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Title: Determination of background levels and pollution assessment for seven metals (Cd, Cu, Ni, Pb, Zn, Fe, Mn) in sediments of a Mediterranean coastal lagoon.

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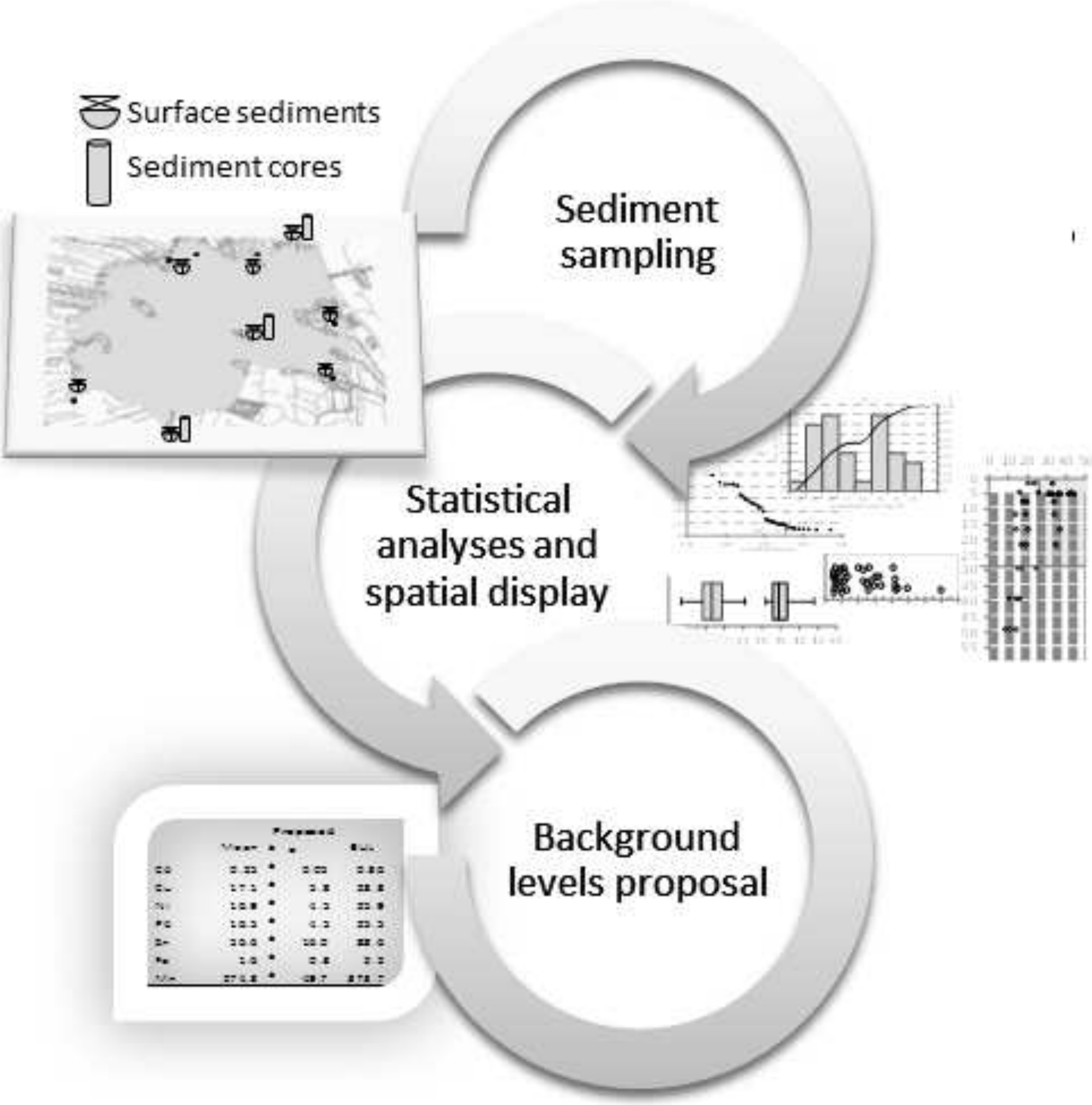
Abstract: The determination of background levels of trace metals in soils and sediments is a key point for the proper assessment of pollution degree. This study demonstrates the suitability of integrating geological and statistical methods for the reliable determination of background levels, applying it to the sediments of Lake Albufera, a wetland of international importance that is highly eutrophic. The procedure followed includes sampling of sediment cores at different points of the lake, including reference sites, and the subsequent statistical analysis of the data, comprising descriptive statistics, probabilistic plots and modal analysis. The final proposal of background levels considers the data subset separated by the statistical analysis and the spatial and age characteristics of sediments, proving the usefulness of jointly using geological and statistical methods. The upper limits of the background populations, defined as the mean+2ű and expressed in mg/kg, are Cd (0.38), Cu (28.8), Ni (25.9), Pb (25.5), Zn (88.6), Fe (2.2%) and Mn (345.7). Background levels proposed for different parts of Spain, found in an extensive literature review, are also provided in this article. Once determined the background levels, the assessment of pollution degree of sediments using pollution indexes indicates that the top 25 to 30 cm of sediments has a pollution level between moderate and severe in the peripheral sites, which are nearest to the pathways of contamination, and that the north zone of the lake is the most polluted by the group of the five metals, including Cd, Cu, Ni, Pb and Zn.

Graphical Abstract (for review)



Highlights:

- We establish background levels for metals to sediments of Lake Albufera.
- An integrated method of geological and statistical approaches has been used.
- The depth to which sediments are contaminated is provided, the upper 30 cm.

Determination of background levels and pollution assessment for seven metals (Cd, Cu, Ni, Pb, Zn, Fe, Mn) in sediments of a Mediterranean coastal lagoon.

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Abstract

The determination of background levels of trace metals in soils and sediments is a key point for the proper assessment of pollution degree. This study demonstrates the suitability of integrating geological and statistical methods for the reliable determination of background levels, applying it to the sediments of Lake Albufera, a wetland of international importance that is highly eutrophic. The procedure followed includes sampling of sediment cores at different points of the lake, including reference sites, and the subsequent statistical analysis of the data, comprising descriptive statistics, probabilistic plots and modal analysis. The final proposal of background levels considers the data subset separated by the statistical analysis and the spatial and age characteristics of sediments, proving the usefulness of jointly using geological and statistical methods. The upper limits of the background populations, defined as the mean+2σ and expressed in mg/kg, are Cd (0.38), Cu (28.8), Ni (25.9), Pb (25.5), Zn (88.6), Fe (2.2%) and Mn (345.7). Background levels proposed for different parts of Spain, found in an extensive literature review, are also provided in this article. Once determined the background levels, the assessment of pollution degree of sediments using pollution

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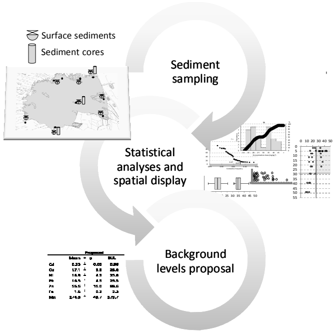

1. Introduction

Trace metals can be found in soils and sediments without human impact, having concentrations derived from rock weathering. These natural concentrations are commonly called “background levels” in environmental studies. Many human activities introduce metals into the environment (e.g., mining, traffic, agriculture, industries, wastewater treatment plants –WWTP–, waste landfills), thus increasing the concentrations of metals in soils and sediments above the background levels. In lentic water bodies, the tendency of metals to bind to the solid phase promotes their removal from the water column by sedimentation, and thus their accumulation in sediments. Therefore, it is important to know the background concentrations to assess the pollution status of sediments, which is also necessary to evaluate the ecological status of water bodies according to the European water framework directive (WFD). Regarding the background level or concentration concept, it is important not to confuse it with the term “baseline value”. The latter refers to the levels currently measured and serves to quantify future changes (Reimann and Garret, 2005).

