Determination of the geochemical background in a metal mining site: example of the mining district of Linares (South Spain)

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Abstract

The study region is situated in the mining district of Linares (province of Jaén, South Spain) and it is characterised by the presence of important seams of galena. The mining, minerallurgic and metallurgic activities in the area, as well as the local geological (metallogenetic) conditions, are important sources of heavy metals in the environment, resulting in considerable soil contamination.

The study area occupies a surface area of 126 km^2, divided into grid squares of 1 km^2 for soil sampling, in order to characterise the geochemical background of this abandoned mining region. The soil samples were analysed for total concentrations of 32 elements; the discussion focuses on eight in particular (Cu, Pb, Zn, Ag, As, Cd, Sb and Mn), these being the main elements associated with human activity. The mean contents of all these elements exceed the Clarke comparison values for trace elements in acid igneous rocks. The total concentrations of Pb, Ag, As, Cd and Sb are especially high. In this very complex zone, on the basis of cluster analysis and of field observations, the local background contents of each geological substrate are defined, distinguishing the different types of activity that took place in the zone and different degrees of intensity.
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1. Introduction

Geochemical maps are of great interest, not just from the scientific or mining standpoint, but also, they constitute an effective tool for environmental planning, and for establishing healthcare policies and promoting sustainable development (Ferguson and Kasamas, 1999). This explains why, in recent years, many governments have promoted research to define geochemical background levels to serve as a basis for legislation to diagnose, prevent and reduce soil contamination (Mielke and Ragan, 1998; Berglund et al., 2000; Rieuwerts et al., 2000). In the USA, background concentrations are often used as soil clean-up criteria following industrial activities. Determining reliable background concentrations of chemical elements in soil is an important issue in environmental sciences, and requires the availability of reliable procedures to distinguish between "natural" and "man-made" element concentrations in soils (Reimann and Garrett, 2005).

The term "geochemical background" has been defined as "the normal abundance of an element in barren earth material" (Hawkes and Webb, 1962). It was introduced to differentiate between normal element concentrations and

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anomalies. By definition, a geochemical anomaly is a departure from the geochemical patterns that are normal for a given area (Hawkes and Webb, 1962). In the same way, the background values for a lithology indicate a typical composition of that rock type.

In regions where hydrothermal processes have given rise to mineralization, the common compositions of local bedrocks are modified, raising metal concentrations (high local backgrounds due to geogenic sources). In addition, ore extraction and mineral processing facilitate metal mobilisation in surrounding areas and increase the average levels of metals in the soil (anomalous values from anthropogenic sources).

The local background levels must be determined for each geologic unit, because its geochemical pattern will be unique and differentiating. The soils that have developed there reflect the geochemistry of the unit over which they have formed (Salminen and Gregorauskiene, 2000; Reimann and Garrett, 2005). A geochemical investigation that is based exclusively on systematic sampling will detect areas enriched in certain trace elements, but will run into difficulties in discerning whether the anomaly is geogenic or anthropogenic (Crock et al., 1992; Darnley, 1997).

