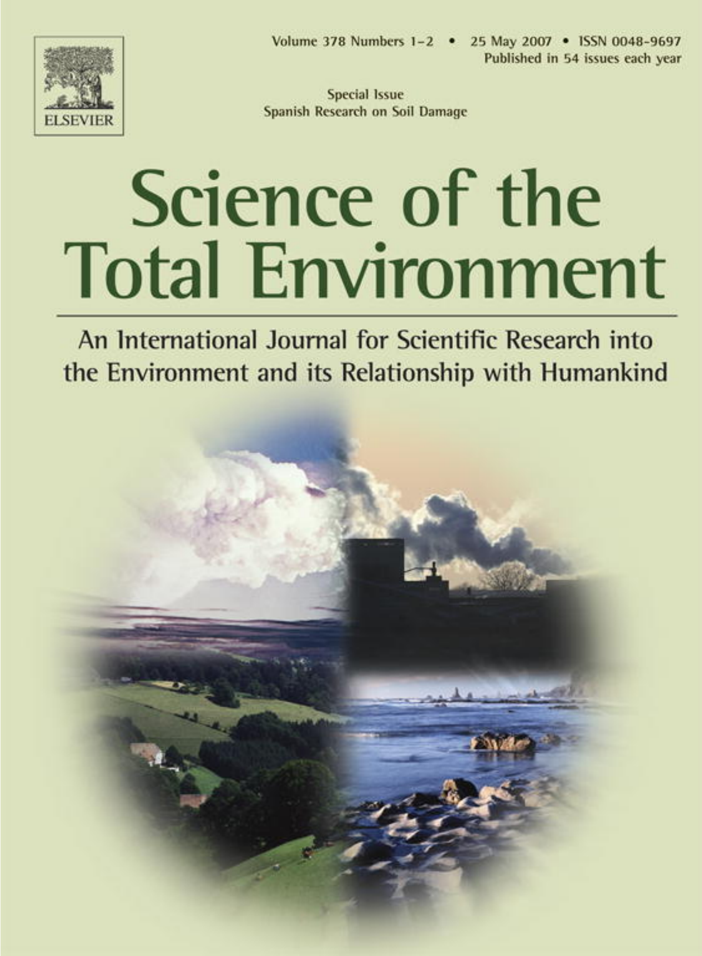

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# Background arsenic concentrations in Southeastern Spanish soils

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## Abstract

The arsenic content in the province of Granada (SE Spain) was quantified, based on 93 soils at two different depths and their corresponding parent materials. The arsenic concentrations fit a log–normal distribution. Four different statistical procedures to estimate the arsenic background range in the region were tested. Upper background limits clearly exceeded limits reported for natural soils when based on the Tukey box plot or means and standard deviations of the dataset ($M \pm 2$sdev) or of the calculated distribution function (Mf$\pm 2\sigma$) but not when based on median values (Md$\pm$2MAD). The relative cumulative frequency curve not only adequately estimates the background range but also delivers a clear and detailed visualisation of the data distribution and identifies subpopulations with specific background ranges related to combinations of parent materials and degree of soil development.

*Keywords:* Soils; Arsenic; Background; Subpopulation

## 1. Introduction

Governments and environmental scientists investigating soil quality use geochemical background as a reference to detect soils contaminated by trace elements. Geochemical background is defined as the concentration of chemicals in soils without human influence but truly uncontaminated soils do not exist in most settings, because of long-range transport and the persistence of contaminants (Chen et al., 2001). In the present study, this background is defined as natural concentrations of arsenic from parent material and natural processes that might also show some influence from diffuse anthropogenic sources and is considered a relative measure to distinguish between natural and anthropogenically influenced (outliers) arsenic concentrations in sets of real samples.

Different statistical approaches have been used to establish levels of trace elements in soils. In exploration geochemistry, values within the range estimated from the $M \pm 2$sdev, where $M$ is the mean and sdev is the standard deviation, have been defined as the geochemical background (Hawkes and Webb, 1962). However, this measure is not valid in environmental studies (Reimann et al., 2005), since the presence of extreme values or *outliers* in the dataset implies that the distribution function will be skewed towards higher values, the data will not be normally distributed, and the mean and the standard deviation will be increased, giving rise to an unreasonably broad range of background values. Various methods have been used to address this problem, including: a) log-transformation of the data to minimize the influence of outliers, adjusting the dataset to a roughly log–normal distribution before the calculation (Ahrens, 1954); b) application of the so-

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called "calculated distribution function" (Matschullat et al., 2000); c) replacement of the mean ($M$) with the median (Md) value, which is not affected by outliers if these are less than 50% of the dataset, and replacement of the standard deviation (sdev) with the median absolute deviation (MAD) (Tukey, 1977); and d) identification of extreme values from a box plot (Tukey, 1977).