Different approaches have been developed to determine geochemical background concentrations. Methods are usually classified into direct (empirical or geochemical) or indirect (statistical or theoretical), and both can be combined, leading to integrated methods (Dung et al., 2013; Galuzska and Migaszewski, 2011). Within each category, several procedures can be found:

- Direct methods. In these methods, the background concentrations are obtained by analysing samples representing the pre-industrial era or pristine areas.
  - Historical aspect. The background concentration is estimated as the mean or median of samples representing the pre-industrial period, such as deep sediments or deep soil horizons, glacial ice cores, archival plants from herbaria or tree rings (Galuzska and Migaszewski, 2011).
  - Contemporary aspect. In this case, it is estimated as the mean or median of samples collected from pristine areas, far away from pollution sources.
- Indirect methods or statistical approaches. These methods consist of sampling a large number of sites and using statistical tools and spatial analysis to separate, within a data set, the background concentration from that related to anthropogenic sources. Samples identified as polluted can be single or multiple outliers, or can represent distinct populations. Several methods of statistical sieving can be used:
  - Tukey boxplots, which identify as outliers any values beyond the whiskers of the boxplot, where the upper whisker = max(x[x<upper inner fence]) and the upper inner fence = Q3 + 1.5 (Q3-Q1), Q1 is the first quartile (25% of data) and Q3 is the third quartile (75% of data) (Reimann et al., 2005; Rodríguez et al., 2006).
  - Empirical cumulative distribution functions (ECDF) or probabilistic plots, the latter representing the accumulated data on a normal probability scale. These permit the detection of deviations from normality and the presence of multiple populations by slope changes and breaks in the plot (Reimann et al., 2005). To avoid subjectivity in identifying the inflexion

point, it is recommended to identify the inflexion point as the value that yields the minimal skewness for the resulting background population (Tobías et al., 1997; Peris, 2006).

- 4σ-outlier test. This requires the removal of potential outliers, identified in the ECDF for example, from the dataset and the calculation of the mean and standard deviation for the remaining sub-set of data. Then, the previously defined outliers can be classified objectively if they are further from the mean than 4σ (Matschullat et al., 2000).
- Iterative 2σ-technique. The mean and standard deviation are calculated for the original data set. Subsequently, all of the values beyond the mean±2σ are omitted, and the procedure is repeated until all remaining values lie within this range (Matschullat et al., 2000). This technique is considered to be mathematically less robust than the outlier test by other authors (Matschullat et al., 2000). Nevertheless, it is better at reducing the upper limit than the 4σ-outlier test and the calculated distribution (described below), and yields realistic and plausible values (Roca et al., 2012).
- Calculated distribution function. The background distribution function is calculated by "mirroring" every single value lower than the median against the original median value by adding the distance from each value to the median, thus obtaining new values larger than the median (Matschullat et al., 2000).
- Maximum likelihood mixture estimation (MLME), also called modal analysis, has been demonstrated to be useful in determining background values for biota and sediments (Carral et al., 1995; Rodríguez et al., 2006). This technique decomposes a multi-mode distribution function into several normal distributions. The sub-populations are centred on the modal values supplied by a previous identification technique. Usually the NORMSEP routine is employed, where the sub-populations are actually different if the separation index (Δmean/Δσ) is higher than 2 (Carral et al., 1995).
- Linear regression between the concentration of an element and one or several conservative factors (e.g., fine fraction, Fe, Al) considered as inert or not influenced by anthropogenic

activities. This tool also allows the identification of values not belonging to the background population, such as those that fall beyond the confidence interval (95%) (Dung et al., 2013).

  - Principal component analysis (PCA) and cluster analysis are also statistical techniques useful for identifying relationships between metals and other variables, and for grouping different populations from a dataset (Rubio et al., 2000; Aloupi and Angelidis, 2001; Micó et al., 2006; Blasco et al., 2010; Esmaeli et al., 2014).

  Once the background population has been separated, the values representing this population should be expressed as a range, which has traditionally been defined as the mean ± two times the standard deviation (mean$\pm 2\cdot\sigma$). However, Reimann et al. (2005) demonstrated that the median ± two times the median of the absolute deviations (median$\pm 2\cdot$MAD) is a more appropriate estimator, even for normal populations.

- Integrated methods combine several direct and indirect approaches. Several authors have demonstrated the convenience of integrating different methods to provide more reliable background thresholds. For instance, Galuzska (2007) sampled clean areas and used statistical analysis, Reimann et al. (2005) proposed a heuristic consisting of sampling different sites and applying statistical and spatial analyses, and Matschullat et al. (2000) applied different statistical tools to data obtained from drill sediment cores.

The use of direct methods is criticized for various reasons: sampling of deep sediment is considered technically difficult and expensive (Carral et al., 1995); it requires expert knowledge of the sampling area and about the geochemical behaviour of the investigated elements, and there may be subjectivity in selecting samples (Matschullat et al., 2000; Galuzska and Migaszewski, 2011). Sampling of deep sediment is also questionable due to the eventual depletion of some elements because of their natural properties, rather than owing to a lack of anthropogenic pollution (Reimann and Caritat, 2005) and it pre-supposes that there have been no post-depositional movements (Carral et al., 1995). Nevertheless, it is a method that is amply used (Blasco et al., 2000; Cobelo-García et al., 2003; Tylmann et al., 2011), and in some cases it is relatively easy to take long sediment cores (i.e., shallow waterbodies). Despite the above drawbacks, this method is advantageous in the sense that the results represent actual data and are not subject to any processing. On the other hand, the sampling of pristine areas is accompanied by the uncertainty of whether they are indeed free of anthropogenic pollution (Galuzska and Migaszewski, 2011).

This study aims to (1) establish background levels for seven metals (Cd, Cu, Ni, Pb, Zn, Fe, Mn) by integrating different methods for sediments from Lake Albufera de Valencia (Spain), a wetland of international importance according to the Ramsar Convention, (2) assess the extent of surface sediment pollution, and (3) compare the proposed background levels with those proposed for other locations in Spain and perform a review of studies of background concentrations for soils and sediments.