The Linares mining district (Spain) (Fig. 1) was selected to analyse the importance of the different geogenic and anthropogenic factors in the present-day composition of the soil. This area has been characterised historically, though the activity has now been abandoned, by the exploitation of seams of galena (PbS). Paragenesis has also given rise to other minerals, including zinc blende (ZnS), calcopyrite ($CuFeS_2$) and barite ($BaSO_4$) (Azcárate and Argüelles, 1971; Azcárate, 1977; Fontboté, 1982). The abundance of these ores enabled the development of a large-scale extractive mining industry, minerallurgic industry (gravimetric and flotation) and smelting industry over hundreds of years. This mining district is located above a substrate in which various geological units can be distinguished, these being mainly constituted of Palaeozoic granites, Triassic lutites and Miocene marls (Fig. 1).
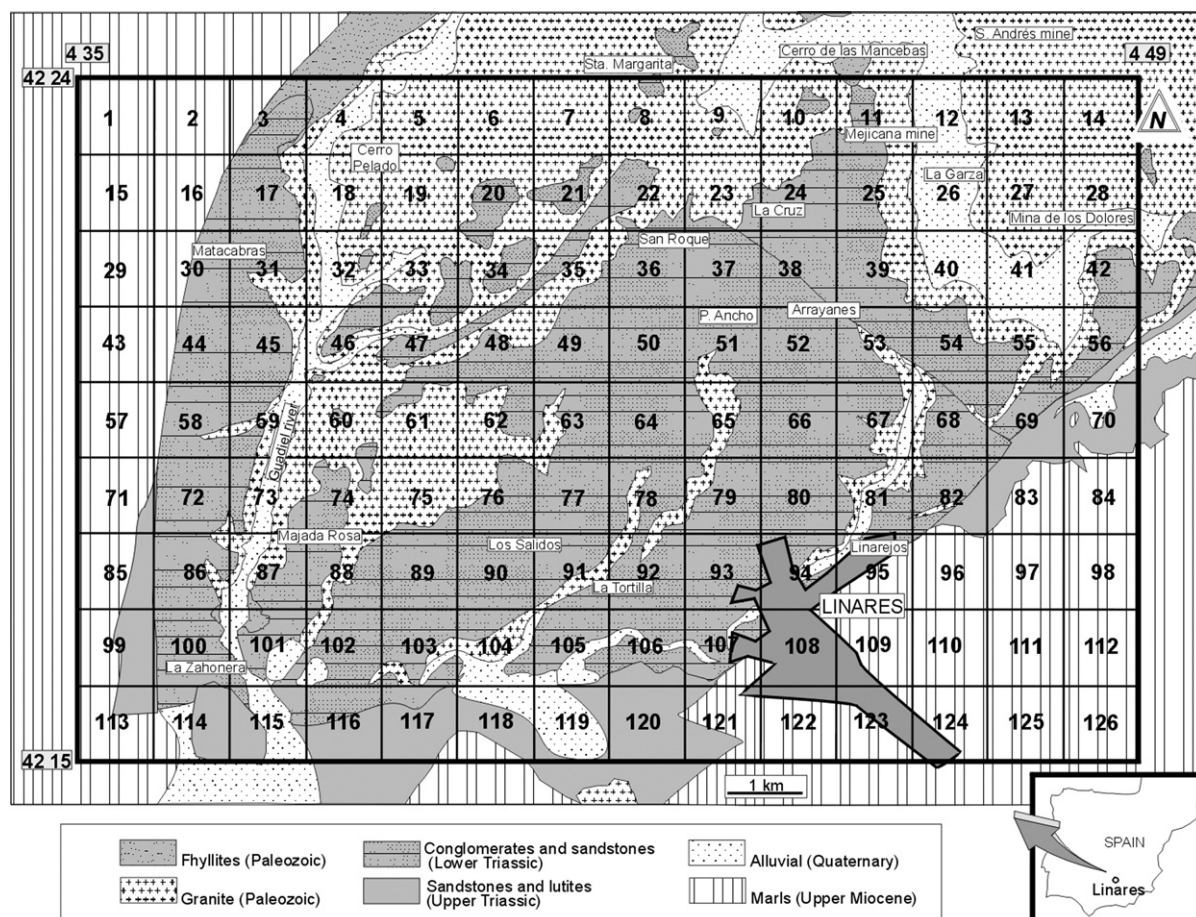

Fig. 1. Geological map of the Linares region and location of the sampling grid squares.

Despite all the human activity and geogenic variability described, to date no detailed studies have been carried out in the region to determine the concentrations of heavy elements in the soil. Therefore, there is a real need to evaluate the levels of concentration of trace elements in the soil of the Linares area and to make this information available, both generically and cartographically, as a matter of public interest and as a reference document for administrations, as a basis for risk studies, among other applications. Taking these factors into account, the present study is focused on the following objectives:

1. Geochemical characterization of this area, to identify the trace elements present in the soils and the incidence of mining activity.
2. To define the local background values of selected trace elements for different geological substrata.
3. To identify the average concentration of the anomalous elements in each geological substratum and discriminate natural and anthropogenic contributions.

2. Materials and methods

2.1. Site description and experimental procedure

The mining district of Linares was divided into 126 grid squares, each measuring 1 km² (Fig. 1). Firstly, after a review of the geologic mapping and having identified the main human activities carried out, three grid squares were selected as representative of the geochemical pattern of the area (Martínez, 2002; Martínez et al., 2006).

On the basis of this pilot study (Martínez et al., 2006), the definitive sampling campaign was designed (i.e. the number of samples and the volume of material to be taken) for the remaining 123 grid squares. Five lots of 1500 g of material were taken from each grid square. Sample collection was carried out in a random fashion using an Auger sample collector, from the top 20 cm of the soil.

2.2. Laboratory analysis

For each of the grid squares, the five lots were combined to form a single compound sample, which was homogenised and passed through two plastic sieves, 2 mm and 63 micron gauge, with the filtered material being collected. One gram of the fraction measuring less than 63 microns was subjected to wet chemical attack in open teflon reactors, with a mixture of 5 ml HNO_3, 10 ml $HClO_4$ and 10 ml HF. The dry residue was redissolved in 5 ml HCl and diluted with distilled water to 100 ml (Martínez, 2002).

Dissolved samples were analysed by Inductively Coupled Plasma Atomic Emission Spectrometry, a technique of simultaneous multi-element analyses, in the Acme Analytical Laboratories Ltd. (an ISO 9002 accredited company) in Vancouver (Canada). The value of the elemental concentration identified for this single sample was assigned as the mean value for the grid square. All the elements analysed are listed in Table 1.

2.3. Statistical analysis

Univariate and multivariate analysis techniques were applied to the matrix of concentration values obtained in this geochemical study. This made it possible to identify interrelations and groupings, to compare data sets and thus to summarise the data obtained, facilitating its subsequent interpretation (Reimann and Filzmoser, 2000; Stanley, 2003; Meloun et al., 2005; Reimann and Garrett, 2005; Burgos et al., 2006).

