ANÁLISIS ESPECTROSCÓPICO DE SEDIMENTOS DE ESTUARIO TROPICAL EN EL NORDESTE DE BRASIL

SPECTROSCOPIC ANALYSIS OF SEDIMENTS FROM A TROPICAL ESTUARY IN THE BRAZILIAN NORTHEAST

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Abstract

The purpose of this work is to characterize the geochemical composition of sediments of the Parnaíba River delta, in terms of trace metal concentrations, using spectroscopic techniques. A profile sampling campaign was carried out in April 2017. The granulometric analysis of the surface sediments showed that the silt + clay fraction added up to 14.31% of the total. The mean concentrations of heavy metals in the profiles were 1.78 mg.kg^{-1} for Cd; 10.57 mg.kg^{-1} for Cr; 11.85 mg.kg^{-1} for Cu; 24.42 mg.kg^{-1} for Ni; 47.90 mg.kg^{-1} for Zn; 152.45 mg.kg^{-1} for Pb; 1887.28 mg.kg^{-1} for Mn; 1.12% for Al and 3.49% for Fe. Scanning electron microscopy/energy dispersive spectrometry (SEM/EDS) applied to the sediments from the coast of Ceará showed the morphological diversity of sediment grains. The infrared spectra presented similar functional groups at all tested points, demonstrating that the clay minerals in the different samples probably have the same origin.

Key words: *Geochemistry, Heavy Metals, Estuarine sediments, Scanning electron microscopy.*

Introduction

Studies related to the measurement of metals in soil and sediments are important to environmental authorities and are used as a way to monitor potentially polluted areas. As a result, determining the concentrations of heavy metals makes it possible to identificy point sources of contaminants, having in mind that the anthropogenic concentrations of trace metals may be higher than accepted quality levels. Several studies have shown a significant increase in the concentration of trace elements in ecosystems in different parts of the world after the industrial revolution (De Paula Filho et al., 2015). When testing the increase of the pollution of a given area, it is common to use sediment profiles as a way of comparing the total quantities of trace elements measured in these areas with values found under natural or pre-industrial conditions. Sediments have been considered to be a compartment of accumulation of pollutants from the water column. An important factor is their high sorption and associated accumulation capacity, where the concentrations become several orders of magnitude higher than the one found in the waters. This allows the use of sediment profiles as an indicator of environmental pollution, both current and distant in time, allowing us to discover the main sources of pollution to a given aquatic system (De Paula Filho et al., 2015).

Materials and methods

The deltaic system of the Parnaíba river is a complex and important ecosystem due to its marine-fluvial dynamics and because it harbors important plant and animal communities. It is characterized by extensive fluvial-marine plains, intersected by channel-forming islands formed by the accumulation of terrigenous materials. Extensive mangrove areas developed under the influence of these environments, representing an important area for the deposition of materials of continental origin. The sampling campaign was conducted in April 2017, and the sampling sites were located in mangrove areas in the estuarine channels. 03 sediment profiles (yellow circles) and 19 surface sediment samples (blue balloons) were collected (Figure 1).

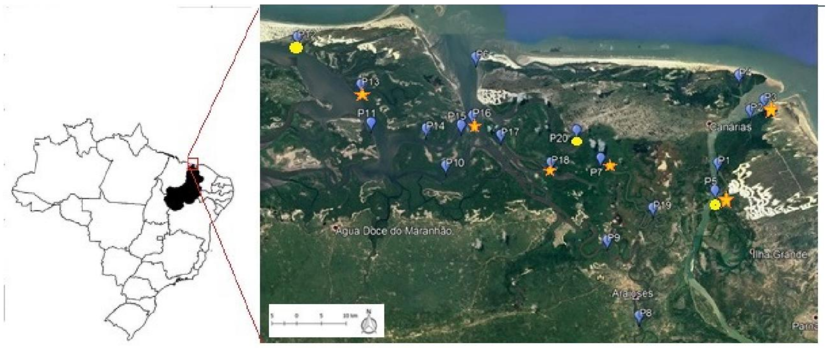

Figure 1. Location map highlighting the sampling points in the Parnaíba River Delta. Profiles (yellow circles) and surface sediments (blue balloons), of these some were analyzed by MEV / EDS (orange stars).