Background levels of trace elements in soils are highly dependent on soil-forming factors (parent material, climate, relief, organisms and time) and soil development processes (Salminen and Tarvainen, 1997; Klassen, 1998; Chen et al., 2001). Thus, an arsenic concentration of 1–40 mg $kg^{-1}$ has been reported in uncontaminated soils, with lowest concentrations in sandy and granite-derived soils, whereas higher concentrations are found in alluvial soils (Mandal and Suzuki, 2002). In regional studies across several ecosystems with different soil-forming factors, natural and human-induced processes lead not only to a broader data range (higher standard deviations) but also to a multimodal distribution in which each *mode* has a specific background range and normal distribution and represents a particular combination of factors and processes (Matschullat et al., 2000). The presence of multiple modes (subpopulations) within the data sets can be assessed by using relative cumulative frequency curves (RCFCs) (Reimann et al., 2005).

The objective of the present study was to assess the background arsenic range of soils in a province in SE Spain (Granada), using different approaches, in order to identify relatively homogeneous subpopulations within the dataset and estimate the background arsenic range in each subpopulation.

## 2. Materials and methods

### 2.1. Study area

Granada province in Southeastern Spain occupies an area of 12,531 $km^2$ (Fig. 1) and has a Mediterranean type climate (Bosque Maurel, 1999). Two large-scale geological units can be differentiated: the Betic Cordillera and the Neogene Basin (Junta de Andalucía, 1995). The Betic Cordillera is divided between a younger External Zone (24% of total area) with a predominance of carbonate materials, e.g., limestones, marbles and dolomites (hereafter "*limestones*"), and an older Internal Zone (20% of total area), with a predominance of metamorphic rocks, e.g., micaschists, quartzites, shales and gneisses (hereafter "*micaschists*"). The Neogene Basin contains the following materials: a) Miocene silts and marls (14% of total area), hereafter designated "*marls*"; b) continental and lacustrine deposits of diverse composition and grain size, divided between *consolidated sediments* (18% of the total area, dating from the late Miocene-Pliocene) and *unconsolidated sediments* (occupying 14% of total area, dating from the Pleistocene); and c) sediments deposited at the bottom of brackish lakes, designated *evaporites* (10% of total area).

### 2.2. Sampling procedure

The province was divided into 93 uniformly distributed sectors of 135 $km^2$ each. A square plot was laid out (10 × 10 m) and georeferenced by Global Positioning System (GPS) at the approximate centre of each sector. Samples were taken from the four corners and centre of each plot at depths of 0–20 cm and 20–40 cm and from the bedrock (BR), and the 5 samples taken at each depth were pooled.

### 2.3. Soil analyses

The pH of the soils was measured potentiometrically in a 1:2.5 soil (fine earth)–water suspension using a CRISON Model Microph 2002 instrument. Soil and BR samples were air-dried and finely ground (<0.05 mm). The parent materials (BR) were also identified in the field by using a petrographic microscope. The $CaCO_3$ equivalent was analysed by manometric measurement of the $CO_2$ released after addition of hydrochloric acid (Williams, 1948). Soil and BR samples were digested in strong acids ($HNO_3+HF+HCl$), and the arsenic concentration in each digested sample was measured by Inductively Coupled Plasma–Mass Spectrometry (ICP–MS) using a PE SCIEX ELAN-5000A spectrometer. The limit of detection of arsenic by ICP–MS was 0.01 μg $l^{-1}$. The accuracy of the method was corroborated by analyses (six replicates) of Standard Reference Material SRM2711 (Simón et al., 2001).

### 2.4. Data processing

The SPSS v.12.0 software package was used for all statistical analyses. The normal distribution of the data (Ahrens, 1954) was checked by frequency histograms and Kolmogorov–Smirnov (K–S) test. A two-way analysis of variance was performed, with depths (0–20, 20–40 cm and BR) and parent materials (6 lithologies: limestones, marls, evaporites, micaschists and unconsolidated and consolidated sediments) as factors, comparing differences between means with Duncan's Multiple Range test, using a significance level of 5% ($P<0.05$).