The following descriptive statistics of centring, dispersion and shape were used: mean, median, standard deviation, variation coefficient (VC), asymmetry coefficient, kurtosis, minimum, maximum, Q_1 and Q_3 (Table 1). The mean gives a better estimate of location even for skewed populations if the outliers truly belong to this population. In environmental data sets they will most likely be an indication of population source. In many cases, the regional distribution of elements is influenced by more than just one process/source, resulting in multi-modal skewed distributions. In this case the median, as a robust estimator of location, is far superior to the mean (Reimann and Filzmoser, 2000).

Table 1 shows the statistical parameters obtained for the 32 elements analysed in this study. To establish a basis for comparison of these first results, Table 1 also includes the values given by Mason (1966) and by Rösler and Lange (1972) as crust "Clarke values" and the average values for trace elements in granite-type 'acid igneous rocks' from Sponza and Karaoglu (2002).

Combining these reference values with the results obtained, the Enrichment Factor (EF) (Chester and Stoner, 1973) was calculated for every element by the formula:

$$EF = \frac{[\text{Concentration Element}]/[\text{Concentration Yttrium}]}{[\text{Clarke Element}]/[\text{Clarke Yttrium}]}$$

where *Concentration Element* and *Concentration Yttrium* are the mean concentration of the element examined and the mean concentration of Y in sampling soils; *Clarke Element* and *Clarke Yttrium* are the Clark values of the element examined and Y, respectively. The EFs

Table 1
Linares mining district data (from 126 compound soil samples): elements analysed, minimum, maximum, mean, median, standard deviation, first quartile (Q_1), third quartile (Q_3) (all data in mg kg^{-1}), variation coefficient (VC), asymmetry value (*a*) and kurtosis (*k*)

Element	Minimum	Maximum	Mean	Median	Standard deviation	VC	*a*	k	Q_1	Q_3	Crust Clarke values	Acid rocks	Enrichment factor (crust)	Enrichment factor (acid rocks)
Mo	1	14.5	1.8	1.5	1.54	0.88	5774	42.05	1	2	15	1.9	0.2	0.9
Cu	14	1654	145	54	242.5	1.67	3.53	14.94	33	128	70	30	2.6	4.5
Pb	27	37,356	4077	1279	7016	1.72	3.11	10.8	267	4866	16	2	324	1852
Zn	26	1988	124	72	206	1.66	6.82	56.2	46	134	132	60	1.2	1.9
Ag	0.25	29	2	0.3	4.29	2.12	4.11	19.43	0.3	1.7	0.1	0.15	26	12
Ni	10	42	20.6	20.7	5.96	0.29	0.47	0.49	15	25	80	8	0.3	2.3
Co	5	39	12	10	6.26	0.51	1.57	2.6	8	14	23	5	0.7	2.2
Mn	194	3981	1211	1086	802.1	0.66	0.94	1.00	530	1608	1000	600	1.5	1.8
Fe	15,900	59,200	32,024	30,900	8863	0.28	0.75	0.44	25,512	36,562	50,000	*	0.8	*
As	2.5	175	26	17	29.23	1.12	3.28	12.12	11	26	5	1.5	6.6	16
Th	4	80	26	21	15	0.59	1.38	1.79	17	31	12	18	2.7	1.3
Sr	60	530	150	122	89.47	0.60	2.35	5.5	103	158	300	300	0.6	0.5
Cd	0.2	32	0.8	0.2	2.86	3.76	10.41	113.38	0.2	0.6	0.15	0.1	6.5	6.9
Sb	2.5	186	11.5	2.5	22.44	1.95	4.88	30.93	2.5	10	1	0.4	14.6	26
V	43	122	72	71	13.44	0.19	0.87	2.45	64	79	150	40	0.6	1.6
Ca	1700	207,600	35,865	14,875	44,882	1.25	1.84	2.68	6600	41125	36,300	*	1.3	*
P	330	2920	848	765	441.4	0.52	2.31	7.54	578	982	1180	700	0.9	1.1
La	17	145	67	69	22.88	0.34	0.12	0.48	52	82	18	46	4.8	1.3
Cr	26	150	50	49	15.37	0.31	2.83	14.94	40	56	200	25	0.3	1.8
Mg	2500	12450	6194	5875	2372	0.38	0.64	0.3	4387	7625	20,900	*	0.4	*
Ba	120	3728	875	705	695.4	0.79	1.94	3.8	369	1024	260	830	4.3	0.9
Ti	1244	6400	3259	3000	1097.7	0.34	0.97	0.34	2575	3662	4400	2300	0.9	1.3
Al	30,100	114,200	63,048	56,400	19,728	0.31	0.88	0.19	48,800	74,200	81,300	81,300	1.0	0.7
Na	1500	16,400	4820	3200	3619	0.75	1.40	0.86	2200	6363	28,300	*	0.2	*
K	10,100	38,450	25312	24,650	6803	0.27	0.01	0.98	19,700	31662	25,900	*	1.2	*
W	2	72.5	5.9	4.5	7.91	1.33	6.02	44.66	2	7	69	*	0.1	*
Zr	36	238	103	100	32.76	0.32	1.04	2.7	86	117	220	200	0.6	0.5
Sn	1	52.5	5.6	4	6.05	1.08	4.46	29.81	2	7	40	45	0.2	0.1
Y	9	48	22	19	8.90	0.40	0.97	0.2	15	28	28	20	1.0	1.0
Nb	5	24	9.6	8	4.45	0.47	1.48	1.5	7	12	24	20	0.5	0.4
Be	0.5	6	3.7	4	1.45	0.39	0.39	0.8	2	5	6	5.5	0. 8	0.6
Sc	6	25	11	10	4.07	0.35	1.50	1.6	9	13	5	7	2.9	1.5

