A rapid field procedure for screening trace elements in polluted soil using portable X-ray fluorescence (PXRF)

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ARTICLE INFO

ABSTRACT

In this work, the potential soil contamination in the abandoned mining area of Rodalquilar (SE, Spain) is studied using portable X-ray fluorescence (PXRF). Measurements were made *in situ*, and data were statistically treated to study the spatial distribution of the anomalous values of trace elements. The elements exceeding the background values of the soils in the area were As, Pb, Zn, and Cu. Intervention levels both for agricultural as well as natural use in the area were exceeded by As concentrations, with 89% and 67% of the samples above these limits, respectively. The field observations and the spatial distribution of the data after the statistical treatment imply that the main mechanism of dispersion of the trace elements in soils of the area were water and wind erosion. PXRF is a useful tool for screening and assessing contaminated areas for quick and easy *in situ* determination of trace-element concentrations. After this study, the mobility and bioavailability of main potentially pollutant element (As) together with toxicity bioassays are necessary to estimate the potential environmental risk of the soils of the area.

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1. Introduction

Environmental pollution by trace elements has become a great concern in recent decades, with increasing research involving control and clean-up operations of polluted sites. Field portable X-ray fluorescence (PXRF) analysers, being a useful tool for screening and assessing contaminated areas, allow *in situ* trace-element concentrations to be determined both rapidly and easily. The detection limits of PXRF are higher than in other techniques used in these types of studies (atomic absorption, inductively coupled plasma, etc.), but these limits are below the regulatory toxicity level for the most common elements (US EPA, 1998).

In this technique, radiation from an electrically excited X-ray tube is used to generate characteristic X-ray emissions from an element in a sample. Several sources of interference are described in PXRF which need to be taken into consideration when soil and sediment samples are analysed (US EPA, 1998): physical-matrix effects such as particle size, homogeneity and surface conditions are a common source of error in the measurement; moisture content affects the accuracy of the analysis, although contents between 5 and 20% have a minimal overall error; chemical-matrix effects cause differences in content between interfering elements (e.g.: the presence of iron reduces Cu but enhances Cr measurements; overlaps occur involving arsenic (As) Kα/lead (Pb) Lα and sulphur (S) Kα/Pb Mα). Therefore, variables affecting sample heterogeneity, contaminant-concentration variability, sample preparation, and analytical variability should be considered and minimized as much as possible.

Trace elements are present in low quantities in the environment, but high concentrations of these elements in soils occur both by natural as well as by anthropogenic processes. Such elements as Zn, V, Se, Mo, Cu, Co, and As are essential to plants or beneficial to animals (Pais and Benton, 1997), but they become toxic when present in high concentrations. Pollution sources can be classified as local or diffuse, and the study of large areas with large numbers of samples is usually required in order to characterize the distribution of the pollution both on the surface as well as in the subsurface.

One of the main sources of trace-element contamination in soils is related to metal mining and smelting/extraction operations (Alloway, 1995). Mine abandonment can result in a degradation of the sites where the wastes are accumulated (dumps, holding ponds, etc.), when potentially pollutant particles are transported by wind or water, contaminating not only soils surrounding the mines but also alluvial soils downstream.

The abandoned mining area of Rodalquilar (SE Spain) provided different metal bearing minerals (Au, Pb, Zn, Cu, and Mn), mainly in the form of sulphides or native elements, during different periods (Hernández, 2005). Au was the main ore mined in the zone (since 1864 up 1990) with different methods over time, from *in situ*

