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BCR sequential extraction procedure study of superficial sediments from floodplain in Educandos (Manaus – Brazil)

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Abstract

Floodplains, highly productive riverside areas, represent between 3-4% of the Amazon region. These areas are annually flooded during the rainy season receiving a high charge of nutrient rich sediment from the Andes Mountains. The enrichment factor (EF) and risk assessment code (RAC) of metal-contaminated sediment samples of Mn, Zn, Cu and Ni from the anthropogenic Educandos floodplain (Manaus, Brazil) in this work was evaluated applying the sequential extraction procedure proposed by the European Community Bureau of Reference (BCR). The sampling site comprised a Negro River floodplain region that has received high concentrations of contaminated industrial and domestic effluents. Ten sediment samples were collected at a depth 5 cm in order to analyze the Mn, Zn, Cu and Ni concentration in the extract obtained by BRC sequential procedure. To calculate the EF and RAC, the Mn, Cu, Ni and Zn concentrations were analyzed with flame absorption atomic spectrometry. EF metal showed high Zn, Cu, and Ni concentration in all sediment samples from the Educandos floodplain. The results of RAC point out the following risks: high to Zn and Ni, ii) moderate to Cu, and iii) low to Mn.

Key words: heavy metal, BCR, sediments, anthropogenic pollution.

INTRODUCTION

Uncontrolled urbanization process accompanied by contaminated wastewater release throughout the city of Manaus has increased over the last years. The city population rose from 1940 (284,118 inhabitants) to 2014 (2,020,301)(G. P. Santana and Barroncas 2007)·(IBGE 2014). The major contamination region has concentrated in the Educandos basin, a region that encompasses a large floodplain. Educandos basin has an area of 46.14 km^2 with a perimeter of 48.11 km corresponding to 10.22% of Manaus's urban perimeter. Its drainage area involves 22 neighborhoods. This region harboring more than 500 industrial enterprises has a high technological index. The electric-electronic sector predominates and is responsible for 55% of all production. The urban and industrial districts are responsible for high sewage discharge into the Educandos floodplain and consequently, into the Negro River. As a result, high contents of heavy metal are found in the aquatic ecosystem (Pio, Souza, and Santana 2014)·(Genilson Pereira Santana 2015), soil (Souza and Santana 2014), fish(G P Santana 2016) etc. Unfortunately, the abundance and persistence of heavy metal explains several cases of worldwide environmental contamination (Li et al. 2014)·(Choobari, Zawar-Reza, and Sturman 2014)·(Zhang et al. 2014). Additionally, heavy metal contamination is an outcome of anthropogenic activity such as industrial, mining and domestic activity.(Reza and Singh 2010)

The ever-increasing Manaus urbanization has increased the heavy metal concentration released into the largest hydrographic basin in the world. The Amazon River basin covers $6.1x10^6$ km^2 encompassing Brazil, Peru, Bolivia, Colombia, Ecuador, Venezuela, and Guyana. The Amazon basin receives an average rainfall of 2460 mm/yr while the mean discharge at the estuary is 209,000 m^3 s^{-1}. This basin has already displayed a problem with mercury contamination since it was detected by renowned scientist Jacques Cousteau in 1985.(Valle et al. 2005) According to Artaxo(Artaxo et al. 2000) an average of 63% of the Hg concentration present in Amazon region has been associated with gold-mining activities. In addition, the metal concentration is greater in the Solimões River, which has shown high levels in particulate sediment.(Seyler and Boaventura 2003)

However, heavy metal contamination level depends upon several factors, such as pH values, redox potentials, particle sizes, composition, environmental compartment, etc. Sediment environmental compartment; heavy metal distributes in different chemical species: soluble, exchangeable, bound to organic matter, occluded in Mn and/or Fe oxides, as a part of carbonates, phosphates, sulfurs, or other secondary minerals, or bound to silicates (residual)(Genilson Pereira Santana 2015),(Manahan 1999),(Devesa-Rey, Díaz-Fierros, and Barral 2010). Therefore, the heavy metal study uses the partition as a fundamental tool to study solid material, such as sediment using selective solutions(Tessier, Campbell, and Bisson 1979),(A. M. Ure 1991).

The International Union of Pure and Applied Chemistry (IUPAC) recognizes sequential selective chemical extraction as a widely used technique for understanding the element distribution in the solid phase. According to IUPAC, the partition is a process of classification of an analyte or a group of analytes from a certain sample according to physical (e.g., size, solubility) or chemical (e.g. bonding, reactivity) properties(Templeton et al. 2000). Sequential extraction answers several metal contamination questions in the sediment such as chemical forms, distribution, and bioavailability(a. M. Ure et al. 1993).

