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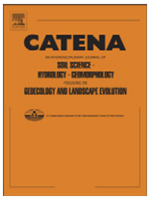

Sequential extraction procedure as a tool to investigate PTHE geochemistry and potential geoavailability of dam sediments (Almadén mining district, Spain)

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ABSTRACT

Sediments from Castilseras reservoir (Almadén) were collected to assess the potential environmental hazards associated with the availability of Potentially Toxic or Harmful Elements (PTHE) in this freshwater environment. PTHE concentrations in sediments were investigated using a four step (F1–F4) Sequential Extraction Procedure (SEP) and the results were evaluated using Principal Component Analysis (PCA) and different risk indexes and criteria. Considering the fractions results and the PCA treatment, two groups of elements can be differentiated in the easily leached by weak acids fraction F1 and these indicate the presence of sulfate and secondary precipitates of carbonates as the main sink for easily accessible metallic elements. In reducible fraction F2, chemical analysis revealed a significant relationship between the majority of the analyzed elements and the Fe oxy-hydroxides, with the exception of Co, Hg and Ni, which are preferentially associated with Mn oxy-hydroxides. In the oxidizable fraction (F3), a significant relationship between Cu, Fe, Hg and Zn (representative metals of the existing ore deposits) and sulfides/organic matter was observed. The environmental assessment based on the aforementioned criteria provides risk levels varying from moderate to high. The risk appears to be higher near the dam, where the higher PTHE levels in sediment are due to a selective accumulation of fine-grained particles.

1. Introduction

Trace metals and metalloids are usually found at background levels in fluviatile sediments, including water reservoirs, except where anthropogenic activities lead to an increase in their concentrations due to air-borne, terrigenous and aqueous inputs (Dhanakumar et al., 2015; Wang et al., 2015). Some of these metals are referred to as “Potentially Toxic or Harmful Elements” (PTHE) (EU, 2001). In particular, mining activities can adversely affect the quality of the fluvial environment by introducing these PTHE in association with particles or in solution. PTHE supply and concentration are highly variable over space and time in the watershed hosting active or dismissed mining areas, and they depend on the characteristics and significance of mine wastes and metal sources as well as the underlying geology, geochemistry and weathering of ore deposits. The amount of PTHE also varies in response to seasonal flow variability, including drought conditions. In particular, mine operations developed over long time periods in historical mining districts have had significant adverse environmental effects in proximity ecosystems (Gosar et al., 1997; Vrhovnik et al., 2013; Resongles et al., 2014). Evidence of contamination can frequently be found beyond the local mined area and in some cases significant contamination can be detected several tens of kilometers away from the source (Pettine et al., 1982; Gosar et al., 1997; Lechler et al., 1997; Gosar, 2008; Covelli et al., 2012; Bavec et al., 2014; Gray et al., 2014; Tornero et al., 2014).

Given the low solubility in water of most of these elements and their tendency to be adsorbed by fine suspended particles (Acosta et al., 2009; Duan et al., 2010), fluvial sediments are important to evaluate the quality of the riverine environment (Yuan et al., 2014). If they are present within the drainage basins, artificial water reservoirs can be considered as important barriers that significantly alter the natural hydrological flow and the transport of materials. These basins promote sedimentation processes and they become significant repositories of PTHE associated with sediments (Loska and Wiechuła, 2003; Rimondi et al., 2012). Moreover, the specific physico-chemical conditions found in these reservoirs when compared to flowing waters may induce the development of biologically mediated transformations of inorganic PTHE into different species that may be more toxic for the environment (Adriano, 2001). Therefore, sediments in the reservoir can be considered as a sink and/or source of contaminants and their ecological risk assessment should be a priority in order to assess the environmental quality of the fluvial compartment (Dević et al., 2016; Fang et al., 2016).

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As a result of previous studies on mining districts throughout the world, aquatic ecosystem contamination by PTHE has been recognized as one of the most important environmental issues related to the toxicity, abundance, persistence and bioaccumulative character of these compounds (Sin et al., 2001; Ruiz et al., 2008). Sediments downstream mining areas provide important information about the impact suffered by the aquatic ecosystems and help to determine the associated risk assessment (Varol, 2013).

In the work described here, the mobility of PTHE in the sediments of the Castilseras reservoir has been investigated by applying a Sequential Extraction Procedure (based on the BCR methodology). In this study several environmental quality indexes, from those available from literature, were applied. The results provide relevant information that enables appropriate strategies to be recommended when planning environmental management of this drainage basin.