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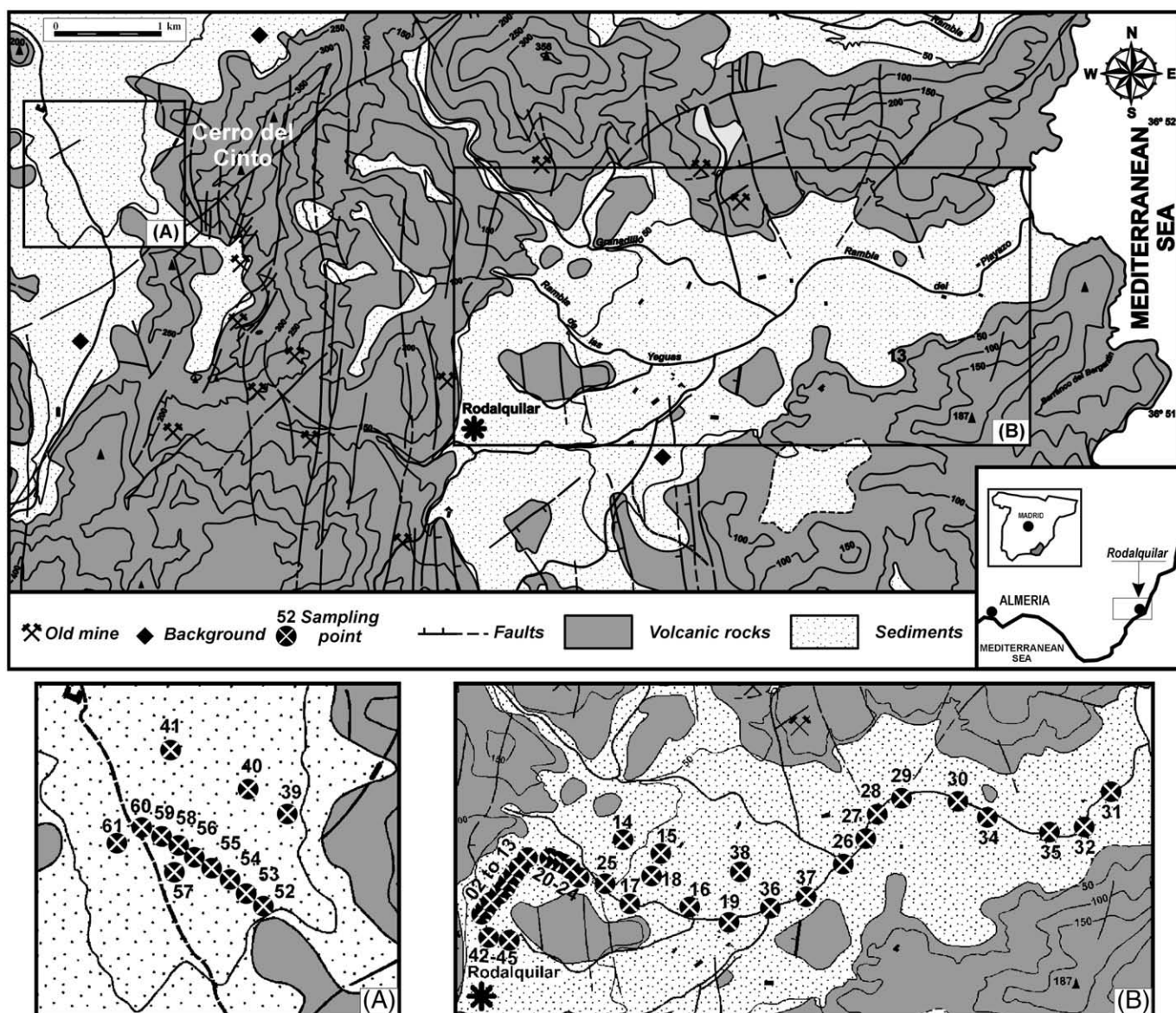 *E-mail address:* fjmartin@ugr.es (F.M. Peinado).

Fig. 1. Location of the Rodalquilar mining area and the two sampling zones. (A) W Zone; (B) E Zone.

amalgamation with Hg (until 1930), to dynamic cyanidation in tanks (approximately 1930–1970) or batch/heap leaching process (1973–1990). Otherwise, most of the non-extractable ore mineralogy in the area is strongly associated with the presence of As, which is usually concentrated in the waste from the mining procedures. Two types of deposits were abandoned in the area after the end of the mining activity: a) waste piles from the heap leaching process, and b) tailing

dump from dynamic cyanidation. In both cases, the unconfined waste deposits were located in the upper part of the basin and exposed to the climate conditions in the area (Oyarzun et al., 2009). In the 90s the tailing dump was partially restored by covering the remaining waste with uncontaminated soil and stabilized with autochthonous vegetation. Anyway, before the recovery of the tailing dump, the erosive agents (mainly wind and water) produced a strong degradation of the waste deposits and high dispersion of the residues over decades (Wray, 1998; Moreno et al., 2007).

The study of the potential contamination in these areas is complex and expensive, mainly due to the large area involved, to the long time required in the sampling and sample preparation, and to the expenses of laboratory analyses. By contrast, PXRF deals with these three main disadvantages by speeding up the screening of large areas, reducing the time in sampling preparation, and strongly reducing the analytical costs. This technique has proved fast, powerful, and cost-effective in the study and characterization of contaminated soils (Kalnicky and Singhvi, 2001; Carr et al., 2008). The present study uses a field portable analyser to explore trace-element concentrations in an area affected by an abandoned

Table 1
Analysis of certified reference material CRM052-050. (SD: standard deviation; RPD: relative percent difference; RSD: relative standard deviation).