Historically, Tessier et al. (Tessier, Campbell, and Bisson 1979) proposed sequential extraction to predict metal behavior in a solid matrix, such as sediment and soil. However, the lack of uniformity in the different sequential extraction used by the various authors made the Community Bureau of Reference of the Commission of the European Communities (BCR) establish a sequential extraction protocol for sequential extraction.(Bacon and Davidson 2008) The result of the metal concentration obtained sequential extraction allows the estimating of the environmental risk in sediments using the Risk Assessment Code (RAC) and the enrichment factor (EF). The RAC assesses the environmental impact caused by metal contamination in sediments(Ghrefat and Yusuf 2006),(Nemati et al. 2011). The ratio exchangeable and/or carbonate-bonded fractions and total metal concentration provide the RAC value. The RAC value receives the following interpretation: i) <1% means no risk; ii) from 1 to 10% low risk; iv) from 11 to 30% medium risk; from 31 to 50 % high risk; and v) > 51 % very high risk to the environment(Rodríguez et al. 2009). Therefore, the RAC metal in urban sediment is an essential issue for understanding the possible change of sediment quality caused by intensive anthropogenic activities.(Yang et al. 2014) EF adjusts the metal variability caused by grain size and mineralogy, identifies anomalous metal contributions, and geochemical normalization of the heavy metal results(Ergin et al. 1991). For calculating ER values the following equation is used:

$$EF = \frac{\left(\frac{M}{Fe}\right) \text{samples}}{\left(\frac{M}{Fe}\right) \text{background}}$$

where $\left(\frac{M}{Fe}\right) samples$ is the ratio of metal and Fe concentration as the sample, and $\left(\frac{M}{Fe}\right) background$ is the ratio of metal and Fe concentration of a background.

In this work, superficial sediment samples of the Educandos basin were analyzed by a BCR metal partition scheme to answer the following questions: i) What are the chemical forms on the metal in sediment and their geochemical variation?; ii) What are the ER values and their consequences?; and iii) What are the results offered by RAC findings?.

MATERIAL AND METHODS

Collection and Sequential extraction procedure

After choosing each sampling showing some environmental characteristics such as access and heavy metal contamination sources, ten sediment samples in an Educandos basin were collected from a depth of 5 cm (Figure 1) in October 2010. The sampling site comprises a floodplain, an ecotone between upland and the Negro River that alternate between aquatic and terrestrial states. This place receives sediments and contaminants from the Manaus Industrial district transported by floodwaters and deposited within riparian zones. Sampling site works as a buffer between upstream and downstream river reach. At the same time, Negro River contributes to the maintenance of the elemental process of the floodplain. The interaction between land and the Negro river is an essential process for riparian ecosystem maintenance and affects fundamental ecological characteristics such as biodiversity water quality and viability of many river species.

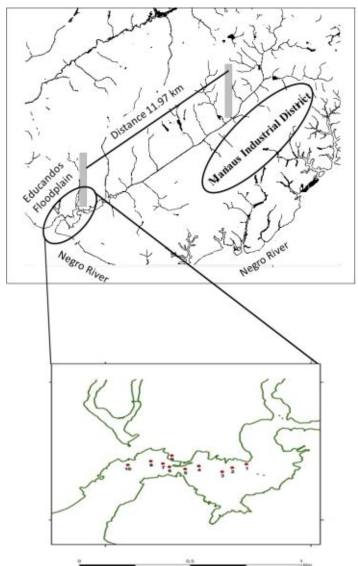

Figure 1. Sampling site located in Educandos basin (Manaus – Brazil).

The BCR sequential extraction procedure was conducted on near 1 g of portions dried sediment ≤ 53 µm in a centrifuge flask of polystyrene at 40 mL and Teflon vessels. The BCR sequential extraction procedure description is:

Setp I (***Extractable fraction – F1***): addition of 40 mL of 0.11 mol L^{-1} CH_3COOH in centrifuge flask, agitation in shaker for 16 hours at laboratory temperature, and separation supernatant and residue by centrifugation.

Setp II (***Reducible fraction –F2***): addition in the residue (***F1***) of 40 mL of 0.5 mol L^{-1} $NH_2OH.HCl$, agitation in shaker for 16 hours at laboratory temperature, and separation supernatant and residue by centrifugation.

Setp III (***Oxidizable fraction – F3***): addition of 10 mL of 30 % H_2O_2 (pH adjusted to 2.0–3.0) in the residue (F2) and heating for 1 hour at 85 ± 2 ^oC. Then, gradual addition of

10 mL of H_2O_2, heating for 1 h at 85 ± 2 °C until volume of 1 mL, addition of 50 mL CH_3COONH_3 at 1 mol L-1, agitation in shaker for 16 hours at laboratory temperature and separation supernatant and residue by centrifugation.