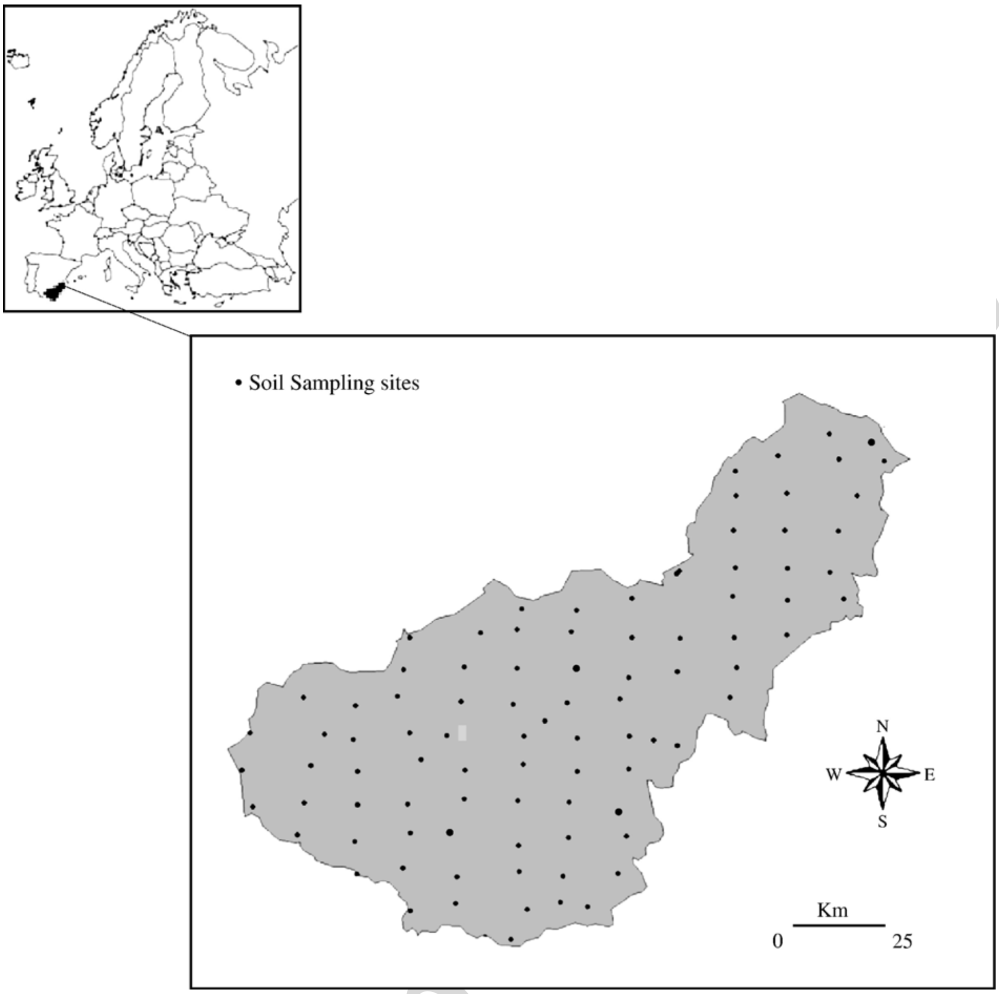

Fig. 1. Location of the study area and distribution of sampling sites.

### 2.5. Background determination and outlier detection

Four statistical methods proposed in the literature for determining general background range and detecting outliers were applied, based on the following:

a) Mean ($M$)±twice the standard deviation (sdev) of the log-transformed dataset ($M$±2sdev; Ahrens, 1954).
b) Mean (Mf)±twice the standard deviation ($\sigma$) of the calculated distribution function (Mf±2$\sigma$; Matschullat et al., 2000). This approach assumes that the lower half of the dataset (values below median) is free from human influence and represents the lower half of the natural background distribution curve. A curve for the distribution function without human influence can be constructed from the lower half of the dataset by extrapolating the inverse curve.
c) Median (Md)±twice the median absolute deviation (MAD), defined as the median of the absolute deviations from the median of all data (Md±2MAD; Tukey, 1977).
d) The Tukey box plot (Tukey, 1977), defining the background as the box (between 25 and 75%) extended by 1.5 times the length of the box towards maximum (upper inner fence) and minimum (lower inner fence) values.Relative Cumulative Frequency Curve (RCFC) was used to evaluate the presence of multiple subpopulations within the datasets that formed distinct straight-line segments on a probability plot with a normal distribution (Bauer and Bor, 1995). Inflection points (*threshold points*) formed by the overlapping of two subpopulations were identified as the end data points for which the resulting population showed a skewness closest to 0 (Fleischhauer and Korte, 1990).