	Certified		Experimental		Accuracy RPD[*] (%)	Precision RSD[*] (%)	Detection limit[*] (mg kg^{-1})
	Mean (mg kg^{-1})	SD	Mean (mg kg^{-1})	SD			
As	14.60	1.71	15.94	1.44	8.9	9.0	7.62
Pb	82.60	5.10	95.63	3.60	−14.6	3.8	14.13
Zn	89.00	8.56	86.80	4.40	2.5	5.1	16.26
Cu	44.20	3.11	43.13	6.80	1.2	15.8	22.44

[*]Estimated from US EPA (2006).

mine. The aim of this work is to propose a rapid methodology for screening potentially polluted areas by *in situ* analyses and data treatment. The discrimination capacity of this methodology will facilitate subsequent detailed studies in the assessment and recovery of the polluted area.

2. Material and methods

2.1. Study area

The mining area of Rodalquilar (Almería, SE Spain) generated two great disposal areas for tailings associated with the different methods of extracting gold over time (Fig. 1), one related to a dynamic cyanidation process in the upper part of a watercourse (E Zone), and other related to the heap leaching process on a smooth slope at the foot of the tailings dump (W Zone).

The arid climate of the area (mean annual precipitations < 250 mm; mean annual temperature ≈ 18 °C) causes the watercourses to remain dry most of the year, but sporadic torrential rain causes overflows and severe soil erosion from runoff water. Wind erosion is also strong in the area, dispersing fine particles from the upper layer of the soils and from holding dumps (Sierra, 2005).

In the E Zone, three types of samples (for a total of 40) were collected: a) tailings from the ore-processing holding dump (Td); b) soils used in the recovery of the dump covering the tailings (Sd); and c) soils related to the riverbed (Sr) starting from the dump and ending at the seaside. In the W Zone, 13 samples were collected; in this case, all samples were from soils with agricultural use, with different positions (close, medium, and far away) in relation to the abandoned waste deposits.

2.2. Sampling preparation and measurement

Soil samples were collected from 0 to 10 cm in depth and located in field by GPS. For the determination of the geochemical background of the soils in the area, three soils were sampled each 10 cm to 50 cm in depth (Fig. 1). Due to the aridity of the study area and the dry conditions of the sampling period (summer), the soil moisture in all cases were below 2% in the uppermost 10 cm of the soil, and below 10% between 10 and 50 cm in depth, so that the overall error from the moisture content in PXRF is considered minimal. Samples were sieved *in situ* to 2 mm; the gravels (>2 mm) and fine-earth (<2 mm) were separated to weigh in the laboratory and calculate the percentage of each fraction. All analyses were made with the fine-earth fraction thoroughly homogenized. Samples were placed in plastic bags and measured directly with PXRF equipment through the bags.

The equipment used in this study is a field portable X-ray fluorescence analyser NITON XLt 792, with a 40 kV X-ray tube with Ag anode target excitation source, and a Silicon PIN-diode with a Peltier cooled detector. The procedure followed the manufacturer's instructions and the recommendations of the Method 6200 (US EPA, 1998). As part of the standard set-up routine, the analyzer was initially calibrated using the silver and tungsten shielding on the inside of the shutter, and the source count time for analysis was fixed in 90 s. The study of the area was made in only one field campaign (two days), including sample collection, preparation, and measurement "*in situ*" of all samples. After data acquisition, the results were downloaded to a portable PC for further processing.

The accuracy of the method was corroborated by analyses (nine replicates) of Certified Reference Material: CRM052-050. According to (US EPA, 2006) the accuracy was estimated by the relative percent difference (RPD) between the concentration in the reference material and the concentration measured by PXRF. The results (Table 1) were excellent (RPD < 10) for As, Zn and Cu, and good (10 < RPD < 25) for Pb. The precision was estimated by the relative standard deviation (RSD)

of nine measurement of the reference material (US EPA, 2006), and the results were excellent (RSD < 5) for Pb, good (5 < RSD < 10) for As and Zn, and fair (10 < RSD < 20) for Cu. Detection limit (DL) was evaluated based on the analysis of sets of nine replicate samples that contained the target element at concentrations near the detection limit estimated in the EPA Method 6200; according to the (US EPA, 2006), detection limits were included in Table 1, and considered as very low (1 < DL < 20) for As, Pb and Zn, and low (20 < DL < 50) for Cu.

