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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 $+ 2\sigma$ 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.

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 Garrett, 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

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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 (Peris, 2006; Tobías et al., 1997).
- 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 (Aloupi and Angelidis, 2001; Blasco et al., 2010; Esmaeili et al., 2014; Micó et al., 2006; Rubio et al., 2000).

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 ± 2 · σ). However, Reimann et al. (2005) demonstrated that the median ± two times the median of the absolute deviations (median ± 2 · 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 (Galuzska and Migaszewski, 2011; Matschullat et al., 2000). 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 de 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 and Prego, 2003; Tylmann et al., 2011), and in some cases it is relatively easy to take long sediment cores (i.e., shallow water bodies). 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 11 °C (Dec–Jan) and 28 °C (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) and Hernández-Crespo and Martín (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