2. Materials and Methods

2.1 Study area

Lake Albufera is a coastal lagoon located 10 km southeast of Valencia (Spain). It has an area of 2400 ha, a mean water depth of 1 m and an average sediment thickness of 70 cm. The climate is Mediterranean, with a low mean annual precipitation (551 mm) and intense storms during autumn (up to 100-300 mm/d). The water temperature of the lake varies between 11ºC (Dec-Jan) and 28ºC (Jul-Aug). Since the 1970s, the lake has been highly eutrophic (with an annual mean chlorophyll-*a* concentration over 100 µg/L) due to several anthropic pressures (urban, industrial and agricultural). Sediments are mainly silty clay, with high contents of organic matter and metals in the layers close to the surface. So far, the concentration of acid volatile sulphide has been sufficient to retain metals as metal sulphides, but the concentration has a decreasing trend (Hernández-Crespo and Martín, 2013). Thus, it is important to establish the background levels to assess the degree of sediment metal contamination.

2.2 Sampling and analytical determinations

Procedures for sampling and chemical analysis are described in detail in Hernández-Crespo et al. (2012, 2013). Briefly, 9 sites inside the lake (identified as 1-7, 10-11 in Fig. 1) were selected for surface sediment sampling (Sep 2008); among these, sites 1, 6 and 11 were selected for sediment core sampling (Sep 2011 and Mar 2012). The peripheral sites 1 and 11 represent areas with higher contamination, while site 6, located in the central area of the lake, is considered as a reference site that is less affected by pollution inputs. With the aim of obtaining vertical profiles, the sediment cores were sectioned into 9 slices of increasing thickness (3x3 cm, 3x5 cm, 3x10 cm). The three sampling campaigns provided a total of 63 samples. Nevertheless, the average values of the two samplings of sediment cores have been utilized for statistical analyses because the results did not differ significantly (p>0.05), thus leaving 27 samples. Gathering the surface (9) and sediment cores (27), a total of 36 samples are available for statistical analysis. Metal content was determined by extraction with aqua regia and quantification by atomic absorption spectrometry (AAS). Quality control was performed by analysing blanks and certified reference material (CRM-320), with the following concentrations and recoveries: Cd (0.47 mg/kg; 98%), Cu (42.0 mg/kg; 100%), Ni (55.0 mg/kg; 95%), Pb (30.0 mg/kg; 93%), Zn (124.4 mg/kg; 110%), and Fe (3.3%; 99%).

2.3 Background assessment

An integrated method, including direct (geochemical) and indirect (statistical) approaches, has been applied to estimate the background concentrations for seven metals (Cd, Cu, Ni, Pb, Zn, Fe, Mn), approximately following the heuristic proposed by Reimann et al. (2005) for data inspection and selection of background thresholds. The steps taken are: (1) Core sediment sampling, to reach unpolluted layers deposited before urban and industrial development of the surrounding area (Hernández-Crespo and Martín, 2013). (2) Probabilistic plots and skewness determination to perform a first inspection and separation of the dataset. (3) Boxplots, histograms and scatterplots are displayed to make a deeper inspection. (4) A MLME is realized, employing FISATII software to apply the modal progression analysis (Gayanilo et al., 2005). This analysis consists of two stages: first, a decomposition of the distribution into their components to identify potential means, using the Bhattacharya's routine; and second, a refinement of results with the NORMSEP routine. Once the populations are separated, new boxplots showing the different populations are represented. (5) Spatial plots, in the form of vertical profiles, are used to support the separation performed with the above techniques. (6) Finally, statistical estimators (mean±2σ and median±2 MAD) are calculated to define the background population.

2.4 Pollution assessment

The pollution degree has been assessed, with the calculation of three widely used indexes (Dung et al., 2013) and taking into account the upper limit of background concentration determined as described above. The indexes calculated are:

Enrichment factor: $EF = \frac{\frac{C_{metal\_sample}}{C_{normalizer\_sample}}}{\frac{C_{metal\_background}}{C_{normalizer\_background}}}$

Geoaccumulation index: $I_{geo} = Log_2\left(\frac{C_{metal\_sample}}{1.5 \cdot C_{metal\_background}}\right)$

Pollution Load index: $PLI = \left(\frac{C_{metal\_1\_sample}}{C_{metal\_1\_background}} \cdot \ldots \cdot \frac{C_{metal\_n\_sample}}{C_{metal\_n\_background}}\right)^{\frac{1}{n}}$

The enrichment factor divides the concentration of metal, in the sample and the background, by a normalizer element. Several constituents can be used as normalizers (Al, Fe, organic matter, clay fraction, etc.) (Rubio et al., 2000). In this study, the normalizer used was Fe because it did not show evidence of an anthropogenic source, as discussed in section 3.1.

3. Results and Discussion

3.1 Background determination

According to the stages described in section 2.3, a first visual inspection was made with probabilistic plots (Fig. 2). The possible break or inflexion points are indicated with arrows on the plot, and the skewness of the population separated by each point is also displayed. As shown in Figure 2, for almost all metals studied, at least one inflexion point was clearly identified, and the data subset selected as the background population was the one with minor skewness (Table 1). For all metals except for iron, the selected sub-population had lower skewness than the population as a whole, suggesting that discrete populations can actually be separated and that iron can be used as a suitable normalizer element because it is not influenced by anthropogenic activities.

Subsequently, the complete dataset was subject to further examination by means of histograms, scatter plots and box-and-whisker plots (Fig. 3). Histograms and scatter plots allowed us to observe polymodality for Cd, Cu, Ni, Pb and Zn, and boxplots indicated a wide variability in the data, with the existence of outliers for Cu, Pb and Mn. The existence of multiple populations was demonstrated by the MLME, employing the NORMSEP routine in the FISATII software, which indicates the existence of different sub-populations if the separation index is higher than 2. The sub-populations extracted are shown in Figure 3 by the new histograms and boxplots. The separation suggested by the NORMSEP routine is in agreement with the polymodality previously observed in the histograms and scatter plots, and agrees as well with the division made by the inflexion points in the probabilistic plots for most metals (see Table 1). The mean±2σ range was selected for characterizing the background population obtained by both tools (probabilistic plots and MLME) because the data subset was normally distributed according to the Shapiro-Wilk test. The statistical estimator median±2MAD was not selected because, although for most metals (Cd, Cu, Ni, Pb, Mn) the difference between both estimators (mean±2σ and median±2MAD) was low, the median+2MAD excluded several samples belonging to the populations defined by the statistical approaches and corresponding to aged or reference sediments for Zn and Fe.

Furthermore, an estimate of background values with the iterative 2σ-outlier test was performed, giving significantly higher values than the other methods tested. Therefore, the authors considered that this technique would be appropriate for characterizing the background population when applied to samples from uncontaminated areas, but not to identify sub-populations (contaminated and uncontaminated).