2.3. Data treatment and statistical methods

To check the fit of the data to a normal distribution, the Kolmogorov–Smirnov (K–S) Test was used. According to K–S Test significance levels $p < 0.05$ show that not all variables are normally distributed. Transformation of the element concentrations to a normal distribution, and standardization of the data (to reduce the various measurement units and the different ranges of the variables) were made to ensure that each variable would have the same influence in the statistical analysis. Transformation was made by assigning ranges to cases based on normal punctuations according to the Tukey's formula:

$$Y = (r - 1/3)/(w + 1/3)$$

where Y is the new standardized variable, r is the range of the data, and w is the sum of the weighing of the cases.

A Hierarchical Cluster Analysis (HCA) was used to classify the dataset samples into categories or clusters based on their nearness or similarity; the dendrogram was constructed using Ward's Method and the city-block distance to dampen the effect of the outliers, as the average differences between dimensions are not squared. This method is considered very efficient (Vega et al., 1998; Kannel et al., 2007) in exploratory data analysis of environmental samples. A statistical procedure of the data set directly measured from the PXRF instrument was followed using the software SPSS v.15.0.

3. Results and discussion

3.1. Geochemical background of the soils

The estimation of the background concentration of an element in soil is essential to define the presence of anomalies or potentially contaminated soils in an area. With this purpose, samples collected to 50 cm deep in the study area were analysed by PXRF to establish the geochemical background of the soils. To avoid the influence of potential contamination processes by surface processes (runoff water or wind erosion), the samples of the uppermost 20 cm were discarded. There are many statistical methods to determine the

Table 2
Concentration of the main trace elements detected in the E Zone. Td: Tailing dump; Sd: Soil of the dump recovery; Sr: Soil of the riverbed. *a, b, c*: statistically significant differences between groups ($p < 0.01$).

		Mean	SD	Min.	Max.
As (mg kg^{-1})	Td	687.90 *a*	329.52	326.83	1211.62
	Sd	127.10 *c*	141.50	25.28	504.45
	Sr	358.87 *b*	169.60	52.95	613.25
Pb (mg kg^{-1})	Td	220.21	89.20	140.27	364.50
	Sd	225.80	649.93	35.99	2744.32
	Sr	283.91	142.11	37.57	635.37
Zn (mg kg^{-1})	Td	164.85	97.17	88.70	283.37
	Sd	149.79	202.27	75.82	931.58
	Sr	114.28	42.04	42.26	230.78
Cu (mg kg^{-1})	Td	72.42	15.79	56.44	96.94
	Sd	65.42	85.77	26.00	384.17
	Sr	69.47	39.01	35.69	226.94
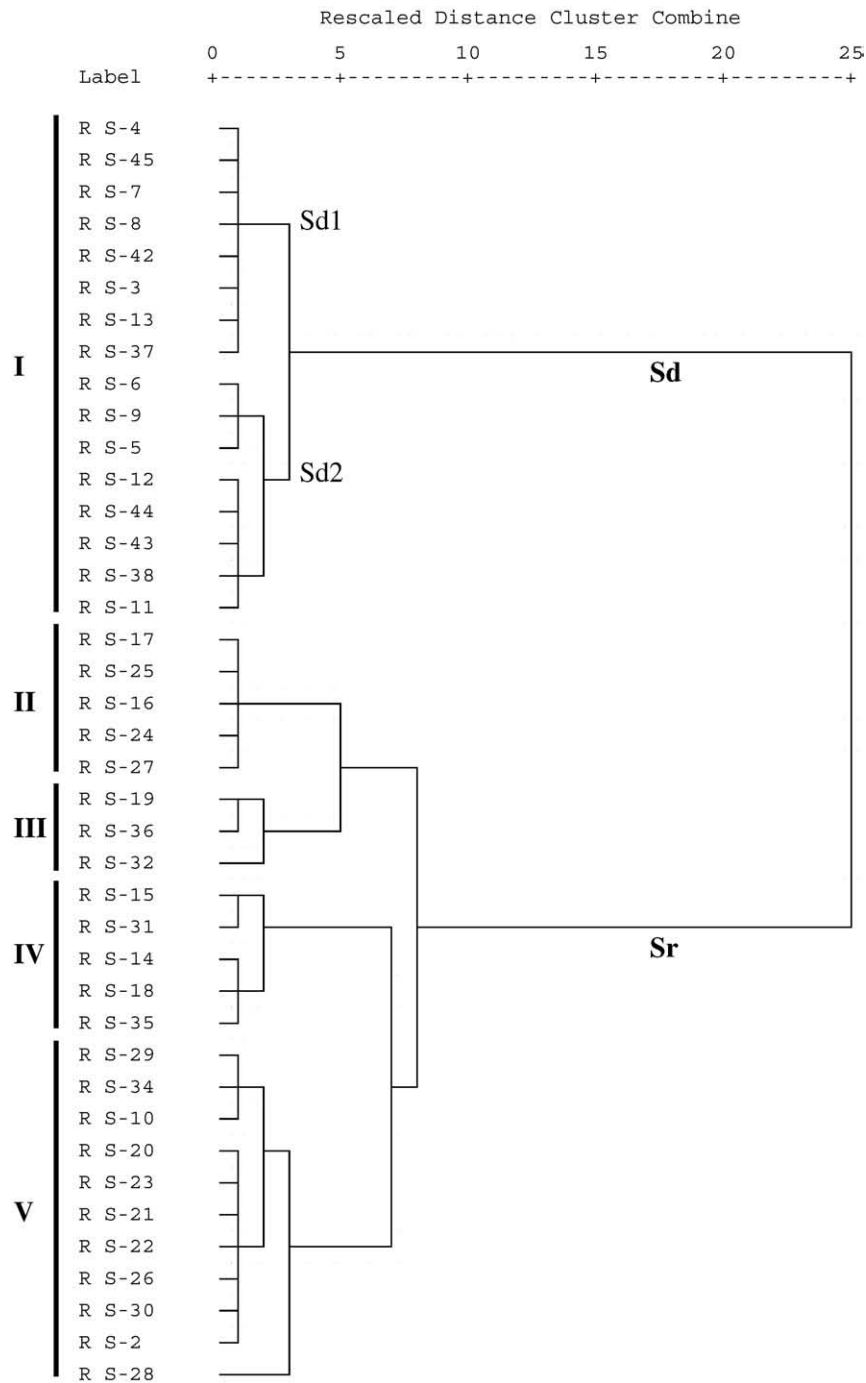
Fig. 2. Hierarchical Cluster Analysis (HCA) of E Zone samples. (Sd: soils used in the recovery of the dump (Sd1: uncontaminated; Sd2: contaminated); Sr: soils in the riverbed; I, II, III, IV, and V: subpopulation discriminated in the HCA).