Reference values for average concentrations in crust and acid rocks (in mg kg^{-1}) and calculated enrichment factors are also included (see Section 2.3).

were calculated with respect to yttrium as a reference element because Y does not form authigenic minerals and is a conservative element. Two EFs were obtained, considering, on the one hand, the average Clarke values and, on the other hand, the Clarke values in acid igneous rocks.

Table 1 includes both calculated Enrichment Factors. These values indicate how many times the concentrations measured exceed the Clarke values.

2.4. Multivariate methods and data transformation

The techniques of multivariate analysis were applied to the matrix of concentration values determined in this geochemical study, making it possible to deduce interrelations and clusters, to compare data sets and, ultimately, to summarise the data for subsequent interpretation.

Clustering techniques were used to separate the individuals into natural groups; by means of proximity criteria, the discrepancies between the individuals in a single group were minimised while the distances separating the groups from each other were maximised. Ward clustering criteria and the measure of the Euclidean distance were applied to measure the divergence. The agglomerative hierarchical clustering was used, separating in each step, from both the groups and the conjunctions of individual specimens, the two groups that were most similar, until a single group was arrived at. Examples of applications of these methods to sediments are common (Huang et al., 1994; Kalogeropulos et al., 1994; Ruiz et al., 1998; Facchinelli et al., 2001; Gallego et al., 2002; Manta et al., 2002; Yongming et al., 2006). All statistical analyses were carried out with the program SPSS 11.0 for Windows and MINITAB Realise 10 for Windows.
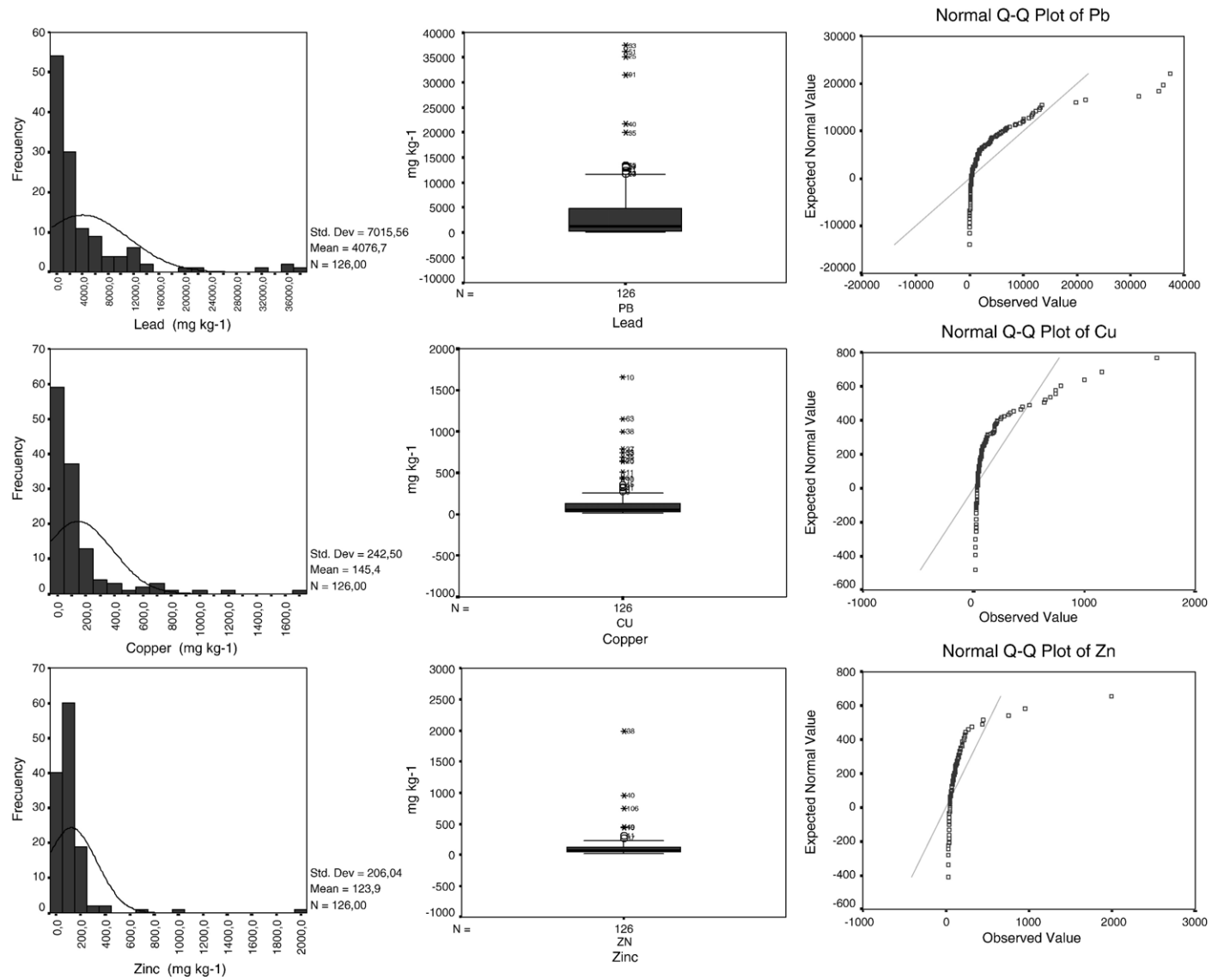
Fig. 2. Histograms, box-plots and Q–Q graphs for lead, copper and zinc to illustrate the whole data set distribution.