## 3. Results

### 3.1. Soil properties

The most representative soils in the area were (in decreasing order of abundance) Entisols, Inceptisols, Mollisols, Aridisols and Alfisols (Soil Survey Staff, 1999). Soil pH ranged from pH 5.80 to pH 8.92 (mean 8.22±0.49), and 50% of samples had a pH>8.37. The $CaCO_3$ content ranged from 0 to 88.50% (mean 35.30±27.3), and 50% of samples had a content>36.35%.

Differences in these two parameters were minimal among soil samples and no statistically significant differences were found between samples taken from 0–20 cm and from 20–40 cm. The most developed soils, those with Bw and Bt horizons, showed partial or complete decarbonation of the soil material (at least in the uppermost 40 cm).

Soil pH and $CaCO_3$ content both showed a significant ($P>0.01$) inverse relationship with log-transformed arsenic data:

$$\mathrm{Log\,As} = -0.191\,\mathrm{pH} + 2.599 \tag{1}$$

$$\mathrm{Log\,As} = -0.007\,\mathrm{CaCO_3}(\%) + 1.290 \tag{2}$$

### 3.2. Arsenic concentration

Mean arsenic concentration (13.0 mg $kg^{-1}$) and range (0.5 – 116 mg $kg^{-1}$) were similar to findings in other countries (Table 1), although the mean level was lower than that reported in soils in Italy and the maximum level was lower than that observed in Hungary and Italy. The median concentration (7.9 mg $kg^{-1}$) was lower than the mean concentration, and the frequency-distribution curve of the data differed from the ideal Gaussian (normal) curve, being positively skewed (skewness=3.53) with a long tail to the right indicating the presence of outliers (Fig. 2a). The distribution curve of the log-transformed data adjusted better to a normal curve, with lower skewness and showing a significance of>0.05 in the K–S test, confirming that the log–normal distribution of the arsenic in these soils (Fig. 2b). Consequently, log-transformed data were used for the different statistical analyses used in this study.

Because Duncan's test results showed no difference in arsenic concentrations between soil samples from 0–20 and 20–40 cm, results for these depths were considered together in the statistical analyses. Significant differences were observed between soils and BR samples ($P<0.05$), with higher arsenic concentrations in soil than in BR.

According to the Duncan's test results, the mean arsenic concentration (5.1 mg $kg^{-1}$) in soil and BR samples from limestones, marls and evaporites significantly differed ($P<0.05$) from the mean value (11.2 mg $kg^{-1}$) in samples from micaschists and consolidated and unconsolidated sediments.

Table 1
Mean and range of arsenic concentration (mg $kg^{-1}$) in soils of different localizations

| Localization | Mean (mg $kg^{-1}$) | Range (mg $kg^{-1}$) | References |
|---|---|---|---|
| Madrid (Spain) | 9.9 | 0.4–86.2 | De Miguel et al. (2002) |
| Aragon (Spain) | 12 | 0.0–58.9 | Navas and Machin (2002) |
| Hungary | 11 | 0.0–230 | Kabata-Pendias and Pendias (2001) |
| UK | 16 | 4–95 | McGrath (1986) |
| Portugal | 17 | 1–82 | Angelone and Bini (2001) |
| Italy | 41 | 4–197 | Angelone and Bini (2001) |
| USA | 7 | <0.1–93 | Shacklette and Boerngen (1984) |
| Japan | 11 | 0.4–70 | Mandal and Suzuki (2002) |

### 3.3. Background range

Broad background ranges were estimated by methods based on means and standard deviations of the dataset ($M$±2sdev) and the calculated distribution function (Mf±2$\sigma$) and by the Tukey box plot method, with values of 0.95–61.7 mg $kg^{-1}$, 0.96–70.3 mg $kg^{-1}$ and 0.68–88.3 mg $kg^{-1}$, respectively. All three methods showed an upper background limit (UBL) of >60 mg $kg^{-1}$ dry sample, higher than the upper limit in uncontaminated soils (40 mg $kg^{-1}$; Mandal and Suzuki, 2002). However, the method based on median values (Md±2MAD) gave a narrower background range (2.05–32.8 mg $kg^{-1}$), with an upper limit below that in uncontaminated soils.