background levels of the soils; the most commonly used methods involve the 95 percentile (Kabata-Pendias and Pendias, 2001), the median and the absolute deviation of the data to the median (Tukey, 1977), and the mean and the standard deviation of the dataset (Hawkes and Webb, 1962). In our study area, the background concentration determined by PXRF and the use of these statistical approaches gave the following levels for the main elements: Pb (23.6–26.2 mg kg^{-1}); As (21.5–23.3 mg kg^{-1}); Zn (43.3–54.9 mg kg^{-1}); Cu (42.2–44.2 mg kg^{-1}). The comparison of these values determined by PXRF with the values described as the baseline in the soils of the province of Almería (Sierra et al., 2007), to which the study area belongs, indicated that the concentrations measured by this method are within the normal range of the region.

3.2. Samples related to dynamic cyanidation process (E Zone)

According to the data provided by PXRF, the main trace elements detected in the samples were Pb, As, Zn and Cu (Table 2). The results indicate increases in trace-element concentrations in the riverbed soils (Sr) in relation to the geochemical background of the area with values exceeding 11- and 16-fold the background level in the case of Pb and As, respectively; although the mean concentration of these elements indicates statistical differences between groups only in the case of As.

The tailings of the dump (Td), located in the upper part of the basin, registered the highest mean values of As, with mean concentrations exceeding 688 mg kg^{-1} and maximum values higher

than 1200 mg kg^{-1}. The uncontaminated soils used in the recovery of the holding dump had the lowest mean values of As (127 mg kg^{-1}), but the highest concentrations in relation to the background level indicate that some samples could be contaminated by the tailings (in the sampling, the thickness of the soil covering the tailings was observed to be lower than 10 cm in some cases). The soils of the riverbed, directly sampled in the middle of the dry watercourse, also have high mean As concentrations (359 mg kg^{-1}), indicating a strong relationship with the source of the pollution, suggesting this eventual watercourse as one of the main ways that trace-elements were dispersed in the landscape.

Hierarchical Cluster Analysis (HCA) was made with the normalized data of the main trace-elements in the soil samples of the area, using the main trace elements (Pb, As, Zn and Cu) to discriminate different subpopulations into the whole dataset (Fig. 2). The first level discriminated between the soils used in the recovery of the dump (Sd), and the soils of the riverbed (Sr); and in a lower discrimination level, 4 different groups were distinguished within the samples, mainly related to the proximity to the holding dump and to the different positions in the riverbed. Clusters II, III, and V are located within the water course and progressively moved away from the origin of the potential contamination (close, middle and far away from the holding dump, respectively). Cluster IV includes samples located outside the main watercourse, but in the flood plain of the riverbed.

