Catena 128 (2015) 174–184

Contents lists available at ScienceDirect

Catena

journal homepage: www.elsevier.com/locate/catena

Assessment of trace element pollution and its environmental risk to freshwater sediments influenced by anthropogenic contributions: The case study of Alqueva reservoir (Guadiana Basin)

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ARTICLE INFO

Article history:
Received 1 November 2014
Received in revised form 3 February 2015
Accepted 4 February 2015
Available online 16 February 2015

Keywords:
Freshwater sediments
Enrichment factor
Geoaccumulation index
Sequential extraction procedure
Risk assessment code
Alqueva reservoir

ABSTRACT

The Guadiana Basin (SW Iberian Peninsula) is affected by acid mine drainage (AMD), a consequence of ancient mining activities in the Iberian Pyrite Belt (IPB). Consequently, the sediments at the Alqueva reservoir (SE Portugal) in the Guadiana Basin are potentially contaminated by trace elements, which make important: (i) to characterize the status of trace element pollution of the sediments; (ii) to evaluate the mobility and the bioavailability of As, Cd, Cu, Cr, Pb and Zn; and (iii) to assess the environmental risk associated with the total and bioavailable concentrations of trace elements, using the sediment quality guidelines (SQGs) and the risk assessment code (RAC). Metal enrichment factors (EF) and geoaccumulation indexes (I_{geo}), determined taking into account the regional background levels, revealed that, among the metals analyzed, Cd contributed the highest to pollution levels followed by Pb and As. Despite the trace element contamination of the Alqueva sediments, the sequential extraction showed that most of them are found in the oxidizable and residual fractions, which indicates that they are sparingly bioavailable, with exception of Cd (acid-labile fraction) and Pb (reducible fraction). Based on the RAC, Cd was the only metal that presented a high risk, while Pb, As and Zn showed a medium risk. Moreover, the SQGs revealed the existence of certain areas of extremely high risk, particularly related to high concentrations of total As and, in less extent, of Pb and Cd, associated with AMD, wastewater discharges and runoff of plant protection products from agricultural fields located near the reservoir.

1. Introduction

Pollution of the natural environment by trace elements is a worldwide problem. With origin in natural sources (e.g., weathering of soil and rock, erosion, forest fires and volcanic eruptions) and anthropogenic activities (e.g., industrial effluents, mining and refining, agriculture drainage, domestic discharges and atmospheric deposition), these elements continuously enter to the aquatic systems, posing serious threat due to their hazardous characteristics (Carman et al., 2007; Chon et al., 2010; Davutluoglu et al., 2011). In fact, one of the most serious environmental issues concerning trace elements, which distinguish them from other toxic pollutants, is that they are resistant to biodegradation and have potential to bio-accumulate and become biomagnified, increasing the exposure of aquatic communities and human populations through the trophic chain (Gao and Chen, 2012; Subida et al., 2013).

As the principal compartment of trace element accumulation, the assessment of sediment quality plays an important role in the good ecological and chemical status of water (Borja and Heinrich, 2005), which is the principal goal of the European Water Framework Directive (WFD) (ECC, 2000). Notwithstanding, this legal document does not mention the sediments as a compartment to be specifically investigated, this matrix constitutes one of the most important source of water contamination by trace elements, as well as, an important carrier of these hazardous substances within the rivers, reservoirs and other waters (Sekabira et al., 2010; Yaun et al., 2014). Consequently, the preservation of this compartment is an important step to maintain the full quality of the water body.

The environmental risk of sediments and its quality could be assessed through the following: (i) pollution indexes, such as the enrichment factor (EF) and the geoaccumulation index (I_{geo}), that characterized the trace element anthropogenic contributions and the contamination levels, comparing the metal enrichment and the unpolluted reference concentrations (background levels) (Christophoridis et al., 2009; Delgado et al., 2010; Mil-Homens et al., 2007); (ii) sediment quality guidelines (SQGs), which relate the pollution status of sediments, considering the total trace element content, with their adverse effects in aquatic organisms,

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http://dx.doi.org/10.1016/j.catena.2015.02.002
0341-8162/

for instance using the threshold effect level (TEL) and the probable effect level (PEL) (Caeiro et al., 2005; Díaz-de-Alba et al., 2011; Saleem et al., 2013); (iii) and methodologies that evaluate the ecotoxicological risk, taking into consideration the mobility/availability of the pollutant, such as, the risk assessment code (RAC; classification that correlates the percentage of the metal more available, with the risk to the aquatic species) (Delgado et al., 2011; Passos et al., 2010; Yuan et al., 2014). Hence, despite the use of total trace element content as a criterion to assess their possible risk to the aquatic ecosystem, it provides insufficient information about the mobility, bioavailability and consequently toxicity, of these hazardous substances to the aquatic and human populations (Gu et al., 2014; Hooda, 2010; Sundaray et al., 2011). Accordingly, the speciation of metals in sediments is therefore a critical factor in assessing their potential environmental impacts (Peng et al., 2004) and can be determined with the use of sequential extraction procedures. Of the many existing schemes, the most widely accepted standardized method was proposed by the European Community Bureau of references (BCR sequential extraction procedure) (Ure et al., 1993) and improved in subsequent works (Rauret et al., 1999; Sahuquillo et al., 1999). The BCR sequential method presents advantages compared with other methods, as high reproducibility and high recovery percentages (Cuong and Obbard, 2006; Pueyo et al., 2008). Further, this procedure has already been applied to assess metal mobility in several types of solid samples, such as sediments (Davutluoglu et al., 2011; Díaz-de-Alba et al., 2011; Delgado et al., 2011 Passos et al., 2010), soils (Martley et al., 2004; Pérez-López et al., 2008; Rao et al., 2008), and sewage sludge (Alvarenga et al., 2007).