Setp IV (***Residual fraction – F4***): addition of 3 mL deionized H_2O, 7.5 mL 6 mol L^{-1} HCl, and 2.5 m L 14 mol L^{-1} HNO_3 in residue (***F3***) and boiled for 2 h.

In each BCR fraction, we analyzed the Mn, Cu, Ni and Zn concentrations with flame absorption atomic spectrometry using a GBC (AVANTA SIGMA) spectrometer model. For metal analysis, we used a fuel-lean air-acetylene flame and reference curves determined from a series already prepared with SpecSol references solutions (Metal concentration 1,000 g ± 0,002 g).

An internal performed check was applied through comparison of the sum F1 + F2 + F3 + F4 with the total concentration obtained by acid digestion in order to validate the obtained results from the sequential extraction procedure:

$$Recovery = \frac{\sum BCR\ fraction\ concentration}{Total\ concentration} x100$$

The recovery results (average ± standard deviation and Coefficient Variation - CV) recorded the following value according to analyzed metal: Mn 99.8±16.6% (CV 16.6%), Cu 81.9±16.1% (CV 19.7%), Zn 122.1±17.5% (CV 14.3%) and Ni 109.9±11.9% (CV 10.9%).

RESULTS AND DISCUSSION

The box plots obtained for the four BCR sequential extraction show low amount outliers indicating high homogeneity in the results (Figure 2). As expected to sediment samples, the box-and-whiskers comprised skewed right and left as well as symmetrically. Therefore, the box plots suggest different behaviors to BCR fraction according to the fraction and metal. The median for BCR sequential extraction point out Ni, Zn and Mn as the metals with major mobility (F1 extract) obeying the following mobility sequence: Zn > Ni > Mn. The box plots display that the lowest metal concentration values are in the residual fraction (F4 extract). These findings point to Zn, Ni, Mn, and Cu as susceptible metals under these chemical and physical environmental conditions. Additionally, high concentrations of Zn, Ni, Mn, and Cu demonstrate that industrial discharges of pollutants from the Manaus Industrial District are received into the Negro River floodplain. For Beckwith et al.[26], our findings are a significant advance in urban Manaus hydrology research because of the pollution source identification in sediment.

The high Zn, Ni and Mn concentrations in the exchangeable fraction show high Zn, Ni and Mn mobility implying insufficiency of important regulatory processes such as precipitation as insoluble sulfides under highly reduced conditions, formation of discrete metal oxides and hydroxides of low solubility, and adsorption to colloidal hydrous oxides of iron and manganese, primarily in aerobic, neutral or alkaline environments.(Gambrell, Khalid, and Patrick 1980),(Tingzong, DeLaune, and Patrick 1997) According to Souza and Santana(Souza and Santana 2014) the Educandos basin has adsorbents with low cation adsorption and the high Zn concentration occurs because of low carbonate concentration. These authors also claim that high contents of Zn have remobilized becoming readily available due to the Ultisol soil low pH values from the Manaus Industrial District. The low pH values explain the release of Zn and Cu from the Educandos basin sediment depending directly on pH variation.

As the depth of sediment samples ≤5cm, our findings express surface enrichment, and consequently, the heavy metal contamination being of recent years. According to Nemati et al.(Nemati et al. 2011) the pollutants are always absorbed into top sediment first and then sink into deeper positions through chemical exchange. In addition, this phenomenon presents as the elements in F1 are of surface sediments, and their distribution depends on the geographical location.

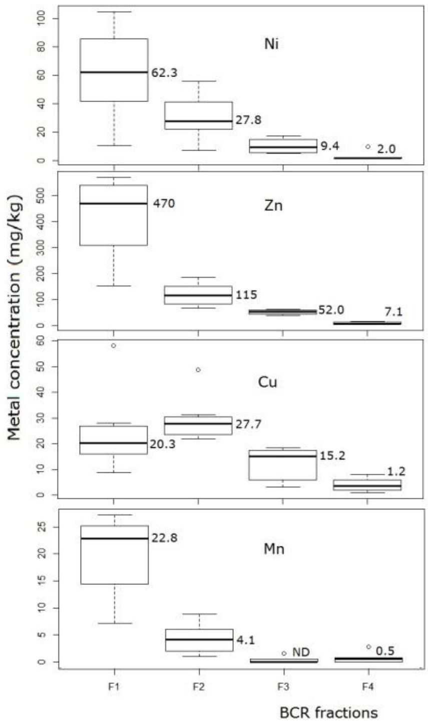

Figure 2. Box plots for the BCR fractions.