### 3.4. Relative cumulative frequency curve

RCFC reflects the multimodal character of the dataset (Fig. 3), distinguishing five subpopulations (denominated as A, B, C, D and E) from the slope changes (*threshold points*) (Table 2).

In accordance with Bauer and Bor (1995), subpopulations A (upper limit<1.5 mg $kg^{-1}$) and E (>33.8 mg $kg^{-1}$), located at opposite ends of the curve, represent samples (*outliers*) below the lower background limit (LBL) and above the UBL, respectively. Accordingly, the background ranged from 1.5 to 33.8 mg $kg^{-1}$ for the whole dataset; and the UBL was similar to that obtained by the Md±2MAD method (32.8 mg $kg^{-1}$). This range, in which three homogeneous subpopulations (B, C, and D) could be distinguished, would include samples without human influence (Reimann et al., 2005). The log-transformed data for each of these subpopulations (Table 2) had a normal distribution (significance level for Kolmogorov–Smirnov test) and showed a linear and

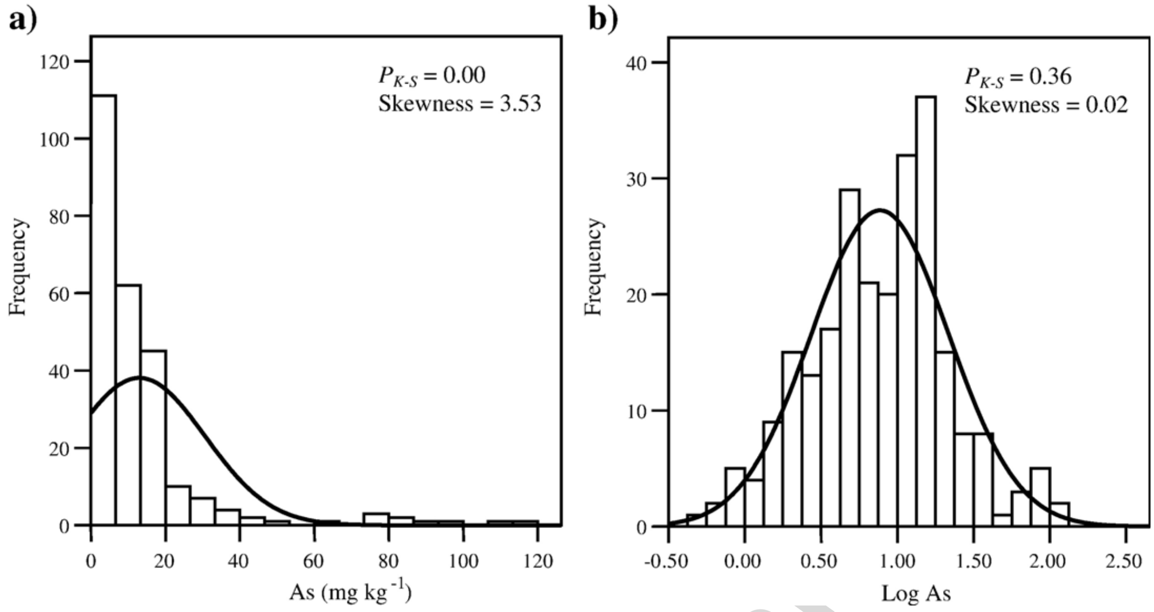

Fig. 2. Frequency histograms and normal curves of non- (a) and log- (b) transformed data for total arsenic concentrations in soils and bedrocks, including skewness and significance level of the Kolmogorov–Smirnov test ($P_{\text{K–S}}$). $P_{\text{K–S}} < 0.05$ indicates that distribution curves are other than normal).

significant ($P < 0.05$) relationship with the cumulative frequency (% CF), as follows:

$$\text{B}: \log \text{As} = 0.0035\%\,\text{CF} + 0.175 \quad r^2 = 0.990 \tag{3}$$

$$\text{C}: \log \text{As} = 0.0075\%\,\text{CF} + 0.549 \quad r^2 = 0.994 \tag{4}$$

$$\text{D}: \log \text{As} = 0.0024\%\,\text{CF} + 1.301 \quad r^2 = 0.968 \tag{5}$$

These data confirm that each subpopulation had a characteristic background range and represented a specific combination of factors and processes (Matschullat et al., 2000).