The granulometry of the surface sediments was determined by dry sieving. The samples were then oven-dried at 80°C and the clods that formed at the drying stage were then pulverized. Acid extracts were obtained from the leaching of about 1.0000 g of the 63 µm fraction in 30.0 ml of a 50% aqua regia solution ($3HCl.HNO_3$). For the profiles we used the bulk fraction (<2 mm). The procedure was performed in a closed system heated to 80ºC for 2 hours (Aguiar et al., 2014). The obtained extracts were tested by flame atomic absorption spectrophotometry (FAAS) using the VARIAN SpectraA 50b spectrophotometer at the Analytical Lab of the Federal University of Cariri. The validation of this method was performed by testing a NIST 1646a Standard Reference Material (National Institute of Standards and Technology). Recovery rates for the metals were 85% for Al, 89% for Cr and Pb, 91% for Cd, 92% for Ni and Mn, 94% for Cu, 96% for Zn and 101% for Fe. The results were compared to the sediment quality criteria for heavy metals as described in CONAMA Resolution No. 454 (CONAMA, 2012). Sediments from six sampling stations (orange stars in Figure 1) were adhered to two-sided carbon adhesive tape over an Al support; the sediments were then covered with a ca. 5-nm layer of platinum. The morphological data and x-ray microanalysis results were obtained using a scanning electron microscope (FEG Quanta 450 Environmental Scanning Microscope with EDS /EBSD). To perform the Infrared Spectroscopy with Fourier Transform, a Perkin Elmer spectrophotometer with a resolution of 3 cm^{-1} was used, with a mode of transmittance by KBr inserts.

Results

The granulometric analysis showed that the surface sediments have fractions with grain sizes that vary from coarse sand to silt + clay, with great discrepancy between their quantities. The mean values were equivalent to 1.53% of coarse sand (600µm < x < 2000µm), 7.05% of medium sand (200µm < x < 600µm), 77.11% of fine sand (60µm < x < 200µm) while the silt + clay fraction was 14.31% of the total (Figure 2).

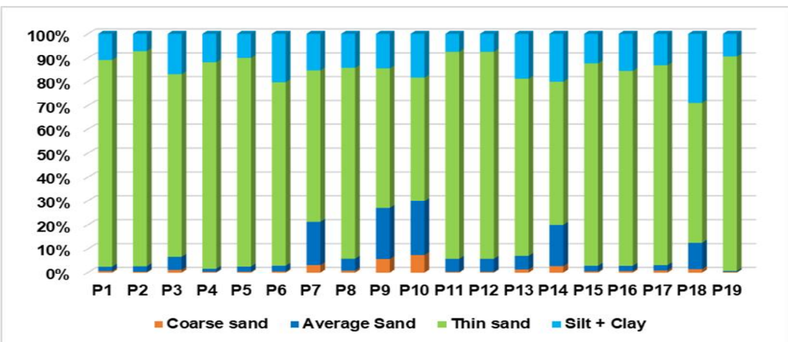

Figure 2. Percentage of grain size represented for each sediment sampling point.

Based on the maximum and minimum values detected for each metal, the concentration data found for Cu, Cr, Mn and Zn are compatible with the quality reference values suggested by CONAMA Resolution No. 454. The P5 profile showed a downtrend for all metal concentrations from the base to the top. In contrast, the P20 profile showed an uptrend in its concentrations, mainly for Cr and Cd. Notably, the P12 profile presented an uptrend of Cu concentrations (Figure 3).

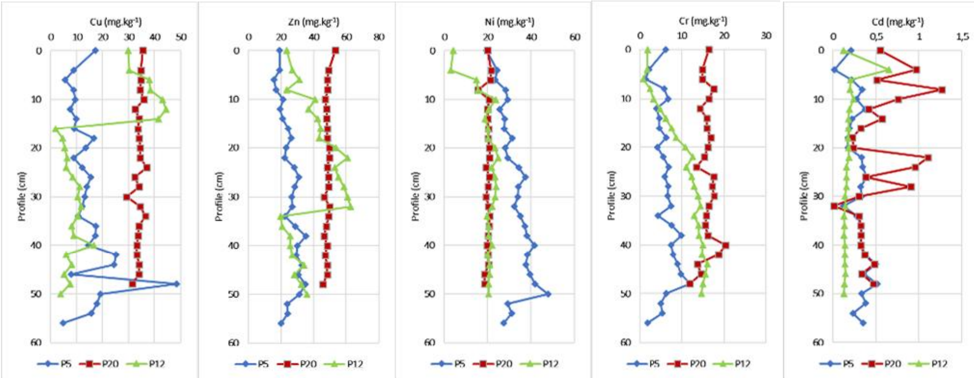

Figure 3. Temporal evolution of metal concentrations in sediment profiles of the Parnaíba River Delta.

The concentrations of Cr ranged from 0.86 to 20.38 mg.kg^{-1}. These values are lower than the threshold effect level (20.38 mg.kg^{-1}) according to the quality reference values suggested by CONAMA Resolution No. 454/12. The evidence collected in point 5 presented values higher than level 1 for Cu only at a depth between 46 and 48 cm, being in its great majority among the values considered without risks to the biota. The three samples showed values higher than level 1 (point 12 presented these values starting at a depth of 4 cm) and higher than level 2 at point 5 (starting at a depth of 24 cm) for Ni, showing an intermediate contamination at the three points, and a higher contamination in point 5. The morphologies of the sediments (Figure 4) were similar, consisting of fragments of biological material, amorphous agglomerates, multifaceted particles, and crystals. The dimensions of these structures varied from nm to mm in length, but micrometric structures predominated.