2. Study area

The Castilseras reservoir is located in the central part of the Almadén Hg mining district (Ciudad Real, central Spain). It was constructed in 1983 and it has a surface area of 97 ha, a water capacity of 5 hm^3 and maximum depth of 14 m. The district covers an area of 120 km^2 and it was the largest producer of Hg at a world level for >2000 years (Hernández et al., 1999). From a geological point of view, the rocks that crop out in Almadén are mainly siliciclastic. Hg mineralizations are hosted by Paleozoic (meta)detritic rocks with a significant volume of interbedded magmatic rocks to form a tectonic structure, the Almadén syncline (Hernández et al., 1999). The Castilseras reservoir is built on Pre-Ordovician (meta)detritic rocks (shales and greywackes) that constitute the Alcudia anticline, located at the south of the Almadén syncline. The dam is located in the Valdeazogues watershed, which is the main river in the mining district. The extensive Hg mining and metallurgical activity developed over centuries, along with other minor mining activities involving Pb, Zn and Ag recovery, has led to significant PTHE inputs in the different environmental compartments of the district (Gray et al., 2004; Molina et al., 2006; Higueras et al., 2006, 2011, 2012; Millán et al., 2006, 2012; Dago et al., 2014). The different inputs from the abandoned mining installations and spoil heaps have been producing adverse effects to ecosystems in proximity to the mining areas for long periods of time. However, the extent of contamination is not strictly limited to the vicinity of mines; contaminated material may be physically remobilized during floods, thus dispersing contaminants over hundreds of kilometers from historical mine sites. The environmental quality of the Valdeazogues River has been negatively affected by run-off waters from the mined areas (Berzas Nevado et al., 2003; García-Ordiales et al., 2014).

The hydrological conditions in the district are mainly determined by the seasonality of the Valdeazogues River, which is controlled by the semiarid climate of the area. The area suffers long periods of drought when the reservoir recharge may reach very low values (approximating zero), enhancing the lentic nature of this lake, and may undergo long periods of evaporation induced by high temperatures and solar radiation. The Castilseras reservoir is the only lentic medium located within the Almadén mining district. This reservoir collects rainwater, mine drainages and leachate from spoil heaps from four of the most important abandoned Hg mines of the district (Las Cuevas, El Entredicho, Nueva and Vieja Concepción, see Hernández et al., 1999 for details). A schematic view of the studied area is shown in Fig. 1 and this includes the main mercury and polymetallic mines and the location of the sediment sampling points in the reservoir.

3. Materials and methods

3.1. Sample collection and chemical analysis

A total number of 12 sampling stations (labelled Cs in Fig. 1) were considered along the main reservoir axis from the dam to the head of the reservoir. Bottom reservoir sediments were collected by means of a Van Veen grab and they were subsampled and homogenized on field, and stored in a refrigerator during transport to the laboratory.

Once in the laboratory, sediments were lyophilized (48 h). Dry samples were then sieved through a 2 mm mesh to discard the coarser fraction (gravel). The resulting <2 mm fraction was subsequently homogenized and crushed in an agate mortar and in an agate ball mill to a size <63 μm mesh, and stored in a refrigerator prior to analysis.

The total Hg content in samples was determined by thermal decomposition followed by Atomic Absorption Spectrometry (AAS) coupled with gold amalgamation (LECO® AMA – 254 Model). Samples were analyzed in the solid state according to the methodology proposed by Costley et al. (2000). Quality control was tested using certified reference materials (CRM): PACS-2, CRM026-050 and CRM042-056. The recovery percentages (RP) for these materials were between 93% and 109%, and the calculated relative standard deviations in % (RSD) for three replicates of each material were <10%.

Major and PTHE were analyzed at Acme Analytical Laboratories Ltd. (Vancouver, Canada) by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS) after digestion of 0.5 g of sample in hot *aqua regia* (95 °C). All elements were analyzed in batches, which included a procedural blank and a certificate reference material (CRM). Each calibration curve was evaluated by analyses of quality control standards before, during and after the analyses of a set of samples. The accuracy for elemental determination was controlled using CRM: STD OREAS45CA, STD DS8 and CRM042-056. RP of the different elements range from 82% to 111% and the RSD was <7%.

The sequential extraction procedure (SEP) applied was based on the BCR methodology (Quevauviller et al., 1997) adapted to a four-step scheme as reported, for instance, by Sahuquillo et al. (1999) and Delgado et al. (2011). Briefly, the different steps of the SEP allowed four fractions to be differentiated: the first fraction (F1), extracted by a solution of 0.11 M acetic acid, that includes the species that are soluble in water, easily leached by weak acids and associated with soluble carbonates; the second fraction (F2), extracted by 0.1 M hydroxylammonium chloride, consists of the easily reducible species, associated with Fe and Mn oxy-hydroxides; the third fraction (F3), extracted by 8.8 M hydrogen peroxide + 1 M Ammonium acetate, includes the easily oxidisable species, mainly associated with organic matter and sulfide minerals (Li and Thornton, 2001); and the fourth fraction (F4), extracted by *aqua regia* + HF, contains those species extracted from silicates or sulfides, with low solubility.

The four fractions were analyzed at the General Research Services of Oviedo University on an ICP-MS by applying EPA method 200.8 (Brockhoff et al., 1999). Quality control was tested using nonspecific CRM: CRM042-056 and PACS-2. The recovery percentages (sum of recovery/total) were in the range between 91% and 106%.

Principal Component Analysis (PCA), performed with Minitab and SPSS statistical software for MS Windows V15 and V17, respectively, were employed to process the SEP results.,

3.2. Risk assessment

Several indexes available in the relevant literature were applied in an effort to estimate the potential environmental risk based on the concentrations and availability of elements in a reservoir sediments (Liu et al., 2009; Michalec, 2012; Tang et al., 2014, among others). Each one of the selected indexes provides important information for a comprehensive risk assessment, comparing the detected values with local, legal and potential risk to the biota levels.

The degree of contamination index (Cd) (Håkanson, 1980; Abrahim, 2005; Yang et al., 2009), is a simple index that allows an assessment of the pollution level due to PTHE or organic pollutants in soils and