The upper limits of background values obtained above were represented in vertical profiles to compare them with those obtained by separating the samples according to their age (Fig. 4). For the latter determination, this technique considered the dating of lake sediments performed by Rodrigo et al. (2010). The discrepancy between statistical methods (probabilistic plots and modal analysis) was solved with the help of this information. For the case of Cd, the resultant upper limit from both methods was very similar, so differences were minor. However, in the case of Cu the difference between both methods was important, and the age of sediment helped us to select the more appropriate background upper limit, this being the one provided by the modal analysis, because it included the older sediments and those from the reference site. In Figure 4, the shaded quadrant is delimited vertically by the selected upper limit of the background concentration, determined with probabilistic plots and/or modal analyses, and horizontally by the sediment depth corresponding to an age of approximately 50 years. Thus, the values falling in this shaded quadrant are above background upper limits, and correspond to concentrations measured in the upper layers of the peripheral sampling sites. Values to the left of the upper limit in the surface layers correspond to the central point taken as a reference point, which is less affected by pollution. Additionally, values below 30 cm depth correspond to sediments accumulated before the development of the surrounding towns, which grew enormously since the 1960s. Therefore, it can be concluded that the statistical analysis performed has provided an appropriate segregation of data and highlights the usefulness of vertical profiles for validating this segregation. The integrated use of statistical techniques and the sampling of uncontaminated sites and sediment cores are advisable to define the background levels with a high level of confidence.

With the aim of comparing the results obtained for Lake Albufera with background levels proposed elsewhere in Spain, a review of scientific literature was performed. Data obtained from different publications are summarized in Figure 5 and Table 2, where technical information such as the analytical extraction procedure and the statistical approach used are indicated. In Figure 5, it can be observed that the background values proposed in this study are generally in the lower-middle range of those proposed for other sites in Spain. A spatial trend that marks zones with higher or lower metal concentrations than the rest is not observed. The differences among locations may be due to actual differences among soils and sediments but also due to the different extraction procedures and statistical techniques employed. This review indicates that there is significant variation among the methods used, not only in analytical determination or statistical techniques but also in the background definition–usually the background level is defined as the mean, and the upper limit is reserved to propose baseline or reference values–and this makes the comparison of data difficult. Hence, a uniform set of procedures should be agreed on to identify differences related to soil and/or sediment. Another noteworthy aspect is that the majority of published studies analyse soils, and a smaller proportion were aimed at studying the sediments. Therefore, it is considered interesting to observe the differences among studies aimed at jointly analysing soils and sediments of water bodies located in the same watershed.

3.1 Pollution assessment

Once the background upper limit (or threshold) is established, pollution indexes can be calculated. In this study, the EF, I_{geo} and PLI were calculated. Figure 6 shows the values obtained for the EF and PLI indexes for the metals Cd, Cu, Ni, Pb and Zn. According to the ranking cited in diverse studies ($EF \leq 1$: no enrichment; $1 < EF \leq 3$: minor enrichment; $3 < EF \leq 5$: moderately enrichment; $5 < EF \leq 10$ moderately severe enrichment; Dung et al., 2013), the level of pollution in the upper 25-30 cm of peripheral sites (sites 1 and 11) was minor (Ni, Pb) or moderate (Cd, Cu, Zn), reaching the moderately severe level for copper and zinc at the second layer (5 cm) of sediments from sites 1 and 11, respectively. I_{geo} was lower in all cases (not shown), classifying the sediment as less polluted than the EF. Other authors have also observed this trend in I_{geo}, where the degree of pollution is minimized because of the numerical factor (1.5) introduced to take into account the possible variations of background levels (Sutherland, 2000; Dung et al., 2013). In this case, as the background level has been defined as an upper limit, the authors consider the use of EF to be more appropriate because the upper limit already takes into account the variability of the background population. Finally, PLI combines all metals into one index, providing an integrated assessment of the pollution degree. According to the PLI results, sediments in the perimeter sites are polluted to the 25-30 cm depth, reaching a higher degree of pollution at site 1, which is consistent with the higher urban pressures found in the north ditches of the lake (Pascual-Aguilar et al., 2013). Average values of organic carbon were 2.7, 3.7 and 2.9% OC, and of fine fraction (<63 µm) were 86.0, 97.0 and 93.1%, for sites 1, 6 and 11, respectively (Hernández-Crespo and Martín, 2013). Significant correlations between the concentrations of metals and organic carbon or fine fraction were only found for data from site 11, where both variables were positively correlated with metals, indicating an affinity of metals to organic matter and the fine fraction.

According to the WFD classification of ecological status, the condition required for non-synthetic pollutants to reach a 'high status' is that the concentrations remain within the range normally associated with undisturbed conditions or background levels. The category of 'good status' is obtained if concentrations are below the Environmental Quality Standards (EQS) proposed as specified in WFD. The categories of 'moderate status' or worse may be applied if these EQS are exceeded (Rodríguez et al., 2006). EQS for sediments have not yet been adopted in Spain, but sediment quality guidelines (SQG) proposed by other authors (MacDonald et al., 2000) can be used as a reference, whereby the surface sediments are around the threshold effect concentration (TEC) for Cd (0.99 mg/kg), Cu (31.6 mg/kg) and Pb (35.8 mg/kg), and near the probable effect concentration (PEC) for Ni (48.6 mg/kg) at site 1 and Zn (459 mg/kg) at sites 1 and 11. In the subsurface layer (second layer from surface) at site 1, Cu, Ni and Pb are very close to the PEL, and Zn exceeds it. Thus, actions on the sediment should be suggested at the peripheral sites. Nevertheless, these SQG can be used as screening tools to identify hot spots, but it is recommendable to perform biological assays and to take into account sediment properties, such as the organic carbon (OC) content or fine fraction (Campana et al., 2013). If Cu concentrations are normalized with respect to OC (2.7-3.7%, Hernández-Crespo and Martín, 2013) and fine fraction (88-97%, Hernández-Crespo and Martín, 2013), only the subsurface sediment at site 1 (5.6 mg <63 µm Cu/g OC) exceeds the no-effect value determined by Campana et al. (5.5 mg <63 µm Cu/g OC). Consequently, further studies are needed to make proper decisions about actions to be performed on the sediments of Lake Albufera.

Note that the decrease of the degree of pollution observed in the uppermost layer of these two sites with respect to the layer immediately below (Fig. 6) is almost certainly related to a decreased input of metals in recent years, thanks to the measures implemented to prevent the arrival of pollutants, such as the proper collection and treatment of wastewaters.

In addition to those measures aimed at avoiding external loads, several measures focused on nutrient internal loads are being carried out to recover the ecological status of the lake, such as treating the lake water in off-shore constructed wetlands (Martín et al., 2013; Rodrigo et al., 2013), or are being considered by stakeholders, such as sediment dredging. This study provides useful information for designing such measures, for instance the thickness of the contaminated layer of sediment. We suggest a prioritization of areas for action, focusing first on the tributary ditches, which are highly contaminated (Hernández-Crespo et al., 2012), and second on a perimeter belt inside the lake, where other measures softer than dredging, such as phytoremediation, could be applied.