3. Results and discussion

3.1. Statistical treatment

The soils of the mining district of Linares contain very high total concentrations of copper, lead, zinc, silver, manganese, arsenic, cadmium and antimony, compared with the Clarke values. Consequently, high Enrichment Factors are also obtained for this area (Table 1).

The EFs for these eight elements exceed the Clarke values; the most notable is Pb at 1852 times the Clarke values (extremely high enrichment), followed by Sb (26), As (16), Ag (12) and Cd (6.9), with significant to very high enrichment. The EF values calculated for Cu (4.5), Zn (1.9) and Mn (1.8) indicate a minimal to moderate enrichment.

In the light of these results Pb, Cu, Zn and Ag were selected as elements of special interest for the study area, these being the main elements associated with mining, minerallurgic and metallurgic activities, together with Cd, As, Sb and Mn, because these are the elements present in the process of mineralization and are, moreover, of considerable importance for the environment.

Each element shows a wide range of concentrations and presents numerous extreme values, and so the means and the medians differ considerably (Table 1). For a better observation of the shape of the distribution of values, Fig. 2 illustrates the histograms for three of the selected elements: Pb, Cu and Zn. Also obtained were box-and-whiskers plots for one-dimensional statistical distributions, in which six parameters are described (Fig. 2): the lower limit, first quartile, median, third quartile, upper limit and extreme values. Q–Q graphs (distribution variable quantiles versus the quantiles of one of the distribution test numbers) show the fit of the values of each variable to the theoretical normal slope (Fig. 2).

The histograms are asymmetric, presenting the highest frequencies in the lowest intervals. The box-plots reveal that the medians coincide with the value of the first quartile and the boxes are displaced towards the minimum values (Fig. 2). In all the elements, there are numerous extreme values above the upper limit. Moreover, the large standard deviations and variation coefficients (CVs > 1), together with the asymmetry and kurtosis values, indicate that the elements have asymmetric distributions with a long tail to the right (high extreme values). Asymmetries are also reflected in the Q–Q graph, where it is apparent that the plots are far from the theoretical normal slope (Fig. 2). In addition, the Kolmogorov–Smirnov test of normality (Chakravarti et al., 1967; Conover, 1971) and the Shapiro–Wilk test give values of zero, indicating that these elements do not follow a normal distribution (Martínez, 2002). Consequently, statistical parameters indicate a multi-modal distribution that reflects the existence of over-lapped values and reveal different data sets.

3.2. Determination of the local background and anomalous values

In order to discriminate different groups of heavy metals as tracers of a natural or of an anthropogenic source, an explorative hierarchical cluster analysis was performed on the available data set (126 grid squares in this study). The results obtained (Fig. 3) enabled five main
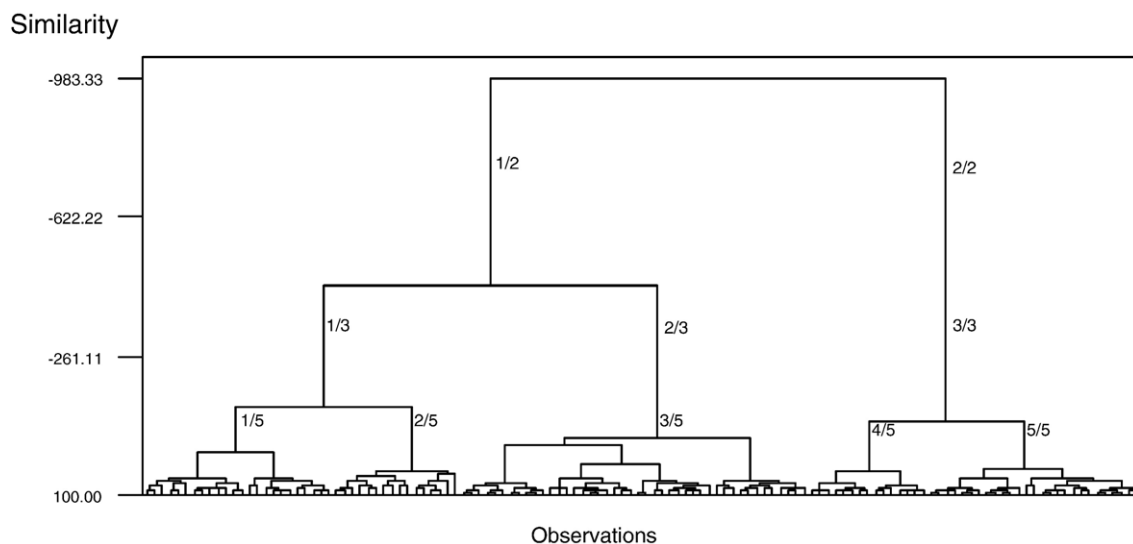

Fig. 3. Cluster analysis of observations.

groups to be identified (numbered 1–5), which were associated with the grid squares according to their respective predominant lithology and depending on the type and degree of soil pollution.