### 3.5. Interpretation of subpopulations

Tukey box plots (Fig. 4) were used to relate the five homogeneous subpopulations identified (Fig. 3) to the origin and depth of samples (Fig. 4a) and their lithology (Fig. 4b).

Subpopulations A and B were exclusively or predominantly (70% of total samples) composed of BR samples; whereas subpopulations C, D, and E were mostly (80–87%) composed of soil samples at the two different depths (Fig. 4a). Limestones and marls were the main BRs of A (86.7%) and B (46.7%) subpopulations, with lesser proportions of other parent materials. Subpopulation C contained the largest number of

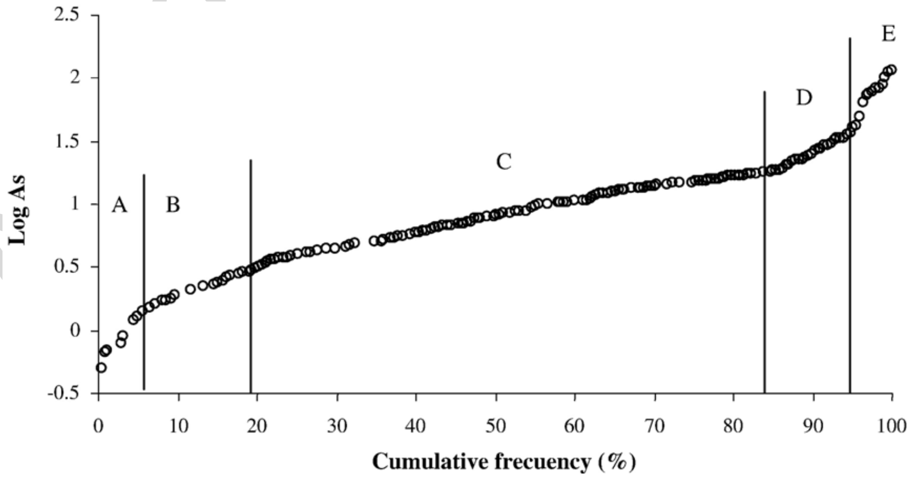

Fig. 3. Relative cumulative frequency curve of log-transformed arsenic, indicating the “threshold points” that separate the different subpopulations.

Table 2
Statistical parameters of arsenic concentrations (mg kg$^{-1}$) in subpopulations B, C and D differentiated by means of relative cumulative frequency curve

| Statistical parameters | Arsenic (mg kg$^{-1}$) | | |
|---|---|---|---|
| | Population B | Population C | Population D |
| Minimum | 1.50 | 3.60 | 20.2 |
| Maximum | 3.50 | 19.3 | 33.8 |
| Mean | 2.35 | 8.84 | 26.6 |
| Median | 2.30 | 9.50 | 27.0 |
| sdev | 0.10 | 4.59 | 4.21 |
| $P_{K-S}$* | 0.791 | 0.067 | 0.813 |

* $P_{K-S}$ = Kolmogorov–Smirnov test, values >0.05 indicate normal distribution curves.

samples (64% of dataset), which represented all soil types and parent materials studied. Most samples (83.3%) in subpopulation D and all samples in subpopulation E were from soil sampled over micaschists and consolidated and unconsolidated sediments.

## 4. Discussion

Because this study included several ecosystems with different parent materials and both naturally- and anthropogenically-induced processes, the arsenic concentration range found was very wide, and the data did not fit a normal frequency distribution curve. Log transformation of the data minimized distorting effects of extreme values and improved the fit of the data-distribution curve. Nevertheless, the range of the log-transformed data was also very broad with a very high standard deviation, compromising calculation of the background from these parameters. Thus, background estimates based on the Tukey box plot or on the means and standard deviations of the dataset ($M\pm2$sdev) or calculated distribution function ($M\pm2\sigma$) give a higher UBL (61–89 mg kg$^{-1}$) than observed in the vast majority of natural soils (40 mg kg$^{-1}$; Mandal and Suzuki, 2002). Consequently, arsenic-contaminated soils could be incorrectly considered natural soils according to the above three methods of calculating background concentrations (Matschullat et al., 2000).