4. Conclusions

The determination of background levels of metals for the sediments of Lake Albufera performed in this study is a significant step toward a proper assessment of the degree of sediments contamination and toward proposing appropriate measures for the recovery of its ecological status. The integrated use of geochemical and statistical methods have been demonstrated to be useful for reliably determining background levels, and this integration of methods has allowed the validation of each other as well. Thus, the authors recommend the use of integrated methods to establish background levels, such as the procedure developed in the present study, especially in shallow lagoons where the extraction of sediment cores does not involve a major effort. The stages to be integrated are: (1) sampling of sediment cores in different sites located near and far from the mouth of pathways for pollutants, (2) to analyse and date the sediments, (3) process the results using several statistical methods of sieving to identify different data subsets (contaminated and non-contaminated) and (4) to define the background values considering the information from both previous stages and using the best suited statistical indicators.

The determination of background levels lets us know, from now on, the extent of sediment contamination, currently being moderate or less (for Cd, Ni, Pb, Fe, Mn) up to 30 cm deep, and moderately severe for copper and zinc in the surface layers (5 cm) of peripheral sites. The study of the vertical profile of sediments provides information about the thickness of the polluted sediment, which is valuable for the design of measures focused on sediment, such as dredging or other remediation measures.

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References

Aloupi, M., Angelidis, M.O., 2001. Geochemistry of natural and anthropogenic metals in the coastal sediments of the island Lesvos, Aegean Sea. Environ. Pollut. 113, 211-219.

Blasco, J., Gomes, T., García-Barrera, T., Rodríguez-Romero, A., González-Rey, M., Morán-Roldán, F., Trombini, C., Miotk, M., Gómez-Ariza, J.L., Joao Bebiano, M., 2010. Trace metal concentrations in sediments from the southwest of the Iberian Peninsula. Sci. Mar. 74, 99-106.

Blasco, J., Sáenz, V., Gómez-Parra, A., 2000. Heavy metal fluxes at the sediment-water interface of three coastal ecosystems from south-west of the Iberian Peninsula. Sci. Tot. Environ. 247, 189-199.

Campana, O., Blasco, J., Simpson, S.L., 2013. Demonstrating the appropiateness of developing sediment quality guidelines based on sediment geochemical properties. Environ. Sci. Technol. 47, 7483-7489.

Carral, E., Puente, X., Villares, R., Carballeira, A., 1995. Background heavy metal levels in estuarine sediments and organisms in Galicia (northwest Spain) as determined by modal analysis. Sci. Tot. Environ. 172, 175-188.

Cobelo-García, A., Prego, R., 2003. Heavy metal sedimentary record in a Galician Ria (NW Spain): background values and recent contamination. Mar. Pollut. Bull. 46, 1253-1262.

De Miguel, E., Callaba, A., Arranz, J.L., Cala, V., Chacón, E., Gallego, E., Alberruche, E., Alonso, C., Fdez.-Canteli, P., Iribarren, I., Palacios, H., 2002. Determinación de los niveles de fondo y niveles de referencia de metales pesados y otros elementos traza en suelos de la Comunidad de Madrid. IGME, Madrid.

Díez, M., Simón, M., Martín, F., Dorronsoro, C., García, I., Van Gestel, C.A.M., 2009. Ambient trace element background concentrations in soils and their use in risk assessment. Sci. Tot. Environ. 407, 4622-4632.

Dung, T.T.T., Cappuyns, V., Swennen, R., Phung, N.K., 2013. From geochemical background determination to pollution assessment of heavy metals in sediments and soils. Rev. Environ. Biotechnol. 12, 335-353.

Esmaeili, A., Moore, F., Keshavarzi, B., Jaafarzadeh, N., Kermani, M., 2014. A geochemical survey of heavy metals in agricultural and background soils of the Isfahan industrial zone, Iran. Catena 121, 88-98.

Galán, E., Fernández-Caliani, J.C., González, I., Aparicio, P., Romero, A., 2008. Influence of geological setting on geochemical baselines of trace elements in soils. Application to soils of South-West Spain. J. Geochem. Explor. 98, 89-106.

Galuzska, A., 2007. A review of geochemical background concepts and an example using data from Poland. Environ. Geol. 52, 861-870.

Galuzska, A., Migaszewski, Z.M., 2011. Geochemical background –an environmental perspective. Mineralogia 42, 7-17.

Gayanilo, F.C., Sparre, P., Pauly, D., 2005. FAO-ICLARM stock assessment tolos II (FISAT II). User's guide. Food and agriculture organization of the united nations.

Hernández, J.A., Fernández, M.T., Alarcón, M.A., 2005. Valores de fondo y valores genéricos de referencia para Cd, Co, Cr, Cu, Mn, Ni, Pb y Zn en suelos del Campo de Cartagena, Murcia (SE España). Edafología 12, 105-114.

Hernández-Crespo, C., Martín, M., 2013. Mid-term variation of vertical distribution of Acid Volatile Sulphide and Simultaneously Extracted Metals in sediment cores from Lake Albufera (Valencia, Spain). Arch. Environ. Contam. Toxicol. 65, 654-664.

Hernández-Crespo, C., Martín, M., Ferrís, M., Oñate, M., 2012. Measurement of Acid Volatile Sulphide and Simultaneously Extracted Metals in sediment from Lake Albufera (Valencia, Spain). Soil Sediment Contam. 21, 176-191.

Jiménez, R., Conde, P., Martín, J.A., García R., 2010. Geochemical background levels and influence of the geological setting on pedogeochemical baseline concentrations of trace elements in selected soils of Castilla-La Mancha (Spain). Estudios Geol. 66, 123-130.

MacDonald, D.D., Ingersoll, C.G., Berger, T.A., 2000. Development and evaluation of consensus-based sediment quality guidelines for freshwater sediments. Arch. Environ. Contam. Toxicol. 39, 20-31.

Martín, M., Oliver, N., Hernández-Crespo, C., Gargallo, S., Regidor, M.C., 2013. The use of free water surface constructed wetland to treat the eutrophicated waters of lake L'Albufera de Valencia (Spain). Ecol. Eng. 50, 52-61.

Matschullat, J., Ottenstein, R., Reimann, C., 2000. Geochemical background –can we calculate it? Environ. Geol. 39, 990-1000.

Micó, C., Peris, M., Recatalá, L., Sánchez, J., 2007. Baseline values for heavy metals in agricultural soils in an European Mediterranean region. Sci. Tot. Environ. 378, 13-17.

Micó, C., Recatalá, L., Peris, M., Sánchez, J., 2006. Assessing heavy metal sources in agricultural soils of an European Mediterranean area by multivariate analysis. Chemosphere 65, 863-872.

Navas, A., Machín, J., 2002. Spatial distribution of heavy metals and arsenic in soils of Aragón (northeast Spain): controlling factors and environmental implications. App. Geochem. 17, 961-973.

Pascual-Aguilar, J., Andreu, V., Picó, Y., 2013. An environmental forensic procedure to analyse anthropogenic pressures of urban origin on surface water of protected coastal of agro-environmental wetlands (L'Albufera de Valencia Natural Park, Spain). J. Hard. Mater. 263, 214-223.

Pérez-Sirvent, C., Martínez-Sánchez, M.J., García-Lorenzo, M.L., Molina, J., Tudela, M.L., 2009. Geochemical background levels of zinc, cadmium and mercury in anthropically influenced soils located in a semi-arid zone (SE, Spain). Geoderma 148, 307-317.

