_test_site.pdf.

Batista, M.J., Nieto, J.M., Bebianno, M.J., Abreu, M.M., Locutura, J., Shepherd, T., Melo, T., DelValls, T.A., Bel-Lan, A., Matos, J., Oliveira, D., Barrosinho, J., Neves, C., Serafim, A., Company, R., Cravo, A., Delgado, J., Blasco, J.M., Kalman, J., Riba, I., Martins, L., 2008. Utilização do Pb como Indicador de vulnerabilidade Ambiental na Faixa Piritosa Ibérica (in Portuguese). Final Report of the SP2.P5-02 INTERREG IIIA Andaluzia-Alentejo-Algarve Programme.

Bengtsson, H., Alvena, G., Nilsson, S.I., Hultman, B., Oborn, I., 2006. Cadmium, copper and zinc leaching and surface run-off losses at the Ojebyn farm in Northern Sweden—temporal and spatial variation. Agriculture, Ecosystems and Environment 113, 120–138.

Blaser, P., Zimmermann, S., Luster, J., Shotyk, W., 2000. Critical examination of trace element enrichments and depletions in soils: As, Cr, Cu, Ni, Pb, and Zn in Swiss forest soils. Science of the Total Environment 249 (1–3), 257–280.

Callender, E., 2004. Heavy Metals in the Environment—Historical Trends. In: Lollar, B. (Ed.), Treatise on Geochemistry Environmental Geochemistry, 9. Elsevier, Amsterdam, pp. 67–105.

Carrol, D., 1959. Ion exchange in clays and other minerals 1959. Geological Society of America Bulletin 70 (6), 749–779.

Carvalho Cardoso, J.V.J., 1965. Os solos de Portugal, sua classificação, caracterização e génese — 1-A sul do Rio Tejo (in Portuguese). Direcção Geral dos Serviços Agrícolas, Lisboa. 310 pp.

Cheng, M., Ma, L.Q., Harris, W.G., Hornesby, A.G., 1999. Background Concentrations of Trace Metals in Florida Surface Soils:Taxonomic and Geographic Distributions of Total-total and Total-recoverable Concentrations of Selected Trace Metals. Florida Center For Solid And Hazardous Waste Management. Report #99-7.

Chevrel, S., Bourguignon, A., Cottard, F., Ittard, Y., 2005. Exploitation of aster imagery in mining-related environmental management. Pecora 16 “Global Priorities in Land Remote Sensing” October 23–27, South Dakota. 10 pp.

Chopin, E.I., Alloway, B.J., 2007. Distribution and mobility of trace elements in soils and vegetation around the mining and smelting areas of Tharsis: Sw spain. Water, Air, and Soil Pollution 182, 245–251.

Cotter-Howell, J., 1996. Lead phosphate formation in soils. Environmental Pollution 93 (1), 9–16.

Davies, B.E., White, H.M., 1981. Environmental pollution by wind blown lead mine waste: a case study in Wales. U.K. Science of The Total Environment 20 (1), 57–74.

Davis, J.C., 1986. Statistics and Data Analysis in Geology. John Wiley & Sons, Inc., N.Y. 646 pp.

Del Río-Celestino, M., Font, R., Moreno-Rojas, R., De Haro-Bailón, A., 2006. Uptake of lead and zinc by wild plants growing on contaminated soils. Industrial Crops and Products 24, 230–237.

Feio, M., 1951. A evolução do relevo do Baixo Alentejo e Algarve (in Portuguese). Communicacoes dos Servicos Geológicos de Portugal XXXII (2), 303–477.

Figueiredo, M.O., Silva, T.P., 2011. The positive Environmental Contribution of jarosite by retaining lead in acid mine drainage areas. International Journal of Environmental Research and Public Health 8, 1575–1582.

Galán, E., Fernández-Caliani, J.C., Aparicio, P., Romero, A., 2008. Influence of geological setting on geochemical baselines of trace elements in soils. Application to soils of South–West Spain. Journal of Geochemical Exploration 98 (3), 89–106.

Garrett, R., 2005. Natural distribution and abundance of elements. In: Selinus, O., Alloway, B., Centeno, J.A., Finkelman, R.B., Fuge, R., Lindh, U., Smedley, P. (Eds.), Essentials of Medical Geology: Impacts of the Natural Environment on the Public Health. Elsevier Academic Press, Amsterdam, pp. 17–41.

Gerritse, R.G., George, R.J., 1988. The role of soil organic matter in the geochemical cycling of chloride and bromide. Journal of Hydrology 101 (1–4), 83–95.

Grimes, D., Carvalho, D., 1994. Geochemical exploration studies in the Portuguese Pyrite Belt. In: Berger (Ed.), US Geological Survey Bulletin, 2081, pp. 53–77.

Grimes, D., Kropschot, S.J., 1998. Geochemical Studies of Rare Earth Elements in the Portuguese Pyrite Belt, and Geologic and Geochemical Controls on Gold Distribution. U.S. Geological Survey Professional Paper 1596–A–B. 40 pp.

