



Heavy metals fractionation and multivariate statistical techniques to evaluate the environmental risk in soils of Huelva Township (SW Iberian Peninsula)

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ABSTRACT

The city of Huelva and surrounding areas are affected by several sources of pollution such as acid mine drainage, industrial complexes, urban wastes and agriculture activities that could pose an important environmental risk. For this reason, the modified BCR (three steps) sequential extraction method was applied to evaluate the mobility and bioavailability of the trace elements in 25 representative samples of the study area. The operational scheme of the BCR was classified into three steps: water/acid soluble fraction, reducible and oxidisable fraction. The mobility sequence based on the sum of three first phases was: Cu (82.01%) > Zn (71.14%) > Cd (68.35%) > Ni (50.44%) > Pb (36.39%) > Cr (29.22%) > As (18.82%). Among metals, Cd poses a serious threat to human health and the environment due to the calculated high percentage of mobility. Additionally, multivariate statistical techniques (principal components and cluster analyses) were applied to the chemical results to evaluate the degree of metallic pollution and the levels of association between the variables (metal-metalloids) at the different steps of sequential extraction and to recognise possible sources of potential contamination. The PCA suggests that the study area is influenced by four sources of anthropogenic contributions: acid mine drainage, industrial activities, traffic, and agriculture, aside from the natural sources characteristic of the zone. Calculated environmental risk index reveal a considerable-high ecological risk in the saltmarshes of the Huelva estuary probably related to acid mine drainage and the industrial complexes located in these areas, while in the north sector of Huelva the metallic content is more closer to the natural sources values. The results obtained suggest the need for corrective remediation measures due to the higher accumulation of potentially dangerous metals, which in most cases exceed the limits established by certain legislation.

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1. Introduction

In recent decades, environmental pollution problems have been a growing interest in the scientific community due to the potentially harmful substances emitted from anthropogenic activity, which can pose a serious hazard to the environment and to the human health. Among the environmental matrices, soils are more easily affected by the negative effect of anthropogenic activities due to their close relationship with the atmosphere and meteoric waters.

The toxicity and mobility of heavy metals in soils depend not only on their concentrations, but also on both their associations, and chemical properties, and on some surrounding environmental conditions such as pH, redox potential, and biological action of the roots and the formation of chelates (Thomson and Frederick, 2002). It has also proven that the contents of clays and of organic matter play important roles on the

behaviour of metals (Otero et al., 1998). For these reasons it is important to recognise the speciation of metals in different fractions of soil to determine their degree of mobility, availability and persistence in the environment. As a matter of fact, soil contamination due to heavy metals and metalloids such as As, Cd, Cr, Cu, Ni, Pb and Zn, represents the source of a severe potential hazard for the ecosystem equilibrium and the health of living beings (Nagajyoti et al., 2010).

Dating back to the 1960's, one of the largest industrial complexes in Spain (Punta del Sebo industrial complex) was built around the city of Huelva (SW Iberian Peninsula). A wide range of industrial products related to the fertiliser and copper smelting can be found in this area affecting the quality of the soils, which could pose a serious risk to the health of resident population and to the environment. A previous study detected high amounts of trace elements in the soils of this area and linked their origin to the industrial activity (Guillén et al., 2011). In addition to the industrial activities, other anthropogenic potential sources of toxic elements (acid mine drainage – AMD, urban wastes, and agriculture activities) are seen in the study area (Barba-Brioso et al., 2010). However, to efficiently evaluate the environmental impact

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of heavy metals accumulated in these soils the chemical state in which the elements are present (easily exchangeable ions, metal carbonates, oxides, sulphides, organometallic compounds, ions in crystal lattices of minerals, etc.) needs to be studied (Pérez et al., 2008; Yu et al., 2010).

There are several analytical techniques to assess the content and behaviours of some metals in soils/sediments (Rauret et al., 2000; Sahuquillo, et al., 1999, 2003). The sequential extraction method should provide quantitative information on the distribution of the various elements in soils/sediments, and implications for metal mobility and bioavailability potential (Sundaray et al., 2011). Determination of bioavailability has been mostly based on metals concentration in the exchangeable/carbonate soil fraction (Karbassi and Shankar, 2005; Vanek et al., 2005).

In recent years, the sequential extraction methods have become the most effective tools to assess the risks generated by metal contamination in soils and sediments. These techniques have been widely applied in environmental geochemical studies aiming to characterise surface sediments (river, lakes and estuaries) and soils (Janoš et al., 2010; Madrid et al., 2007). Furthermore, studies on toxic metal fractionation (Cu, Pb, Fe, Mn and Sn) in urban soils (Hursthouse et al., 2004; Madrid et al., 2002, 2004) have discriminated natural and anthropogenic sources. For these reasons, the objectives of this study were to investigate the mobility of the most harmful elements (As, Cd, Cu, Cr, Hg, Ni, Pb and Zn) in the soils of Huelva municipality, by applying a modified European Community Bureau of Reference, (BCR) sequential extraction scheme, and to determine the mineral reactivity occurring in the different fractions of the soils. Additionally the application of statistical techniques besides ecological indexes, have allowed us to establish monitoring strategies to support future action/remediation plans on the study area.