Peris M (2006). Estudio de metales pesados en suelos bajo cultivos hortícolas de la provincia de Castellón. PhD thesis. Valencia: Universitat de València.

Reimann, C., de Caritat, P., 2005. Distinguishing between natural and anthropogenic sources for elements in the environment: regional geochemical surveys versus enrichment factors. Sci. Tot. Environ. 337, 91-107.

Reimann, C., Filzmoser, P., Garrett, R.G., 2005. Background and threshold: critical comparison of methods of determination. Sci. Tot. Environ. 346, 1-16.

Reimann, C., Garrett, R.G., 2005. Geochemical background –concept and reality. Sci. Tot. Environ. 350, 12-27.

Roca, N., Pazos, M.S., Bech, J., 2012. Background levels of potentially toxic elements in soils: A case study in Catamarca (a semiarid region in Argentina). Catena 92, 55-66.

Roca-Pérez, L., Gil, C., Cervera, M.L., Gonzálvez, A., Ramos-Miras, J., Pons, V., Bech, J., Boluda, R., 2010. Selenium and heavy metals content in some Mediterranean soils. J. Geochem. Explor. 107, 110-116.

Rodrigo, M.A., Alonso-Guillén, J.L., Soulié-Märsche, I., 2010. Reconstruction of the former charophyte community out of the fructifications indentified in Albufera de València lagoon sediments. Aquat. Bot. 92, 14-22.

Rodrigo, M.A., Martín, M., Rojo, C., Gargallo, S., Segura, M., Oliver, N., 2013. The role of eutrophication reduction of two small man-made Mediterranean lagoons in the context of a broader remediation system: effects on wáter quality and plankton contribution. Ecol. Eng. 61, 371-382.

Rodríguez, J.G., Tueros, I., Borja, A., Belzunce, M.J., Franco, J., Solaun, O., Valencia, V., Zuazo, A., 2006. Maximum likelihood mixture estimation to determine metal background values in estuarine and coastal sediments within the European Water Framework Directive. Sci. Tot. Environ. 370, 278-293.

Rubio, B., Nombela, M.A., Vilas, F., 2000. Geochemistry of major and trace elements in sediments of the Ria de Vigo (NW Spain): an assessment of metal pollution. Mar. Pollut. Bull. 40, 968-980.

Sánchez, M.I., 2003. Determinación de metales pesados en suelos de Medina del Campo (Valladolid): contenidos extraíbles, niveles fondo y de referencia. PhD thesis. Universidad de Valladolid.

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.

Tobías, F.J., Bech, J., Sánchez Algarra, P., 1997. Establishment of the background levels of some trace elements in soils of NE Spain with probability plots. Sci. Tot. Environ. 206, 255-265.

Tylmann, W., Lysek, K., Kinder, M., Pempkoviak, J., 2013. Regional pattern of heavy metals content in lake sediments in Northeastern Poland. Water Air Soil Poll. 216, 217-228.

Table 1. Descriptive statistics of background populations according to the separation performed with probabilistic plots and modal analysis, and final proposed values (mg/kg; except Fe, %). N: subpopulation size. *p* (S-W): significance level of Saphiro-Wilk normality test. BUL: background upper limit (Mean+2σ).

	Probabilistic plots						Modal analysis						**Proposed**
	N	*p* (S-W)	Mean	±	σ	BUL	N	*p* (S-W)	Mean	±	σ	BUL	**BUL**
Cd	13	0.944	0.26	±	0.06	0.38	12	0.746	0.25	±	0.05	0.36	**0.38**
Cu	8	0.894	11.5	±	1.3	14.2	18	0.097	17.1	±	5.8	28.8	**28.8**
Ni	21	0.847	16.9	±	4.5	25.9	21	0.847	16.9	±	4.5	25.9	**25.9**
Pb	20	0.428	16.5	±	4.5	25.5	20	0.428	16.5	±	4.5	25.5	**25.5**
Zn	15	0.166	56.6	±	16.0	88.6	15	0.166	56.6	±	16.0	88.6	**88.6**
Fe	36	0.374	1.6	±	0.3	2.2	36	0.374	1.6	±	0.3	2.2	**2.2**
Mn	34	0.654	266.7	±	39.5	345.7	34	0.654	266.7	±	39.5	345.7	**345.7**

Table 2. Review of background values proposed for different sites in Spain. GM: geometric mean, GSD: geometric standard deviation.

					Concentration (mg/kg; except Fe in %)								
Authors	Place	Analytical method	Background estimation		Cd	Cr	Cu	Hg	Ni	Pb	Zn	Fe	Mn
Carral et al., 1995	Galicia (coast)	HNO_3+HF	Sediment surface samples - Modal analysis	Upper limit (CI95)		32	28		32	53	122	2.6	275
Cobelo-García et al., 2003	Galicia (Ría Ferrol)	HNO_3+HF	Sediment core sampling - Linear regression	Mean$\pm\sigma$		63± 14	12± 3		26± 10	27± 7	55± 11	2.4± 0.5	
Rubio et al., 2000	Galicia (Rías Bajas, Vigo)	HNO_3+HF+ $HClO_4$	Sediment surface samples - PCA	Mean		34.0	29.4		30.3	51.3	105.3	3.5	244.3
Rodríguez et al., 2006	Basque country (coast)	HNO_3+HCl	Sediment surface samples - Modal analysis, geographical display	Upper limit (mean+2.7σ)	0.45	71	64		57	66	248	5.4	447
Tobías et al., 1997	Cataluña	X-ray fluorescence	Soil profiles - Probability plots	Antilog(GM+2·GSD)		275	145		83	91	326		
Navas et al., 2002	Aragón	HNO_3+H_2O_2	Soil deep samples - Descriptive statistics, geographical display	Median	0.46	19.2	8.4		17.4	5.9	48.2	1.6	284
De Miguel et al., 2002	Madrid	HNO_3+HCl	Soil surface samples - descriptive statistics	Upper limit (p95)	0.30	34	20	0.09	20	31	75		710
Sánchez, 2003	Valladolid (M. Campo)	HNO_3	Soil profile - Descriptive statistics, PCA, cluster	Upper limit (mean+2σ)	0.44	16.1	9.4		9.8	13.8	33.4		
Jiménez et al., 2010	Castilla la Mancha	X-ray fluorescence	Soil profile - Descriptive statistics	Upper limit (mean+2σ)		113.4	27		42.6	44.2	86.5		
Peris, 2006	Castellón	HNO_3+HCl	Soil surface samples - Probability plots, descriptive statistics	Upper limit (mean+2σ)	0.63	42.9	50.4		29.2	51.3	154.9	2.6	517
This study	Valencia	HNO_3+HCl	Sediment core sampling - Probability plots, modal analysis, descriptive statistics	Upper limit (mean+2σ)	0.38		28.8		25.9	25.5	88.6	2.2	345.7
Micó et al., 2007	Alicante	HNO_3+HCl	Soil surface samples - Descriptive statistics	Upper limit (mean+2σ)	0.7	36	28		31	28	83	2.0	402
Roca-Pérez et al., 2010	Eastern Spain	HNO_3+HF+HCl+ H_2O_2	Soil surface samples natural soils - descriptive statistics	Upper limit (GM/GSD^2, $GM·GSD^2$)	0.97	217	46		50	137	246	12.4	2691
Pérez-Sirvent et al., 2009	Murcia (Campo de Cartagena)	HNO_3+HF	Soil surface samples - PCA, cluster and discriminant analysis	Median (p95)	0.30 (0.43)			0.4 (1.5)			40 (93.5)		
Hernández-Bastida et al., 2005	Murcia (Campo de Cartagena)	HNO_3+HF	Soil surface samples - Descriptive statistics, geographical display	Upper limit (median+2σ)	0.53	89	40		38	44	105		628

Table 2. Review of background values proposed for different sites in Spain (cont.).