The other methods used did not present this drawback. The Md±2MAD and RCFC methods both gave a narrower background range and an UBL (around 33 mg kg$^{-1}$) below the range of the natural soils. By the former method, 16.2% of study samples were classified as outliers (9.7%<LBL and 6.5%>UBL) compared with 11.3% of samples by the latter (5.7%<LBL and 5.6%>UBL). Samples identified by these methods as outliers due to excessively high levels (>UBL) were from plots close to abandoned but formerly important mines (Alquife and Conjuro), presumably the source of their contamination. In contrast, excessively low arsenic levels (<LBL) were found where the parent material was especially poor in arsenic, since the Mediterranean climate does not favour arsenic solubilization and migration processes that might lead to arsenic depletion. Consequently, these two methods proved to be suitable

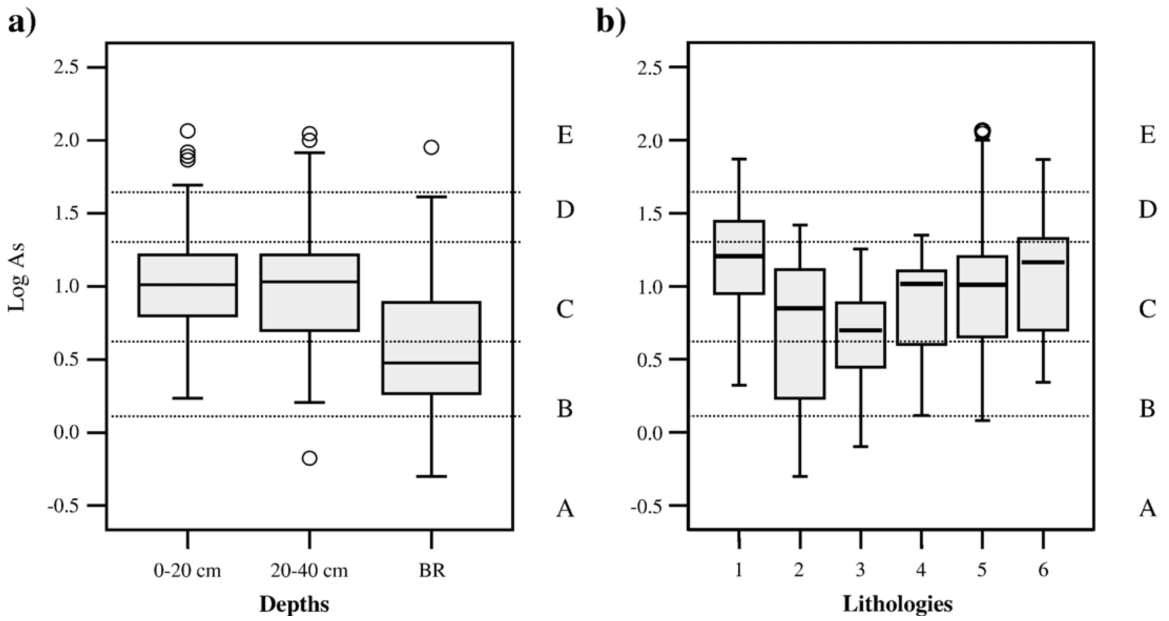

Fig. 4. Tukey Box plot of log-transformed arsenic data against: a) depth of samples (soil samples at 0–20, 20–40 cm and BR), and b) lithology (1 = micaschists, 2 = limestones, 3 = marls, 4 = evaporites, 5 = unconsolidated sediments, 6 = consolidated sediments). Relationship of box plot with subpopulations (A, B, C, D and E) of data set identified in RCFC are shown.

for estimating the upper limits of the arsenic background in the study area.