2. Materials and methods

2.1. Area of study

The Huelva municipality is situated in the southwest of the Iberian Peninsula (Fig. 1). The soils in the area of study are mainly affected by the production activity in two important industrial complexes which could release a number of contaminants into the surrounding environment (e.g. inorganic acids, fossil fuel combustion residues, detergents, metallurgic product residues, animal food and fertilizers among others). Furthermore, contaminants released to the environment as atmospheric emissions, can affect surface soils as a result of atmospheric fall out. Besides industries, the intense agriculture activity and urban waste management are other potential sources of pollutants. On the other hand, Huelva estuary, where the city of Huelva is located, has been historically affected by acid mine drainage (AMD) generated in the inner zones of the basin, so it is considered one of the most contaminated estuaries in the world (Nieto et al., 2007; Sarmiento et al., 2009).

Geologically, the study area is characterised by the presence of recent Holocene sediments overlying a siliciclastic Tertiary succession whose ages range from Miocene to Pliocene (Fig. 1). The more recent Holocene sediments are mainly constituted by clay and sand as is typical of sediments in estuarine systems; the Tertiary succession, deposited in marine and continental environments (Civis et al., 1987) consists of a basal gray-blue marlstone corresponding to the Gibráleon Clay Formation (GCF) and of a upper fine sands and gray-yellow silt corresponding to the Huelva Formation (López-González et al., 2006).

2.2. Sample collection and pre-treatment

During the fall of 2007, 25 from a total of 150 soil samples were determined using a modified BCR-sequential extraction procedure. Soil samples were obtained from industrial sites, urban and periurban areas according to Guillén et al. (2011). The operation included parks, open spaces, mud flats, farmlands and industrial areas. From the 25

soil samples studied in this work, 2 were recollected in agricultural zones, 6 from saltmarshes areas, 8 from sites close to industrial activities and the rest were sampled in urban areas. Due to the heterogeneous nature of the samples in this work, we do not discriminate whether or not they are sediments or soils (Fernández-Caliani, 2012). The location of each sampling point (Fig. 1) was chosen to be representative of areas affected by industrial activity or/and influenced by the chemistry of some effluent of the Odiel and Tinto rivers, which carrying an important heavy metals load (Sarmiento et al., 2009). Approximately 3 kg of soil were collected between 0 and 15 cm depth, by combining five individual specimens collected at the centre and vertices of a 2 m wide cross. The samples were stored in polyethylene bags following internationally adopted methods (Salminen et al., 1998). In the laboratory, the samples were ground, oven-dried (40 °C) until completely dry, homogenised, sieved (<2 mm), and stored in polyethylene containers. Because of the strong association of trace elements with fine-grained soil components, we used the <63 µm soil fraction for the sequential extraction and total acid digestion methods (Cuong and Obbard, 2006). Based on previous results (Guillén et al., 2011) 25 samples from this study were selected to evaluate mobility and availability of trace elements in soil by a BCR-sequential extraction combining with statistical analyses. Additionally, the metal concentrations obtained by Guillén et al. (2011) were used for mapping the distribution of the potential ecological risk in the study area.

2.3. Reagents

Double-deionised water (18.2 µΩ) was used for preparing the solutions and to clean the instrumental. Analytical grade acetic acid (Qemical®), hydroxylamine hydrochloride (Merck®), hydrogen peroxide (Panreac®) and ammonium acetate (Panreac®) were used in the sequential extraction procedure. Suprapure hydrochloric and nitric acids (Merck®) were used for the sequential extraction and to extract the chemical elements for measure the pseudo-total content. All glassware and plastic material used were first treated with a 10% (v/v) suprapure nitric acid solution for 24 h and rinsed with distilled water before use.

2.4. Procedures

2.4.1. Chemical analysis and quality control

Chemical analyses of soil samples (Table 1) were carried out, at Acme Analytical Laboratories Ltd (Vancouver, Canada) accredited under ISO 9002, by ICP-MS and ICP-AES. Using Acme's Group 1F-MS package (ultratrace aqua regia digestion) a total of seven elements (As, Cd, Cr, Co, Ni, Pb and Zn) were reported for a 15 g sample analysed by ICP-emission spectrometry following an aqua regia digestion. To ensure the reproducibility of the results, the analysis sequence consisted of calibration of standards, blind standard solutions analysis as an unknown (quality control solutions), method blanks and one certified reference (STD-SD7). In addition, a total of 13 replicates were used. Accuracy was calculated on Acme's in-house reference material, (STD-SD7).

The results obtained for extractable concentrations in the sequential extraction procedure (SEP) were compared with indicative or certified values, following the procedures for the standard reference material (BCR-701). They showed that certified (or indicative) and obtained values were not significantly different. The recovery rates (Eq. (1)) for heavy metals in the standard reference material were between 70 and 104% (Table 2).

$$\% \text{ Recovery} = (F1 + F2 + F3 + R/\text{Pseudo-total concentration}) \times 100 \quad (1)$$

Where: Pseudo-total concentration refers to the values obtained by Acme Laboratories and F1, F2, F3 and R (residual fraction)

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