Assessment of trace metals contamination in estuarine sediments using a sequential extraction technique and principal component analysis

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ABSTRACT

Fractionation of the metals Cd, Cr, Cu, Ni, Pb and Zn in sediments was performed for samples collected from eight locations in the Poxim river estuary of Sergipe State, northeast Brazil, using the 3-stage sequential extraction procedure proposed by the European Community Bureau of Reference (BCR). The extraction method was found to be satisfactory for analysis of certified reference material BCR-701, with recovery values ranging from 85% (Cu) to 117% (Cr). The detection limits obtained were 0.001 to 0.305 μg g^{-1}. Zn exhibited greatest mobility and bioavailability, indicative of anthropogenic sources, while Cr was mainly found in the residual fraction and could be used as an indicator for the contribution from natural sources. Cd, Cu, Ni and Pb were associated with the oxidizable fraction, and Pb, Cr and Ni with the reducible fraction. Principal component analysis (PCA) clearly separated the metals into three groups: I (Zn); II (Pb); III (Cd, Cu, Cr and Ni). These groupings were mainly due to different distributions of the metals in the various fractions, in sediments from the different locations. Risk assessment code (RAC) analysis indicated that although the metals presented a moderate overall risk to the aquatic environment, nickel showed a low risk (RAC<10%) at three sites, while zinc presented a high risk (RAC>30%) at four other sites.

1. Introduction

Investigations concerning the metals present in sediments have increased in recent years, and whereas previously sediments have been considered as reservoirs into which chemical species are deposited, they are now viewed as an active aquatic compartment that performs a fundamental role in redistribution of these species to aquatic biota [1–3].

It is accepted that determination of the total concentrations of metals in sediments is not sufficient to be able to predict the capacity for mobilization of these elements. The environmental behavior of trace metals is critically dependent on their chemical form, which influences mobility, bioavailability and toxicity to organisms. Consequently, there is considerable interest in understanding the associations of these elements with the solid phase [4,5].

In the absence of anthropogenic influences, trace metals in sediments are mainly associated with silicates and primary minerals, and therefore have limited mobility. Chemical elements introduced from human activity show greater mobility, and are associated with other sediment phases, such as carbonates, oxides, hydroxides and sulfides [6].

Although time-consuming, the use of sequential extraction provides detailed information concerning the origin, mode of occurrence, biological and physico-chemical availabilities, mobilization and transport of trace metals. The procedure simulates the mobilization and retention of these species in the natural environment using changes in environmental conditions such as pH, redox potential and degradation of organic matter [4]. A series of reagents is applied to the sample, increasing the strength of the extraction at each step, in order to dissolve the trace metals present in different sediment phases. The extractants are inert electrolytes, weak acids, reducing agents, oxidizing agents and strong mineral acids [7].

The three-stage sequential extraction procedure proposed by the European Community Bureau of Reference (BCR) was developed in an attempt to standardize the various schemes described in the literature [8–10], since the use of different procedures, varying in the number of steps, types of reagent and extraction conditions, hindered comparisons of results obtained in the many studies of trace metal chemical fractionation in environmental samples [11].

The BCR method has been widely adopted by various authors, and applied to a range of types of solid samples including fresh water sediments [12–14], salt water sediments [15–17], soil, sewage sludge and particulate matter [18–20].

The rationale of the sequential extraction procedure is that each successive reagent dissolves a different component, so that the resulting elemental distributions can be used to infer information

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about the mobility and bioavailability of an element, or the potential risks posed to the environment [4,7,11]. In some studies [21–23] the risk assessment code (RAC) has been used to assess environmental risks and estimate possible damage to benthic organisms caused by contaminated sediments. This is because in sediments, metals are bound to both different fractions and with different bonding strengths, with the latter influencing the bioavailability of the metal in the environment [7,11]. The RAC considers the percentage fraction of metals that are exchangeable and associated with carbonates. In this fraction, the metals are weakly bound to the sediment, and present a greater environmental risk since they are more available to the aquatic system. The RAC classification defines risk levels as zero, low, medium, high and very high, depending on the percentage value [21,24].

The present work presents the distributions of the trace metals Cd, Cr, Cu, Ni, Pb and Zn in surface sediments of the Poxim river, Sergipe State, northeast Brazil, obtained using the optimized three-stage BCR extraction procedure of the Standards, Measurements and Testing Programme (SM&T), proposed by the European Community Bureau of Reference. Interpretation of results was based on the reduction of metal bioavailability or mobility at each successive extraction step. The first three fractions contained the most labile metals, and the residual fraction the least bioavailable/mobile metals. The RAC was determined for each metal, and multivariate principal component analysis (PCA) applied to the results in order to identify groupings between the metals.