					Concentration (mg/kg)								
Authors	Place	Analytical method	Background estimation		Cd	Cr	Cu	Hg	Ni	Pb	Zn	Fe	Mn
Sierra et al., 2007	Almería	HNO_3+HF+ $HClO_4$	Soil profile - ECFD	Upper limit (ECDF)	0.3	123	47.2	1	70.9	93.9	129		
Díez et al., 2009	Granada	HNO_3+HCl+HF	Soil profile - ECFD	Upper limit (ECDF)		110	40		56	50	135		
Blasco et al., 2000	Huelva (Odiel estuary)	HNO_3+HCl+HF	Sediment core sampling - descriptive statistics	Mean (deep sediment)		112	1975					11.4	346.1
	Cádiz (Bay Cádiz)					97.4	21.3					4.2	402.8
	Cádiz (Barbate estuary)					60.4	14.8					2.3	278.0
Galán et al., 2008	Andalucía (Ossa-Morena Zone)	HNO_3+HF+HCl+ $HClO_4$	Soil profile - Descriptive statistics	Upper limit (p95)		182	143		73	200	327		

Figure 1. Location of Lake Albufera and sampling sites.

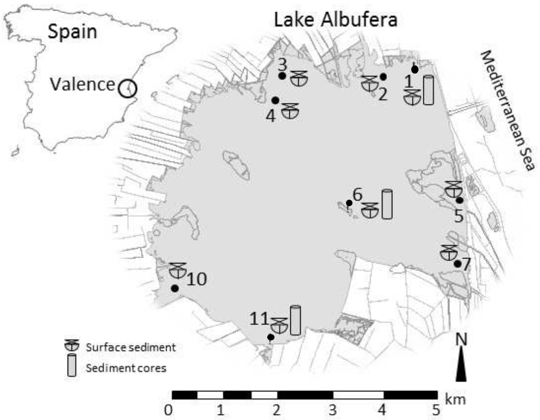

Figure 2. Probabilistic plots for the original dataset. Arrows indicate possible inflexion points, and the values are the skewness coefficients associated with the subpopulations separated by each inflexion point.

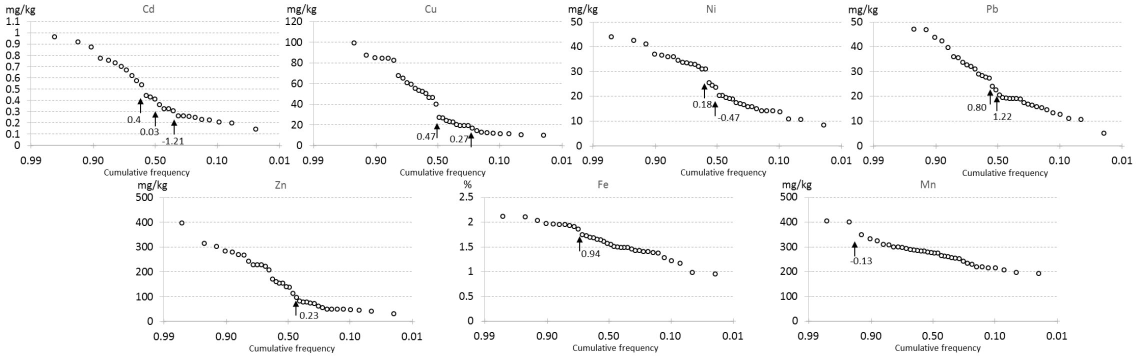

Figure 3. Top down: (a) histograms, scatter plots and box-whisker plots for the original dataset, (b) histograms and box-whisker plots for normal distribution of data subsets extracted by modal analysis.

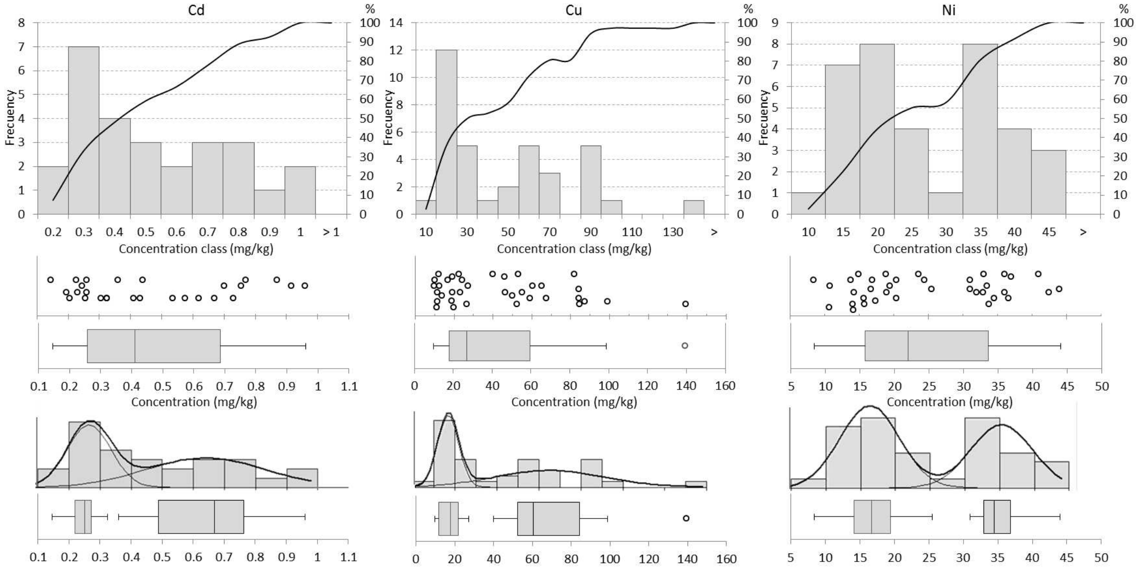

Figure 3 (cont.). Top down: (a) histograms, scatter plots and box-whisker plots for the original dataset, (b) histograms and box-whisker plots for normal distribution of data subsets extracted by modal analysis.

