Marine Pollution Bulletin 127 (2018) 1–9

Contents lists available at ScienceDirect

Marine Pollution Bulletin

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

Geochemical behavior, environmental availability, and reconstruction of historical trends of Cu, Pb, and Zn in sediment cores of the Cananéia-Iguape coastal system, Southeastern Brazil

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ARTICLE INFO

Keywords:
Valo Grande channel
Metals
Sediments
Sequential extraction
Sedimentation rate
Mining

ABSTRACT

The Cananéia-Iguape system is located in a coastal region of southeastern Brazil, recognized by UNESCO as an Atlantic Forest Biosphere Reserve. This system has suffered substantial environmental impacts due to the opening of an artificial channel and by past intensive mining activities. In this paper was performed the sequential chemical extraction of Cu, Pb, and Zn, on previously described sediment cores, and the statistical treatment of the data, allowing to estimate the remobilization geochemical behavior, the available content and the trend of accumulation between 1926 and 2008. The maximum available level (sum of all mobile fraction) were, in mg kg^{-1}, 18.74 for Cu, 177.55 for Pb and 123.03 for Zn. Considering its environmental availability, Pb remains a concern in the system. It was possible to recognize the anthropic contribution of Pb, being the mining activities considered the only potential source of this metal in the region.

1. Introduction

The Cananéia-Iguape system is located in the interior of a coastal region in southeastern Brazil, known as Lagamar. This region is recognized as an Atlantic Forest Biosphere Reserve by UNESCO (United Nations Educational, Scientific and Cultural Organization). This system, characterized by its outstanding set of environmental attributes, has undergone dramatic changes over the last 150 years, since the opening of the Valo Grande artificial channel, which connected the system to the Ribeira de Iguape River (Mahiques et al., 2009). The canal was built between the years of 1827 and 1852 (Geobrás, 1966), to facilitate the transport of agricultural products, reducing the distance to the region leading export port. However, in addition to freshwater, the Ribeira River discharged through this channel a high load of fine suspended sediments (Tessler and Souza, 1998), affecting the physical-chemical characteristics and deposition of sediments in this region (Mahiques et al., 2013). With the intense mining activity in the Ribeira Valley between the 40s and 90s, the Ribeira River basin was affected, reaching the Cananéia-Iguape system through the Valo Grande channel. The Ribeira Valley presents an extensive history of mining activities, with several mines and a refinery (company Plumbum) operating for decades. The company Plumbum was active from 1945 to 1995 with the purpose of Pb ore beneficiation and refining, produced in the mines of the region or imported from other countries (Di Giulio et al., 2008). The processes of ore beneficiation and smelting in this region were usually rudimentary and without control over the consequent impacts on the environment, with the slag resulting from the activities launched during 40 years in the waters of the Ribeira River (Guimarães and Sígolo, 2008). Several studies in sediments, carried out since the 80's, showed that the Ribeira River basin was affected by mining and metallurgical activities (e.g., Tessler et al., 1987; Moraes, 1997; Silva, 1997; Corsi, 1999; Guimarães and Sígolo, 2008). Other studies also showed the anthropogenic contribution of metals in the Cananéia-Iguape system, with mining activities indicated as the only source of pollution in the region (Mahiques et al., 2009; Mahiques et al., 2013; Tramonte et al., 2016).

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https://doi.org/10.1016/j.marpolbul.2017.11.016
Received 28 August 2017; Received in revised form 9 November 2017; Accepted 11 November 2017
Available online 22 November 2017

The adverse effects caused to the environment by mining activities have being studied recurrently around the world (e.g., Kovács et al., 2012; Maftei et al., 2014; Resongles et al., 2014; Omanović et al., 2015; Othmani et al., 2015; García-Ordiales et al., 2016; Obiora et al., 2016; Idaszkin et al., 2017). Given this scenario, the importance of the chemical fractionation of metals in sedimentary records of the Cananéia-Iguape system is evident, mainly to estimate the geochemical behavior regarding remobilization in the case of changes in environmental conditions, as well as their environmental availability and, also to reconstruct these elements accumulation tendency.

The study of metals in sediments is a relevant topic in environmental research since, besides being a reservoir for chemical species, sediments are considered active aquatic compartments that play a significant role in the redistribution of these chemical species to the biota (Cotta et al., 2006; Cuong and Obbard, 2006). Although the accumulation of heavy metals in sediments provides temporary improvement in the quality of overlying water, polluted sediments can be considered as "time bombs" (Kelderman and Osman, 2007), since the contaminants are not permanently fixed in them (Förstner, 1979; Calmano et al., 1996; Zoumis et al., 2001).

The mobility, transport, and fractionation of heavy metals are a function of the chemical element form, which in turn is controlled by the physicochemical and biological characteristics of the system (Sakan et al., 2009). According to Förstner (2004), aquatic sediments can present several functions such as memory effect, the monitoring of biological and chemical quality, and the prognostics for remobilization risks.

The aim of this work was to present a study focused on the geochemical behavior, the environmental availability and the reconstruction of the accumulation of Cu, Pb, and Zn in sediment cores of the Cananéia-Iguape system, which deposition occurred during the period of intense mining activity in the Ribeira Valley, between the 1940s and the 1990s.