Group 1 comprised the grid squares with outcropping granite with mining activity and several grid squares with evergreen oak groves. Group 2 grouped the grid squares with Triassic lutites and/or granite lithology, where there had been intensive mining and metallurgic activity. Group 3 is very heterogeneous, with grid squares over Triassic soils dedicated to crop growing, but also urban land and areas affected by mining. Group 4 included the grid squares with an undifferentiated Triassic–Miocene soil and no mining impact. Group 5 represents the grid squares where only Miocene marls outcrop, and where there has been no mining activity (Martínez, 2002).

Fig. 4 shows the spatial distribution by groups, in which there is clearly a good correlation between the groups deduced by analysis of the grouping and of the outcropping lithologies (Fig. 1). Considering these groups, it is possible to determine the local background for each lithology and also the anomalous load due to anthropogenically influenced factors.

3.2.1. Miocene marls

Miocene marls are related to Group 5 (Figs. 3 and 4). Using the original database, a new one was created containing only the grid squares that were classified by the grouping analysis as Group 5 (i.e. there were 27 such grid squares in this case). The normality curves were created for all the variables and their logarithms and they all followed a normal distribution. The trends were similar to the normal probability plots of the log of Pb and Cu, included in Fig. 5. After having tested the normality of this distribution, and to avoid the influence of extreme values, the median concentration of the element was then taken as the local background value (Table 2).

The median concentrations in mg kg^{-1} of Cu, Pb, Zn, Ag, Mn, As, Cd and Sb were 35, 116, 47, 0.3, 322, 10, 0.2 and 2.5, respectively. These concentration levels are comparable to those recorded in other "world average" reference values (Reimann and de Caritat, 1998; Manta et al., 2002; Yongming et al., 2006).

3.2.2. Triassic lutites

Triassic lutites have been related to Group 3 (Figs. 3, 4 and 5). In this group, the lithology is associated with human activities (mining, crop growing, urban development). Using the original database, a new one was created, containing only the 33 grid squares that had been classified by the grouping analysis as belonging to Group 3. The normality curves and their logarithms for all the variables, except for Mn, showed the existence of two populations in this group.

Fig. 5, which illustrates the normality tests for Pb and Zn, shows that the distribution of points undergoes an inflection. This feature of the graph can be used to