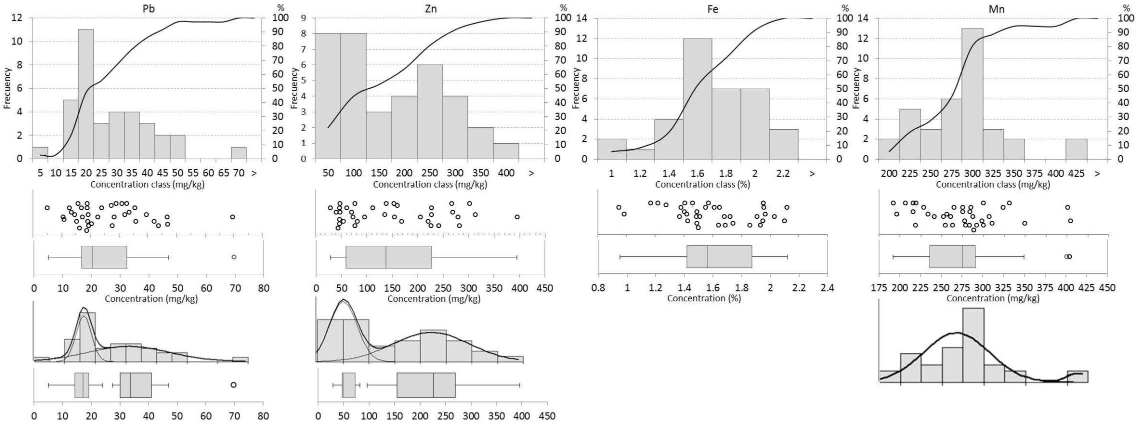

Figure 4. Vertical profiles of sediment age and concentrations of metals. Data for sediment age is adapted from Rodrigo et al. (2010). Vertical lines represent the upper limit of background levels (BUL) obtained by statistical approaches. Horizontal solid lines represent the depth below which the sediment was deposited prior to urban and industrial development.

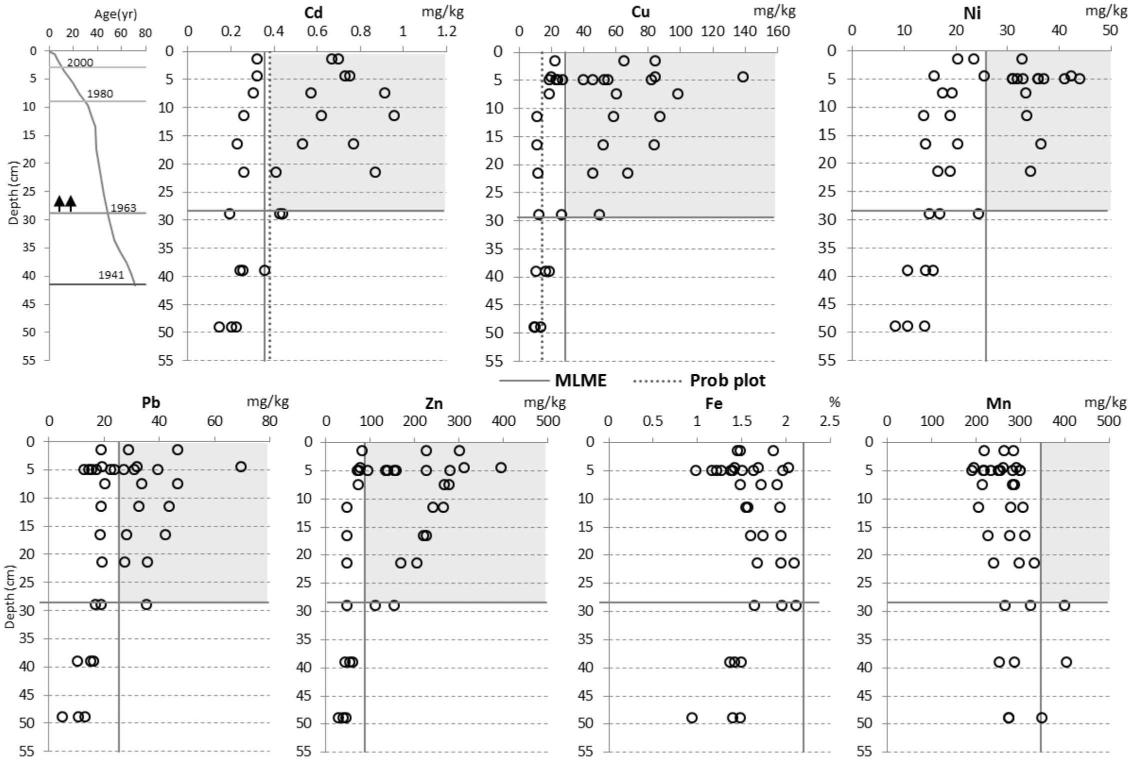

Figure 5. Spatial representation of background values proposed in different locations in Spain. The legend indicates the upper limit of concentration, represented by each size of circle (mg/kg, except Fe in %).

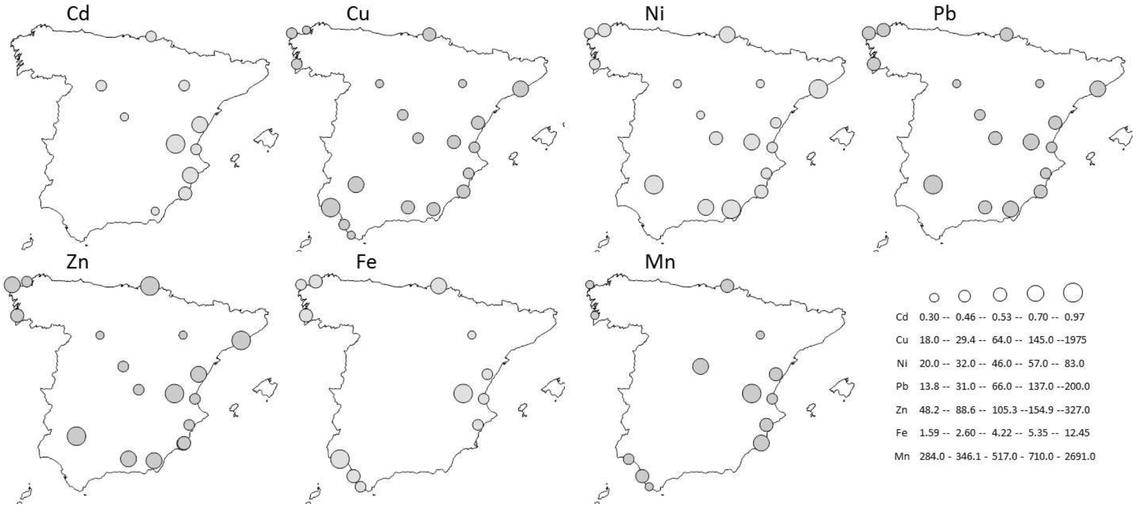

Figure 6. Vertical profiles of Enrichment Factor of sites sampled in Lake Albufera. Results of surface samples are represented by open diamonds. EF scale: EF≤1: no enrichment; 1<EF≤3: minor enrichment; 3<EF≤5: moderately enrichment; 5<EF≤10 moderately severe enrichment.