The calculation of the EF points to several values > 1.0 according to sampling site, except Mn (Figure 3). The EF proposition interpretation suggested by Sutherland[25] established five categories of classification: i) EF~2 Depletion to minimal enrichment suggestive of no or minimal pollution. ii) EF 2 – 5 Moderate enrichment, suggestive of moderate pollution. iii) EF 5 – 20 Significant enrichment, suggestive of a significant pollution signal. iv) EF 20 – 40 Very highly enriched, indicating a very strong pollution signal. v) EF140 Extremely enriched, indicating an extreme pollution signal. As our sampling sites have received high concentration of contaminated sediment since 1969, all five EF categories are obviously expected to be found. However, the Zn, Cu, and Ni EF values point to high contamination caused by release of domestic and industrial effluents.

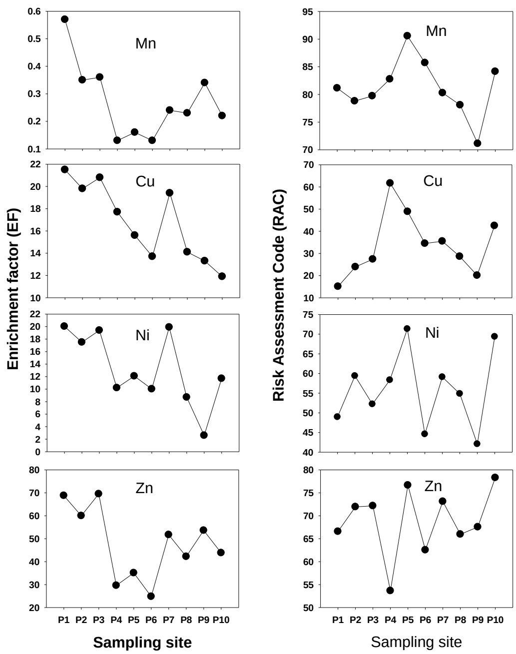

Figure 3 – EF and RAC of the sediment samples.

Generally, heavy metal in anoxic sediments has been considered non-toxic because of the formation of stable and insoluble metal sulfides, consequently, metals have low bioavailability, mobility, and potential risk.(Wang et al. 2016) However, the RAC values show a high environmental risk due to Mn, Zn, and Ni (Figure 3). Our results point to the following mobility and bioavailability order: Zn (69%) > Ni (56%)> Cu (33%) > Mn (4%). This RAC sequence indicates a significant risk level of Zn, Ni, and Cu. Commonly. RAC values above 50% indicate very high as well as dangerous risk, with metals being easily able to enter the food chain.(Nemati et al. 2011) Unfortunately, these metals have entered into the food chain and can cause deleterious effects to aquatic systems. Indeed, high Zn and Cu concentrations were found in muscle and live from *Hoplosternum littorale*, fish species survivor in the Educandos basin.(G P Santana 2016)

The Santana findings obtained in the Manaus Industrial District also have high RAC values. Figure 3 suggests that high concentration of Zn, Cu and Ni pollutes all the hydrology of the

Educandos basin arriving into the Rio Negro floodplain. RAC values show that Zn maintains the same risk along all hydrologies of the Educandos basin. This result supports a high mobility of the Zn release from the Manaus Industrial District. Ni has the greatest RAC value of the Manaus Industrial District region. On the other hand, the Cu presents the greatest risk in the Educandos floodplain. This result shows that the Manaus Industrial District contributes significantly to polluting the Educandos basin as well as Negro River.

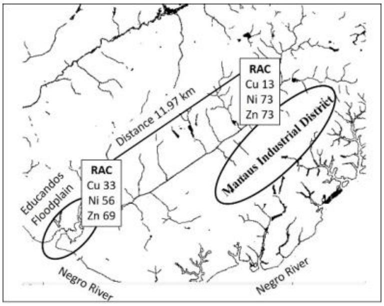

Figure 3 – RAC value found in Manaus Industrial District region and Educandos Floodplain.

CONCLUSION

The interaction between land and the Negro river constitutes an essential process to riparian ecosystem maintenance and affects fundamental ecological characteristics such as biodiversity water quality and viability of many riverine species. However, our results showed Zn, Ni, and Cu contamination of the sediment riparian zone. This affirmation has as support the high EF of Zn, Cu and Ni found in all sediment samples from the Educandos floodplain and the RAC that point out high risk to Zn and Ni, moderate risk to Cu and low risk to Mn.

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