Fig. 4. Spatial distributions of the five groups deduced from the cluster analysis (the grid squares of Fig. 1 have been used). 1: Palaeozoic granite (mining and evergreen oak groves). 2: Palaeozoic–Triassic granite–lutites (mining–metallurgy). 3: Triassic lutites (mining–urban). 4: Triassic–Miocene lutites and marls. 5: Miocene marls.
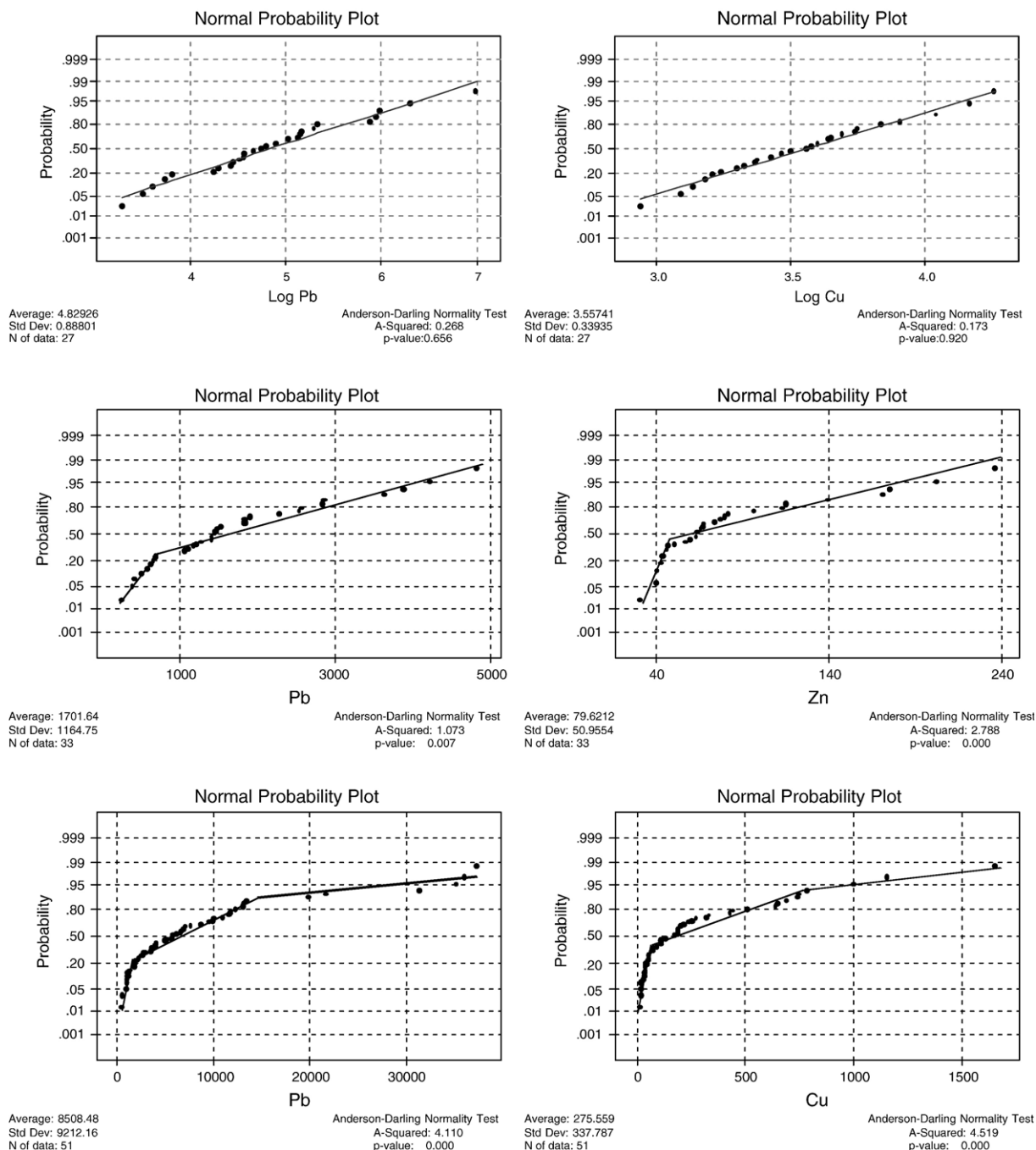
Fig. 5. Normality test of log Pb and log Cu for the Miocene marls (top plots), normality test of Pb and Zn for the Triassic soils (middle plots) and normality test of Pb and Cu for the granite (lower plots).

distinguish between natural or geogenic values (the first population, with low values) and anthropogenically influenced samples (high concentrations). This latter subset is interpreted as representing the result of mining activity. Having deduced these two populations, the next step is to extract the Triassic grid squares associated with mining activity (24 in total) and those that are not (9 cases). From the variables studied, the values of the means and the medians for each population are derived. The median values obtained for the first and the second population are the local background and the anomalous concentrations, respectively. A net anomalous value can

Table 2
Local background values for the Miocene marls

Element	N	Mean	Median
Cu	27	37	35
Pb	27	190	116
Zn	27	53	47
Ag	27	0.27	0.25
Mn	27	340	322
As	27	10	10
Cd	27	0.25	0.2
Sb	27	2.8	2.5

N is the number of soil samples and the mean and the median are expressed in mg kg^{-1}.

be deduced for Group 3 (Triassic) by subtracting the local background from the anomalous content.

Table 3 presents the local background, the anomalous content and the net anomalous value deduced for the Triassic soils (Group 3). The median values for the local background for Cu (38 mg kg^{-1}), Zn (47 mg kg^{-1}), Ag (0.3 mg kg^{-1}), As (15 mg kg^{-1}), Cd (0.2 mg kg^{-1}) and Sb (2.5 mg kg^{-1}) are very close to those obtained for the Miocene marls. However, the median concentration of Pb (567 mg kg^{-1}) clearly exceeds the range of this reference value. These materials are younger than the granite intrusion and were not affected by the mineralization that led to a natural enrichment by sedimentary processes during the Triassic (the granite is a source for the detritic Triassic rocks). Therefore, the local background for Pb probably reflects the "ambient background" (sensu Reimann and Garrett, 2005).

In addition, significant net anomalous values are deduced for Cu (37 mg kg^{-1}), Zn (18 mg kg^{-1}) and As (4 mg kg^{-1}) and a very high anomalous concentration value is obtained for Pb (1262 mg kg^{-1}). The distribution pattern of these metals suggests that intensive mining activity represents the most important contaminant source over Triassic outcrops. These metallic contents must have been derived from surface disper-

sion by the action of water or wind acting on surface-level mining waste tips.

3.2.3. Granite

The granite is present in Groups 1 and 2. However, in these groups the predominant factor, rather than the lithology, is human activity (mining, minerallurgy and metallurgy). The two factors (lithology and human activities) are interrelated, because granite constitutes the lithological and structural metallotect of the mineralization.

Using the database for the original variables, a new one containing only the grid squares classified by factorial analysis as belonging to Groups 1 and 2 (in this case, 51 grid squares) was created. The normality curves for the variables present three slopes (three populations): the first one represents the local background values of the variables and the second and third populations are in relation with the mining activity (Figs. 4 and 5).