Although the UBL estimated by these two methods is useful for general studies and regulatory purposes, it is of less value for specific and detailed studies. In the latter cases, the RCFC can discriminate the multimodal character of the data set, allowing the ready identification and segregation of modes (subpopulations) for further analysis (Fleischhauer and Korte, 1990) and detecting extreme outliers as single values (Reimann et al., 2005). Thus, in this study of Granada province, degree of soil development and parent material were the two main parameters that influenced the arsenic concentrations in samples and the segregation of the dataset into different subpopulations. The weathering of BR samples increases the arsenic concentration in soil samples, presumably because depletion of more soluble elements leaves a higher percentage of those with less mobility (Zhang et al. (2002). This increase (Table 3) was especially marked in soils developing over limestones (mean almost 5-fold higher than that of BR) and marls (mean more than 2-fold higher than that of BR), in which development of partially or completely decarbonated Bw and Bt horizons increase the arsenic concentration (Palumbo et al., 2000). The significant inverse relationship between the arsenic and $CaCO_3$ content of samples (Eq. (2)) confirmed this process. Moreover, arsenic concentrations significantly differed among parent materials, with lowest values in limestones and marls and highest in micaschists (Table 3).

The subpopulations identified by RCFC were consistent with the above findings (Fig. 4). Thus, 85% of subpopulation A samples were BRs (limestones and marls) with very high $CaCO_3$ contents (>60%). The majority (55%) of subpopulation B was also made up of BR samples (limestones, marls and unconsolidated sediments with very high $CaCO_3$ contents) alongside soil samples formed from weakly weathered carbonate materials (mean $CaCO_3$ content ≈ 56%). Most of the samples analysed belonged to subpopulation C and comprised BRs with no or little $CaCO_3$ content and moderately weathered soil samples (mean $CaCO_3 \approx 32\%$). Population D included only 8% of the dataset and mainly comprised decarbonated and strongly developed Bt horizons formed over micaschists, limestones, and consolidated and unconsolidated sediments. Finally, all samples of population E were located near old iron ore mines (mostly goethite, hematite and siderite) in Alquife and Conjuro, and their high concentration can be attributed to contamination processes rather than to the parent material or degree of soil development.

Table 3
Statistical parameters of arsenic concentrations (mg $kg^{-1}$) in BR and soil samples of different lithologies

| Lithology | Samples | Mean | Maximum | Minimum | sdev |
|---|---|---|---|---|---|
| Micaschists | Soils | 15.42 | 74.30 | 2.86 | 0.365 |
| | BR | 10.91 | 30.13 | 2.10 | 0.400 |
| Limestones | Soils | 9.31 | 26.18 | 0.67 | 0.327 |
| | BR | 1.65 | 7.10 | 0.50 | 0.351 |
| Marls | Soils | 5.86 | 17.91 | 1.60 | 0.222 |
| | BR | 2.28 | 1.67 | 0.80 | 0.272 |
| Evaporites | Soils | 9.62 | 22.28 | 2.80 | 0.283 |
| | BR | 4.58 | 12.79 | 1.30 | 0.447 |
| UCS | Soils | 13.37 | 115.88 | 3.40 | 0.400 |
| | BR | 5.51 | 89.54 | 1.20 | 0.455 |
| CS | Soils | 17.99 | 73.45 | 5.00 | 0.388 |
| | BR | 4.70 | 19.32 | 2.20 | 0.390 |

(UCS: unconsolidated sediment; CS: consolidated sediment).

According to this study, arsenic concentrations <3.5 mg $kg^{-1}$ characterize highly carbonated materials and very weakly-weathered soils developed on them (Entisols); arsenic concentrations of 3.5–20 mg $kg^{-1}$ define most of the other parent materials and soils of the region; arsenic concentrations of 20–33.8 mg $kg^{-1}$ characterise the Bt horizon of the most developed soils (Alfisols); and arsenic concentrations >33.8 mg $kg^{-1}$ represent outliers in the dataset. The upper limit of arsenic background in the region can be established at around 33 mg $kg^{-1}$. Nevertheless, contamination may be indicated by arsenic concentrations below this upper limit under certain conditions, e.g., by >3.5 mg $kg^{-1}$ in weakly weathered and highly carbonate soil samples from limestone and marls or by arsenic concentrations >20 mg $kg^{-1}$ in soil samples other than strongly weathered and decarbonated Bt horizons.

## 5. Conclusions

In regions characterized by a wide variety of soil-forming factors and soil development, there is a broad range of arsenic concentrations but the dataset can be divided into homogeneous subpopulations that have each a characteristic background range. Consequently, although an overall upper limit of arsenic background can be established for the region, it may be misleading. Thus, a sample that falls below this regional limit may not necessarily indicate absence of contamination, since it might exceed the upper limit of the subpopulation to which it belongs.

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