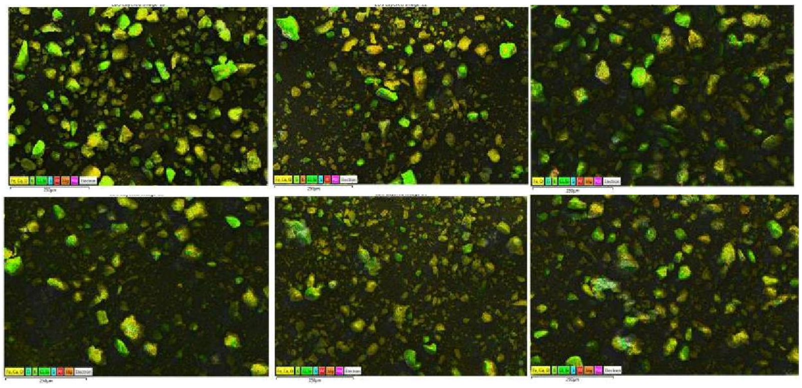

Figure 4. Scanning Electronic Microscopy images from the sampling stations.

SEM generates images of individual sediment grains and information about the formation, habit, porosity, and growth of minerals. The morphology showed by the SEM/EDS allowed us to identify various minerals on the Parnaíba Delta (Figure 5).

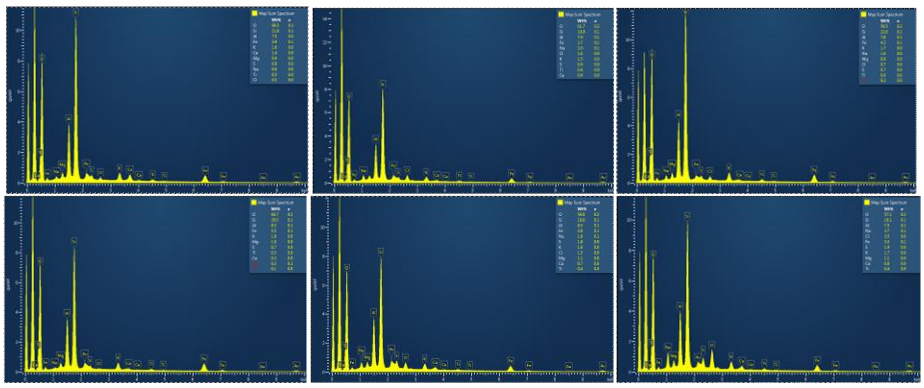

Figure 5. Disperse energy spectra from sampling stations in the Parnaíba River Delta.

The SEM/EDS x-ray microanalysis of the sediments from the Parnaíba River Delta showed silicates, oxides, carbonates, and sulfates. At the same time, this method increased the quantification of metals in the sediments from the northeast coast of Brazil. The similarity between the spectra demonstrates that the clay minerals present in the different samples probably have the same origin. That is, the sediments deposited in the different channels of the estuary of the Paraíba Delta present a common mineralogical composition (Figure 6).

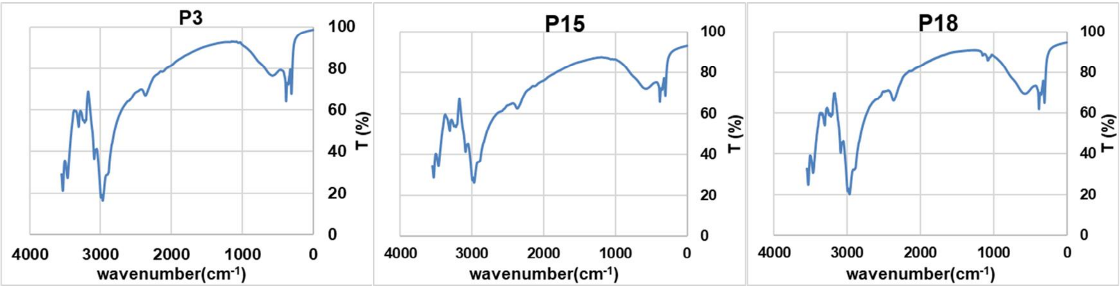

Figure 6. Infrared spectra of surface sediments of the Parnaíba River Delta.

According to Almeida (2010), small streaks between 400 and 800 cm^{-1} can be observed in the spectra, which may correspond to the stretching vibrations of the Mn-O bond (they are poorly diagnostic and suffer intense interference from the silicate bands). Large streaks between 2900 and 3550 cm^{-1} are also observed, which according to Almeida (2010) refer to stretching and angular vibrations of the OH group and are related to the adsorbed water and hydration water present in the clay.

Conclusions

In general, the granulometric testing indicated that the surface sediments had 14.31% of silt + clay and 77.11% of fine sand, with a larger sandy fraction in the granulometric constitution. The sediment profiles showed variability in the enrichment trend of metals from top to bottom. Cr showed a marked downtrend. The SEM/EDS x-ray microanalysis of the sediments identified silicates, oxides, carbonates, and sulfates. At the same time, this method increased the quantification of metals in the sediments from the Parnaíba River Delta in the Northeast coast of Brazil.

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