2. Materials and methods

2.1. Study region

The Poxim river, located in Sergipe State, northeast Brazil, is part of the Sergipe river hydrographic basin, that drains approximately 16.7% of the State, an area of 3,673 km^2, and has average flows of 560,000 m^3 day^{-1} and 70,000 m^3 day^{-1} in the rainy and dry seasons, respectively [25]. The Poxim is formed after the confluence of the Poxim-Açu and Poxim-Mirim rivers, and near its mouth is joined by the Pitanga river. In its final reaches, it flows through urban areas of the municipalities of São Cristóvão, Nossa Senhora do Socorro and Aracaju, the State capital, where it receives discharges of untreated domestic and industrial waste [26].

The study area extended over 7 km, covering the lower estuary of the Poxim, between latitudes 10° 55′ S and 10° 57′ S, and longitudes 37° 03′ W and 37° 05′ W. The cities of Aracaju and São Cristóvão are located in this region, with ~592,000 inhabitants (~30% of Sergipe's total population). Industrial activities include food processing, metallurgical plants, and production of plastics, textiles and ceramics. Besides domestic and industrial effluents, there are impacts from deforestation, municipal landfills, tourism and agriculture. In the vicinity of Aracaju city, the Poxim receives untreated waste from surrounding residential neighborhoods and industrial districts [25].

2.2. Sampling and sample preparation

Eight surface sediment samples were collected from the estuarine region of the Poxim river in March 2004. Site locations are illustrated in Fig. 1. The core sampler used was composed of cellulose acetate butyrate, and the upper 5 cm of sediment were removed at each site. Samples were stored in closed plastic vessels, and kept in ice until arrival at the laboratory. They were then immediately dried in a forced air circulation cabinet at 60 °C for 72 h (until constant mass was achieved), and homogenized to a fine powder in a porcelain mortar. They were then stored under refrigeration in pre-cleaned glass flasks, prior to analysis.

2.3. Reagents and glassware

All reagents used were analytical grade or better (Merck, Germany), and ultrapure water (18 MΩ cm) was supplied from a Millipore Milli-Q system. Stock standard solutions, containing 1000 mg L^{-1} of the metals, were prepared from standard vials (Tritisol, Merck) containing 1.000 g ± 0.002 g of metal. Working standard solutions were prepared at the time of analysis by dilution of the stock solutions. All glassware were previously decontaminated using HNO$_3$ (50%, v/v), followed by repeated rinsing with ultrapure water.

2.4. Determination of method efficiency

The efficiency of the sequential extraction method was determined by analysis of four replicates of certified sediment reference material (BCR-701, European Community Bureau of Reference). For each extraction step, the concentration of each metal obtained was compared with the reference value, and the recovery calculated as the ratio (%) between measured and certified values.

2.5. Determination of detection limits

Detection limits (DL) were determined for the six trace metals in each fraction, following the procedure of Miller and Miller [27]. Ten analytical blanks were analyzed for each step of the extraction process. The DLs were calculated as $3\sigma/a$, where a is the slope of the calibration curve, and σ is the standard deviation (in absorbance units) calculated from ten readings of the sample blank. DL values took into account the use of 1 g portions of sample in extractions, and any necessary dilutions.

2.6. Sequential extraction of trace metals

Sequential extraction was performed using the optimized BCR procedure [28]. A detailed description of this procedure is provided below.

Stage 1 (fraction soluble in acid — metals that are exchangeable or associated with carbonates): To each 1 g of sample was added 40 mL of a 0.11 mol L^{-1} solution of acetic acid, with agitation for 16 h at 22 °C. The extract was separated from the solid phase by centrifugation at 3000 rpm for 20 min, and the supernatant stored for later analysis.

Stage 2 (reducible fraction — metals associated with oxides of Fe and Mn): To the residue from Stage 1 was added 40 mL of a 0.5 mol L^{-1} solution of acid hydroxylammonium chloride (pH 1.5). The suspension was then agitated for 16 h at 22 °C. The extract was separated from the solid phase by centrifugation, as described for Stage 1.

Stage 3 (oxidizable fraction — metals associated with organic matter and sulfides): To the Stage 2 residue was added 10 mL of 8.8 mol L^{-1} H$_2$O$_2$ solution (pH 2–3), and the mixture left at room temperature for 1 h. It was then heated to 85 °C for 1 h in a water bath, until the volume was reduced to 2–3 mL. Another 10 mL portion of 8.8 mol L^{-1} H$_2$O$_2$ solution was added, and the mixture heated to dryness at 85 °C for 1 h. After cooling, 50 mL of a 1.0 mol L^{-1} solution of ammonium acetate (pH 2) was added to the residue, with subsequent agitation for 16 h at 22 °C. The extract was separated from the solid phase by centrifugation, as above.

Stage 4 (residual fraction — metals strongly associated with the crystalline structure of minerals): The Stage 3 residue was digested using a mixture of the acids HNO$_3$ (4 mL), HCl (2 mL) and HF (4 mL) to determine the total concentrations of metals. The residues were digested in closed Teflon receptacles for 2 h at 140 °C. After cooling, the receptacles were opened, and then heated at 210 °C until completely dry. The final residue was dissolved in 10 mL of 0.5 mol L^{-1} HCl, and the volume made up to 50 mL.