To study the fractionation and the availability of metals in sediment cores of the Cananéia-Iguape system, we adopted the sequential extraction method proposed and optimized by the European Community Bureau of Reference (BCR), currently named Standards, Measurements and Testing Program (SM&T). This method is considered one of the most popular (Abollino et al., 2011), and establishes three distinct phases, in which the associated metals are sequentially released by the chemical action of specific reagents for each of the phases, simulating the remobilization of metals in sediments in the case of variation in the environmental conditions.

2. Materials and methods

2.1. Study area

The Cananéia-Iguape system is located between latitudes 24°40′S and 25°05′S and longitudes 47°25′W and 48°00′W, in the southeastern coastal region of Brazil, known as Lagamar (Fig. 1). This system is formed by a complex of estuarine and lagoon channels that surround islands and mangroves. With an approximate extension of 100 km, the main communication of the system with the open ocean are the inlets of Barra de Cananéia and Barra de Icapara (Bernardes and Miranda, 2001). Its circulation is mostly driven by tides, the flow of fresh water from rivers and wind influence (Miyao et al., 1986). The tide in this system is the primary forcing that is responsible for the processes of mixing and exchanges that take place between the ocean and the estuary, becoming an active agent in the sediments transport process and the renovation of estuarine waters (Miyao and Harari, 1989).

The Ribeira de Iguape River, with a contribution through the Valo Grande channel, is the primary supplier of fresh water to the system, which together with the tidal cycles cause considerable variation in the salinity amplitude. It is estimated that after the opening of this channel, about 60% of this River flow was directed to the Cananéia-Iguape system, leading to a drastic decrease in salinity (Mahiques et al., 2009). It is important to note that in addition to freshwater, the Ribeira de Iguape River also discharges a high load of fine suspended sediments (Tessler and Souza, 1998).

The climate of this system shows characteristics of a humid tropical climate, varying from humid tropical without a dry season to humid tropical with a cool summer and, due to the climatic and geomorphological characteristics of the region, the vegetation cover is marked by salt marshes and mangroves in the margins of mixohaline bodies of water and by the dune vegetation of the Atlantic forest in the highest areas (Mahiques et al., 2013).

2.2. Sampling

Five cores, CAN: 02, 04, 05, 07 (these four cores were earlier described in Mahiques et al., 2013), and CAN 10 were collected in 2008 along the Cananéia-Iguape system (Fig. 1, Table 1) with the aid of a Rossfelder VT-1 vibracorer. These were fractionated into slices, which were freeze-dried and kept in a closed plastic container until analyzed. For each of the cores, six samples were selected, at depths between 0 and 50 cm, totaling 30 sediment samples that were submitted to the sequential extraction procedure. According to the geochronology data, the sedimentary deposition of the selected layer contemplates the period of highest intensity of mining activities in the Ribeira Valley.

2.3. Sequential extraction of metals

The levels of Cu, Pb, and Zn, were determined for the geochemical fractions in the sediment samples. Their quantification was performed through the ICP-OES (Inductively Coupled Plasma - Optical Emission Spectrometry) technique (Varian analyzer, model MPX 710-ES). The quantification limits (QL) were 0.64 mg kg^{-1} for Cu; 1.90 mg kg^{-1} for Pb and 1.40 mg kg^{-1} for Zn. For the determination of the elements of interest in these fractions, it was applied the sequential extraction procedure based on the protocol developed and optimized by the European Community Bureau of Reference (BCR) (currently named Standards, Measurements and Testing Programme - SM&T). Below it is presented a synthesis of the applied procedure based on the method described on Pueyo et al. (2001):

- Step 1: acid-soluble fraction (F1) - 20 mL acetic acid 0.11 M was added for each 0.5 g of sediment sample. This suspension was agitated for approximately 16 h at room temperature and then centrifuged to separate the liquid extract and the solid phase.
- Step 2: reducible fraction (F2) - 20 mL hydroxylamine hydrochloride 0.5 M was added to the solid residue from step 1. Agitation, centrifugation, and separation of the solid and liquid phases were performed according to the described in step 1.
- Step 3: oxidizable fraction (F3) - 5 mL hydrogen peroxide 30% (v/v) was added to the solid residue from step 2. Initially, the extraction was performed at room temperature and then under heating. Afterward, another aliquot of 5 mL hydrogen peroxide was added under heating. After reducing the volume and cooling of the suspension, it was added 25 mL ammonium acetate 1 M (pH = 2) to it. Agitation, centrifugation, and separation of the solid and liquid phases were also performed according to the described on step 1.

Those above-described extractions were carried out with dry sediment, and the residues were washed with Milli-Q water, under agitation, before the use of the aliquots on the subsequent steps. The liquid extracts obtained in each step were kept under refrigeration until the moment of analysis.

The certified reference material (CRM) number 701, from the Institute for Reference Materials and Measurements (IRMM), was used to evaluate the efficiency of the extraction procedure. The observed RSD for this method was inferior to 15% for all elements and the