Table 4 shows the concentration (mean and median) in mg kg^{-1} of the eight elements for three sets: the first population represents the local background, the second population is Group 1 (anomalous values from the moderate impact of mining activity) and the third population is Group 2 (anomalous values from the intensive impact of metallurgic activity). As for the Triassic lithologies, net anomalous values were deduced by subtracting the local background from the anomalous concentrations.

To determine the local background component for granite (the first population), grid squares 5, 55, 60, 13, 14, 28, 18, 61, 42, 62, and 75 were studied. These are identified as granite "with evergreen oak groves" and they presented no impact from mining (Martínez, 2002). The variables present a normal distribution of values, and so the local background value adopted for granite was the median value obtained (Table 4). Note the high local background levels for Pb (1149 mg kg^{-1}) and Mn (1141 mg kg^{-1}) in the granitic soils. The granitic

Table 3
Local background values, anomalous contents and net anomalous values obtained for Triassic soils

Element	Triassic (Group 3)			Triassic local background (first population)			Triassic anomalous content (second population)			Net anomalous values
	N	Mean	Median	N	Mean	Median (a)	N	Mean	Median (b)	($b-a$)
Cu	33	76	68	9	49	38	24	86	74.5	36.5
Pb	33	1702	1442	9	525	567	24	2143	1829	1262
Zn	33	80	64	9	56	47	24	88	65	18
Ag	33	0.7	0.6	9	0.3	0.3	24	0.8	0.7	0.4
As	33	18	18	9	16	15	24	19	19	4
Cd	33	0.3	0.2	9	0.3	0.2	24	0.3	0.2	0
Sb	33	5.3	5	9	2.7	2.5	24	6.2	5.7	3.2

N is the number of samples and the concentrations are expressed in mg kg^{-1}.

Table 4
Local background values, anomalous contents and net anomalous values for the granite

Element	Granite (evergreen oak groves)		Group 1		Group 2 high		Group 1	Group 2
	Local background		Anomalous values		Anomalous values		Net anomalous values	Net anomalous values
	Mean	Median (a)	Mean	Median (b)	Mean	Median (c)	(b−a)	(c−a)
Cu	34	34	159	164	634	578	130	544
Pb	1212	1149	6053	5689	18127	12642	4540	11493
Zn	100	98	163	122	367	219	24	121
Ag	0.3	0.2	2.3	1.9	10.2	6.4	1.7	6.2
Mn	1182	1141	1505	1419	2291	2300	278	1159
As	18.1	18.5	30	25	83	60	6.5	41.5
Cd	0.3	0.2	0.7	0.6	3.6	1.5	0.4	1.3
Sb	25	25	11	10	54	41	−15	16

N is the number of samples and the concentrations are expressed in mg kg^{-1}.

bedrock was affected by hydrothermal processes that promote galena veins and a gangue of impure calcite, rich in Mn. Consequently, these high levels of Pb and Mn are interpreted as reflecting natural enrichment by weathering and pedogenesis processes.

The elements giving significant net anomalous values for Group 1 are Cu (130 mg kg^{-1}), Pb (4540 mg kg^{-1}), Zn (24 mg kg^{-1}) Mn (278 mg kg^{-1}) and As (6.5 mg kg^{-1}), in relation with historical mining activity. For Group 2, the eight elements studied have high values indicative of anomaly: Cu (544 mg kg^{-1}), Pb (11493 mg kg^{-1}), Zn (121 mg kg^{-1}), Ag (6 mg kg^{-1}), Mn (1159 mg kg^{-1}), As (42 mg kg^{-1}), Cd (1.3 mg kg^{-1}) and Sb (16 mg kg^{-1}), in relation with the historical metallurgy activity carried out in this area.

4. Conclusions

The results obtained in this study demonstrate that statistical techniques combined with element concentration analysis can be a useful tool to identify different geogenic and anthropogenic sources affecting soil composition, provided that local geochemical backgrounds are correctly established.

Soil samples from the Linares mining district show high Cu, Pb, Zn, Ag, Mn, As, Cd and Sb concentrations. The high degree of dispersion of the total concentration is associated with the different lithologies, with paragenesis and with the greater or lesser influence of mining-metallurgic activities.

In order to discriminate the local background levels for each rock type, a cluster analysis was performed and normality curves derived. Five groups, associated with lithology and degree of soil pollution, were identified.

The Miocene marls are related to Group 5. The normality curves for all the variables in this group and

their logarithms show only one original population and the median concentrations are accepted as local background values. Metal contents in soil samples are comparable to those recorded in other "world average" reference values.

The Triassic lithologies are related to Group 3. The normality curves for all the variables in this group and their logarithms revealed two populations, one original and the other overlapped. This fact has been interpreted as the result of the mining activity that took place. The median concentrations of the first population are accepted as local background values for the Triassic. The net anomalous values were deduced by subtracting the local background from the anomalous concentrations.

Granite is present in Groups 1 and 2. The normality curves for all the variables and their logarithms revealed three populations: the first is indicative of the local background, while the second and third are in relation with different degrees of mining impact (mining and metallurgic activity). The median concentrations of the first population are accepted as local background values for granite. The net anomalous values of Groups 1 and 2 were deduced by subtracting the local background from the anomalous concentrations.

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