A variance analysis (ANOVA) and multiple-comparison test (Tukey Method) were performed between the different clusters and the main trace elements in order to determine statistical differences ($p < 0.05$) between groups. The main pollutants in the area were As and Pb and, according to this test, both elements had statistical differences between the subpopulations separated within the cluster (Table 3).

The different subpopulation discriminated by the HCA were also studied by the means of the As and Pb concentrations, and their location in the landscape. According to the box-plot (Fig. 3), the lowest As concentration belonged to Cluster I, including the soils used in the recovery of the dump (Sd). This group has several anomalous values, and when the cluster was examined in detail (Fig. 2), the group was split in two different subpopulations (Sd1 and Sd2). Sd1 represents the soil samples used in the recovery of the dump, with As concentrations (17.0 ± 3.9 mg kg^{-1}) similar to the geochemical background of the soils in the area. Sd2 includes the soil samples used for the tailing dump recovery, but partially contaminated by the tailings below during the soil sampling due to the scarce thinness (less than 10 cm in some cases) of the soil layer. In Sd2 group, the mean As concentration is higher (48.0 ± 10.4 mg kg^{-1}) than in Sd1 group, with three outliers samples (R S-5, R S-6, and R S-9) presenting As concentrations around 80 mg kg^{-1}.

The highest As concentrations were found in Cluster II, which includes the samples located closest to the holding dump, just below the retention dam, where mean values reached 378.4 mg kg^{-1}. Cluster III is located in the middle part of the dry watercourse, with mean As concentrations (288.1 mg kg^{-1}) significantly lower than the samples located upstream. Cluster V includes samples located in the final part of the riverbed and samples of the retention dam (presenting a mixture of soils used in the recovery of tailings from the dump), with mean As concentrations (256.2 mg kg^{-1}) not
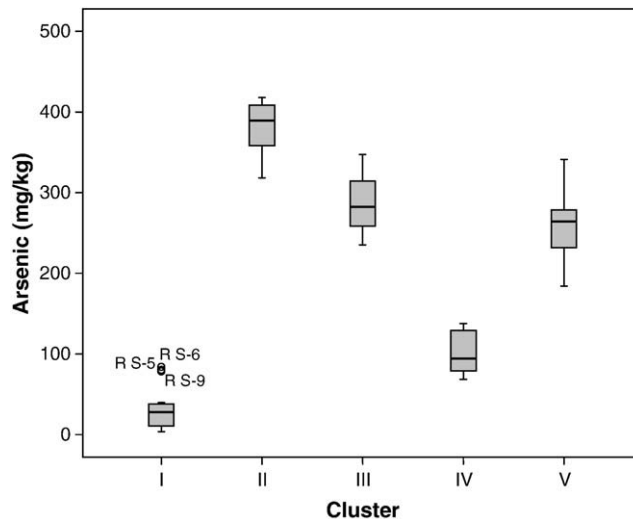

Fig. 3. Box-plot diagram of As concentration in E Zone according to the subpopulations of the hierarchical cluster analysis of Fig. 2.

significantly lower than Cluster III. Finally, Cluster IV includes the samples located outside the main water course, but in the flood plain of the riverbed, with mean As concentrations (101.8 mg kg^{-1}) significantly lower than the other samples related to the main water course.

According to the results, and with the data obtained in field directly measured by PXRF, we can deduce that there are two main processes involved in the dispersion of the potential contamination in the area. On one hand, the water erosion leached the main pollutants (As and Pb) downstream, with statistical differences according to the position into the riverbed in relation to the contamination source (holding dump); on the other hand, the wind erosion dispersed the pollutant, increasing the concentration of these elements in adjacent areas outside the riverbed.

3.3. Samples related to the heap leaching process (W Zone)

The main trace elements detected by PXFR in the samples were the same as in the E Zone (Pb, As, Zn and Cu). The results indicate an increase in the trace element concentrations of the soils in relation to the geochemical background of the area, with values exceeding 8- and 6-fold the background level in the case of Pb and As, respectively (Table 4). The mean concentrations of these elements indicate lower values in this area than in the samples related to the holding dump; the mean concentration of As in these soils is 124.5 mg kg^{-1}, the mean concentration of Pb is 206.6 mg kg^{-1}, and in the case of Cu, the concentrations were not statistically different from the background values of the soils in the area.