This work was developed in the sediments of the Alqueva reservoir (the biggest artificial lake of the Iberian Peninsula) in the Guadiana Basin, which is one of the most important rivers of the Iberian Peninsula and drains the western part of Iberian Pyrite Belt (IPB), one of the world's most important metallogenic sulfide provinces, where mining dates back to the Third Millennium B.C. (Delgado et al., 2011; Nocete et al., 2005). Associated with these mining areas are acid leachates containing metals, metalloids and sulfates, which constitute the acid mine drainage (AMD). Presently, the mining activity is limited to a small number of active mines (Neves Corvo and Aljustrel), but the environmental impact of the AMD still exists, due to the some abandoned mines which need to be rehabilitated (Matos e Martins, 2006), and several authors have reported AMD as an important anthropogenic source of trace elements in the Guadiana Basin (Fernández-Caliani et al., 2009; Guillén et al., 2011; Nieto et al., 2007). On the other hand, the intensive agricultural activity and the discharge of untreated or inefficiently treated domestic wastewater may constitute other sources of metals in this water body (Palma et al., 2014a, 2010; Silva et al. 2011).

Previous studies developed at the Alqueva reservoir have characterized the textural structure and organic content of the sediments, the levels of nutrients, the total contents of As, Cd, Cr, Cu, Ni, Pb, Zn, Fe and Mn; and some ecotoxicological effects (Palma et al., 2014a, 2014b). Currently, it is important to understand, which amounts of trace elements are arising from anthropogenic sources, as well as their mobility and bioavailability in the sediments, and try to correlate these results with the toxicological risk for the reservoir and for the populations. In this scenario, the main aims of the present study were as follows: (1) to characterize the status of pollution of the sediments, in terms of potentially toxic trace element contents, based on the specific geochemical regional backgrounds, and using as pollution indexes, the EF (which estimates the anthropogenic impact, on sediments, of each of the element analyzed) and the I_{geo} (based on geochemical data, that makes possible to map the areas according to their pollution degree); (2) to investigate the mobility and the bioavailability of the most potentially toxic elements (As, Cd, Cu, Cr, Pb and Zn); (3) to assess the environmental risk associated with the total and bioavailable trace element contents in the sediments, using available SQGs (TEL and PEL) and the RAC; (4) to identify, among the trace elements analyzed, which are those with higher risk for the aquatic communities.

The results of this study, in combination with the outcomes obtained in previous ones, are intended to help the water resource managers and regulatory authorities to establish priority actions aimed at achieving the chemical and ecological status objectives, outlined in the Water Framework Directive. Further, this research intended to demonstrate the usefulness of diverse tools to estimate the real environmental risk of pollutants, which could become an innovative and useful approach to be applied in risk assessment of water environments.

2. Materials and methods

2.1. Study area and sampling sites characterization

The Alqueva reservoir is located in southern Portugal, along 83 km of the main course of the Guadiana River Basin. The river is divided from the morphological point of view in five distinct sections (Batista et al., 2012; Feio, 1951): Alto Guadiana or Ruidera lagoons, the Miocene aged Mancha plain, the "Monte do Toledo", the Central Extremadura and, finally, the Portuguese section, where the Alqueva reservoir is located.

The lithology of the Guadiana Basin, which influences both sediment composition and grain size distribution, is dominated by greywacke, schist, and a volcano-sedimentary complex with polymetallic sulfide complexes of Cu, Pb and Fe–Mn and carbonate rocks (Mil-Homens et al., 2007).

The hydrologic regime of the Alqueva reservoir reflects the regional expression of the Mediterranean climate, which is characterized by dry and hot summers as well as mild and wet winters with concentrated rains (Morales, 1993). Further details about its physical and hydrodynamics characteristics can be found elsewhere (Palma et al., 2014a, 2010).

Five sampling sites were established at the Alqueva reservoir: three upstream, Ajuda (Aj; 38°46′28.56″N, 7°10′47.00″W), Alcarrache (Ac; 38°19′1.53″N, 7°19′51.10″W), Álamos (Al; 38°20′30.00″N, 7°34′40.00″W), and two at the middle, Mourão (Mr; 38°23′60.00″N, 7°23′25.80″W) and Lucefécit (Lf; 38°33′6.32″N, 7°17′52.86″W), of the reservoir (Fig. 1), selected taking into account previous studies (Morais et al., 2007; Palma et al., 2010).

2.2. Sampling

Sampling was carried out approximately every two months from February 2011 to November 2012 (12 sampling campaigns). The wet season included the months of November (Nv), February (Fb) and April (Ap), and the dry season included the months of June (Jn), July (Jl) and September (Sp) (ARHAlentejo, 2011).

At each sampling location, 5 L of surface sediments (<10 cm) were collected, gathered using a stainless steel van Veen grab of 0.05 m^2. The sediments at Lf, Mr, Ac, and Al were collected at a water column depth of 25, 48, 37, 27 and 30 m, respectively. All the samples from Aj were collected from the shore. The sediment samples were packed in polyethylene bags and transported to the laboratory, in a cooler at 4 °C, where they were preserved and stored until the analysis following the requisites for sediment conservation (USEPA, 2001).

2.3. Trace element analysis

Total trace element concentrations in the sediment were determined after digestion of the samples with aqua regia according to ISO 11466 (1995). Flame atomic absorption spectrometry (FAAS) or electrothermal atomic absorption spectrometry (ETAAS) was used in the analysis, using a Varian apparatus (SpectrAA 220FS, 220Z and 110Z). The methodology was described in Palma et al. (2014a).