Hagberg, L., Löfgren, E., 2007. Soil and Plant Contamination by Textile Industries at ZFILM, Managua. Minor Field Study 126. Uppsala University, Sweden. 64 pp.

Hansmann, W., Köppel, V., 2000. Lead-isotopes as tracers of pollutants in soils. Chemical Geology 171, 123–144.

Johnson, B., 1990. Effect of pH, temperature, and concentration on the adsorption of cadmium on goethite. Environmental Science and Technology 24, 112–118.

Jung, M.C., 2008. Heavy metal concentrations in soils and factors affecting metal uptake by plants in the vicinity of a Korean Cu–W mine. Sensors 8, 2413–2423.

Kabata-Pendias, A., Pendias, H., 2001. Trace Elements in Soils and Plants, 3rd edition. CRC Press, Inc., Boca Raton, Florida. 413 pp.

Ketterer, M.E., Peters, M.J., Tisdale, P.J., 1991. Verification of a correction procedure for measurement of lead isotope ratios by inductively coupled plasma mass spectrometry. Journal of Analytical Atomic Spectrometry 6, 439–443.

Ketterer, M.E., Lane, D.A., Jordan, J.A., 2010. Unusually radiogenic lead (Pb) in Ashtabula River Sediments: an isotopic tracing case study using quadrupole ICP-MS. The Open Chemical and Biomedical Methods Journal 3, 202–209.

Komárek, M., Ettler, V., Chrastný, V., Mihaljevič, M., 2007. Lead isotopes in environmental sciences: a review. Environment International http://dx.doi.org/10.1016/j.envint.2007.10.005.

Kovalevskii, A.L., 1979. Biogeochemical Exploration for Mineral Deposits. Oxonian Press PVT, Nova Deli. 136 pp.

Lai, C.H., Gao, C.K., Lin, T.T., Yeh, S.H., Chen, C.Y., Wang, M.K., 2006. Simulation of lead ions adsorption onto the iron-coated medium: dependent on temperature and pH. Practice Periodical of Hazardous, Toxic, and Radioactive Waste Management 10, 28–32.

Leistel, J.M., Marcoux, E., Thieblemont, D., Quesada, C., Sanchez, A., Almodovar, G.R., Pascual, E., Saez, R., 1997. The volcanic-hosted massive sulphide deposits of the Iberian Pyrite Belt: review and preface to the thematic issue. Mineralium Deposita 33, 2–30.

Levinson, A.A., 1980. Introdution to Exploration Geochemistry. Applied Publishing Ltd., Wilmette, Illinois, USA. 924 pp.

Leyva, F., Ramirez, J, 1979. Mapa geológico y memoria explicativa de España a escala 1/50.000. Hoja nº 998 Ayamonte; Instituto Geologico e Minero the España.

Li, M.S., Luo, Y.P., Su, Z.Y., 2007. Heavy metal concentrations in soils and plant accumulation in a restored manganese mineland in Guangxi, South China. Environmental Pollution 147 (1), 168–175.

Manjunatha, B.R., Balakrishna, K., Shankar, R., Thiruvengadasami, A., Prabhu, K.R., Mahalingam, T.R., Iyengar, M.A.R., 1996. The transport of elements from soils around Kaiga to the Kali river, southwest coast of India. Science of the Total Environment 191 (1–2), 109–118.

Marcoux, E., 1998. Lead isotope systematics of the giant massive sulphide deposits in the Iberian Pyrite Belt. Mineralium Deposita 33, 45–58.

Memon, A.R., Aktoprakligül, D., Demür, A., Vertii, A., 2001. Heavy metal accumulation and detoxification mechanisms in plants. Turkish Journal of Botany 25, 111–121.

Sociedade Mineira Rio Artézia, 1992. Área de Pomarão-Odeleite Unpublished report. LNEG Arquive, 50 pp.

Nelson, Y.M., Lion, L.W., Ghiorse, W.C., Shuler, M.L., 1999. Production of biogenic Mn oxides by Leptothrix discophora SS-1 in a chemically defined growth medium and evaluation of their Pb adsorption characteristics. Applied and Environment Microbiology 65 (1), 175–180.

Pereira, J., Guimarães-Silva, A., Júnior, H., Pacheco-Silva, E., Lena, J., 2007. Distribuição, fracionamento e mobilidade de elementos traço em sedimentos superficiais (in Portuguese). Quimica Nova 30 (5), 1249–1255.

Plano de Bacia Hidrográfica do Rio Guadiana, 2001. Final Report (in Portuguese). Hidroprojecto, Engenharia e Gestão S. A., Coba, Consultant, Hidrotécnica Portuguesa. 367 pp.

Póvoas, I., Barral, M.F., 1992. Métodos de Análise de Solos (in Portuguese). Com. do Inst. de Inv. Cient. Tropical, Série de Ciências Agrárias, N.° 10, Instituto de Investigação Científica Tropical, Lisboa. 61 pp.