Hierarchical Cluster Analysis (HCA) was made with the normalized data of the main trace elements (Pb, As, Zn and Cu) in the soil samples of the area, to discriminate different subpopulations within the general dataset (Fig. 4). The first level discriminated between the soils closest to the abandoned slagheap (cluster I) and the other soils;

Table 3
Multiple-comparison test (Tukey Method) between subpopulations. Values are in mg kg^{-1}; *a, b, c, d*: statistically significant differences between groups ($p < 0.05$).

Cluster	As	Pb
I	32.5 *a*	68.3 *a*
II	378.4 *b*	267.2 *b*
III	288.1 *c*	392.4 *c*
IV	101.8 *d*	209.7 *b,d*
V	256.2 *c*	160.3 *d*

Table 4
Concentration of the main trace elements detected in the W Zone.

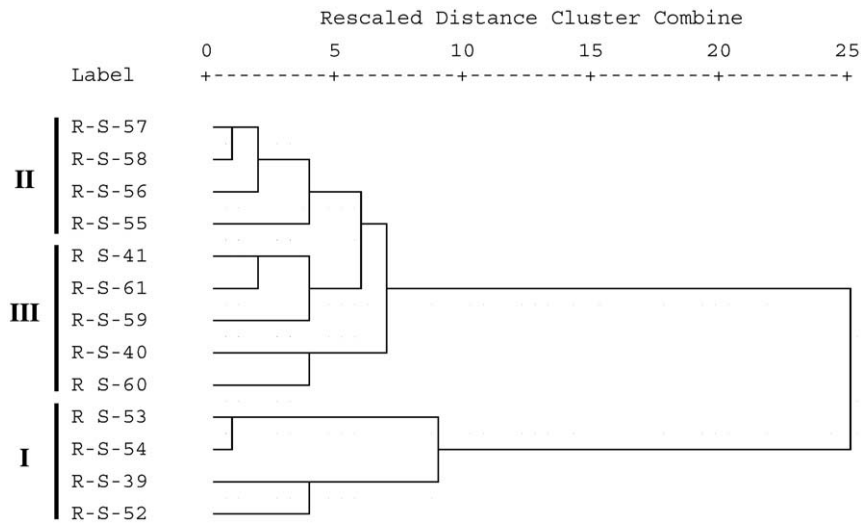|	Pb (mg kg^{-1})	As (mg kg^{-1})	Zn (mg kg^{-1})	Cu (mg kg^{-1})
Mean	206.57	124.54	124.62	45.00
SD	100.89	82.41	41.87	11.18
Min.	107.96	49.33	48.00	29.09
Max.	440.95	331.42	201.35	71.79

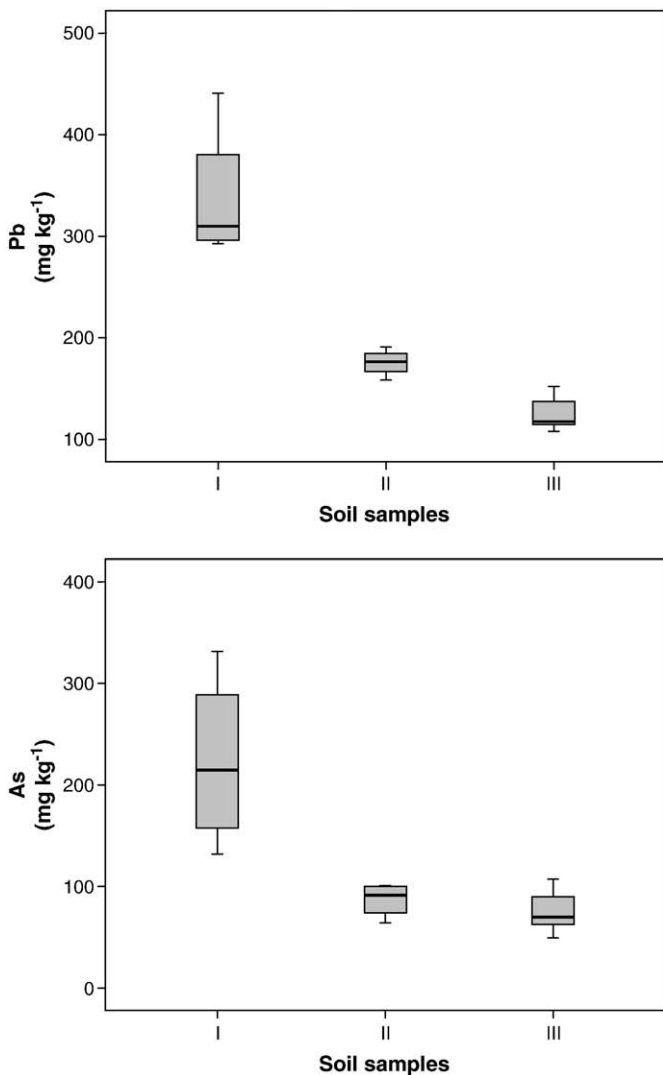**Fig. 4.** Hierarchical Cluster Analysis (HCA) of W Zone samples.

Fig. 5. Box-plot diagram of Pb and As concentrations in W Zone according to the subpopulations of the hierarchical cluster analysis of Fig. 4.

in a second level, the discrimination was between the soils far away from the slagheap (cluster III), and the one located in an intermediate position (cluster II).

A variance analysis (ANOVA) and multiple-comparison test (Tukey Method) were made between the different subpopulations obtained in the HCA and the main trace elements studied, to determine statistical differences ($p<0.05$) between groups. According to this test, the As and Pb were the only elements with statistical differences between subpopulations, creating two groups.

The soils closest to the abandoned slagheap (cluster I) had the highest As and Pb concentrations of the area (223.1 and 338.3 mg kg^{-1}, respectively), and the other soils, although not statistically significant, registered lower values, depending on the distance to the slagheap, with the lowest concentrations of As and Pb (75.8 and 125.9 mg kg^{-1}, respectively) being reached in the soils far away from the slagheap (cluster III). The decline in the As and Pb concentrations in relation to the distance to the slagheap was also evident in the Box-Plot (Fig. 5), so that the distribution of the potentially contaminated soils, could be strongly related to the main geomorphologic processes in the area (mainly wind and water erosion).

3.4. Potential contamination of the soils

According to the background concentration of the soils in the two studies areas the levels of the main trace elements studied were many-fold the levels of these concentrations, especially in the case of Pb and As, so that the values measured by PXRF could be considered significantly higher.

The potential contamination of the soils was determined by a comparison between the trace element concentrations and the intervention levels (Table 5) proposed to the Environmental Agency of the Regional Government of Andalusia (Aguilar et al., 1999).

Table 5
Intervention levels in soils of Andalusia region (Aguilar et al., 1999). Values are in mg kg^{-1}.

Element	Agricultural use		Natural areas	Industrial areas
	pH<7	pH>7		
As	50	50	100	300
Cu	300	500	500	1000
Pb	350	500	1000	2000
Zn	600	1000	1000	3000

These levels are defined depending on the different soil use, and the comparison between the values measured in soils and the intervention levels in this table shows the significance of the anomalous trace-element concentrations in the soils of the study area. The element with the highest anomalous values is the As, exceeding the intervention level for agricultural use (50 mg kg^{-1}) in 89% of the samples; and in the area related to the heap leaching process (with soils used exclusively for agriculture) only one sample had a concentration slightly below this limit (48 mg kg^{-1}). The intervention level for natural areas (100 mg kg^{-1}) was exceeded by 67% of the samples; meanwhile the intervention level for industrial areas (300 mg kg^{-1}) was surpassed by 43% of the samples. For Pb, 8% of the samples exceeded the intervention level for agricultural use, while no samples exceeded the limits for either natural or industrial areas.

The high As concentrations detected by PXRF in most of the samples, indicated that the soils of the area could be potentially polluted by this element, and the total concentrations measured could be related to a potential toxicity with hazardous environmental implications. Therefore, detailed studies on the retention and immobilization capacity of this element in the soils of the area, on the potential mobility and bioavailability of As in this media, and on toxicity-risk assessment are strongly recommended.

4. Conclusions

The determination of trace elements in soil samples by PXRF is a quick and useful tool for screening potentially polluted soils. The treatment of the raw data by a simple statistical approach (HCA and ANOVA) can differentiate anomalous concentrations and discriminate several degrees of potential soil pollution according to the spatial distribution of the samples. The element exceeding the intervention levels both for agricultural and natural use in the area was the As, with 89% and 67% of the samples above these limits, respectively. According to this methodology and field observations, the main mechanism of dispersion of trace elements in soils of the area can be assumed. Two processes are believed to participate in the spreading of the potential pollution: on one hand, water erosion, making it possible to differentiate subpopulations with statistically lower concentrations of As farther from the pollution sources (holding dumps); on the other hand, wind erosion, with soil samples outside the water course presenting As concentrations above the background values of the area and with higher concentrations than subsurface samples.

Studies regarding the mobility and bioavailability of the trace elements detected (mainly As), together with toxicity bioassays, are necessary to estimate the potential environmental risk of these elements in the soils of the area.

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