Querol, X., Alastuey, A., Viana, M.M., Rodriguez, S., Artiñano, B., Salvador, P., Garcia do Santos, S., Fernandez Patier, R., Ruiz, C.R., de la Rosa, J., Sanchez de la Campa, A., Menendez, M., Gil, J.I., 2004. Speciation and origin of PM10 and PM2.5 in Spain. Journal of Aerosol Science 35 (9), 1151–1172.

Reimann, C., Flem, B., Arnoldussen, A., Englmaier, P., Erik Finne, T., Koller, F., Nordgulen, O., 2008. The biosphere: a homogeniser of Pb-isotope signals. Applied Geochemistry 23, 705–722.

Relvas, J.M.R.S., Barriga, F.J.A.S., Longstaffe, F., 2006. Hydrothermal alteration and mineralization in the Neves-Corvo volcanic-hosted massive sulfide deposit, Portugal: II. Oxygen, hydrogen and carbon isotopes. Economic Geology 101 (4), 791–804.

Ribeiro, A., Quesada, C., Dallmeyer, R.D., 1990. Geodynamic Evolution of the Iberian Massif. In: Dallmeyer, R.D., Garcia, E.M. (Eds.), Pre-Mesozoic Geology of Iberia. Springer-Verlag, Berlin, pp. 383–395.

Richards, D.G., 1995. Environmental Geochemistry of Heavy Metals in a Portuguese River Basin. Thesis submitted to the University of Liverpool in fulfilment of the degree of M. Phil., 192 pp.

Rodda, D.P., Johnson, B.B., Wells, J.D., 1996. Modeling the effect of temperature on adsorption of lead(II) and zinc(II) onto goethite at constant pH. Journal of Colloid and Interface Science 184 (2), 365–377.

Salazar Rincón, A., 2006. Mapa geológico 1/50.000 de Huelva-Los Caños. Instituto Geologico e Minero the España.

Sharma, N., Sahi, S., 2006. Physiology of Lead Accumulation and Tolerance in a Lead Accumulating Plant (*Sesbania drummondii*). Trace Elements in the Environment. In: Prasad, M.N.V., Sajwan, K.S., Naidu, R. (Eds.), Biogeochemistry, Biotechnology and Bioremediation. Taylor & Francis Ed., pp. 425–438.

Sierra, M., Martínez, F.J., Aguilar, J., 2007. Baselines for trace elements and evaluation of environmental risk in soils of Almería (SE Spain). Geoderma 139, 209–219.

Sposito, G., 2008. The Chemistry of Soil, 2nd ed. Oxford University Press. 330 pp.

Stanley, C.R., Noble, R.R.P., 2007. Optimizing geochemical threshold selection while evaluating exploration techniques using a minimum hypergeometric probability method. Geochemistry: Exploration, Environment, Analysis 7 (4), 341–351.

Tack, F.M.G., Singh, S.P., Verloo, M.G., 1999. Leaching behaviour of Cd, Cu, Pb and Zn in surface soils derived from dredged sediments. Environmental Pollution 106, 107–114.

Tebo, B.M., Bargar, J.R., Clement, B.G., Dick, G.J., Murray, K.J., Parker, D., Verity, R., Webb, S.M., 2004. Biogenicmanganese oxides: properties and mechanisms of formation. Annual Review of Earth and Planetary Sciences 32, 287–328.

Tornos, F., 2006. Environment of formation and styles of volcanogenic massive sulfides: the Iberian Pyrite Belt. Ore Geology Reviews 28, 259–307.

Tornos, F., Casquet, C., Relvas, J.M.R.S., 2005. Transpressional tectonics, lower crust decoupling and intrusion of deep mafic sills: a model for the unusual metallogenesis of SW Iberia. Ore Geology Reviews 27, 133–163.

Turpeinen, R., Salminen, J., Kairesalo, T., 2000. Mobility and bioavailability of lead in contaminated Boreal Forest Soil. Environmental Science and Technology 34, 5152–5156.

Ulrich, T., 2007. Biogenic manganese oxides: formation mechanisms, mineralogy and environmental relevance. Term paper: Biogeoch. Pol. Dynamics. 21 pp.

Van der Veer, G., 2006. Geochemical soil survey of the Netherlands. Atlas of major and trace elements in topsoil and parent material; assessment of natural and anthropogenic enrichment factors. Netherlands Geographical Studies, NGS, 347. 245 pp.

Vreca, P., Pirc, S., Sajn, R., 2001. Natural and anthropogenic influences on geochemistry of soils in terrains of barren and mineralised carbonate rocks in the Pb–Zn mining district of Mezica, Slovenia. Journal of Geochemical Exploration 74, 99–108.

Ziaii, M., Pouyan, A.A., Ziaei, M., 2009. Neuro-fuzzy modelling in mining geochemistry: identification of geochemical anomalies. Journal of Geochemical Exploration 100, 25–36.