



SEDIMENT-DISTRIBUTED METAL FROM THE MANAUS INDUSTRIAL DISTRICT (MID) REGION (AM - BRAZIL)

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ABSTRACT: Sediment samples from a major Manaus stream (Igarapé do Quarenta – IQ40) were collected from nine sites in the Manaus Industrial District (AM-Brazil) in order to be submitted to a sequential chemical extraction for the partitioning of heavy metals (Cu, Co, Cr, Fe, Zn, Pb and Ni). The samples were treated with solutions of several different pH, and the contents of the metals were determined by flame atomic absorption spectrometry (FAAS). Our findings show the association of Fe, Cu, and Zn with sulfides, carbonates and organic fractions. The sequential extraction proposed showed the influence of the pH values on the bioavailability of heavy metals in contaminated sediments. Additionally, sequential extraction showed the pH value to release of Zn, Cu and Fe in the IQ40 sediment.

KEYWORDS: Sequential extraction; Heavy metal; Bottom sediment; FAAS.

1. INTRODUCTION

The distribution of heavy metals in the environment depends on several factors, such as pH values, redox potentials, particle sizes, composition and amount of the soil/sediment source, cation exchange capacity, anthropogenic activity, etc.. Therefore, it is hard to achieve a clear understanding of all interactions involving the metal ions and the sediment and water. In sediments, metals can exist in different forms: soluble, exchangeable, bound to organic matter, occluded in Mn and/or Fe oxides, as a component of carbonates, phosphates, Sulphurs, or other secondary minerals, or bound to silicates (residual) (Devesa-Rey *et al.*, 2010).

During several years, the literature showed that most sediment studies concerning environmental impact supported their findings in the total metal concentration (Bacon and Davidson, 2008). As an attempt of improving the metal environmental study, it is

possible to find several strategies reported on the metal speciation in soils/sediments. (Das et al., 1995) in the review paper suggested some methods based on sequential extractions to establish the heavy metal environmental distributions. Substances that are able to change the redox potential of the sample and to form complexes, depending on the pH, encompass the sequential extraction of specific metal (Ure, 1991). The method recommends as a sequential procedure for portioning metal the scheme developed by *the European Community Bureau of Reference (BCR)*. This operational speciation permits to answer some questions as the chemical forms of the metals in the sediments and their geochemical variations; the sediment dominant characteristics that influence the metal distribution; and the bioavailability of metal (Ure et al., 1993). However, inferences concerning bioavailability based on sequential extraction findings present some problems. It is reasonable to expect that metal liberated in a sequential extraction have the potential for more immediate environmental impact than the exposure route. The usefulness of sequential extraction has several applications and its continued usefulness, in particular for environmental monitoring, requires researchers to be aware of the limitations (Bacon and davidson, 2008; Ferreira and Santana, 2012).

As an attempt to test a new sequential extraction procedure, we decided to evaluate a chemical extraction sequence of several sediment samples from the Industrial District of Manaus, in order to estimate the potential remobilization of some heavy metal ions.

2. MATERIAL AND METHODS

2.1. Sampling sites

This study was carried out in the Igarapé do Quarenta (IQ40) basin, located at the Educandos hydrographic basin (03°07'16.6 S and 59°59'08.0 W), encompassing an aquatic system formed by 12 small streams (Figure 1). The streams usually are 1.30-4.00 m wide and 0.30-1.6 m deep along its 38 km length. The IQ40 is located in the central area of the city of Manaus (250,000 inhabitants), and crosses the Industrial District (MID), which was constructed on a plateau and houses over 400 high-throughput state-of-art industrial companies. The electric-electronic sector represents 55% of the whole MID production. Large amounts of organic (domestic waste) and inorganic (heavy metal) sewage have been discharged into the IQ40 (Ferreira et al., 2012; Pio *et al.*, 2014; Souza and Santana, 2014). As a result apart from being the population's main water source, it is also affected by all the untreated waste products being discharged into it IQ40.

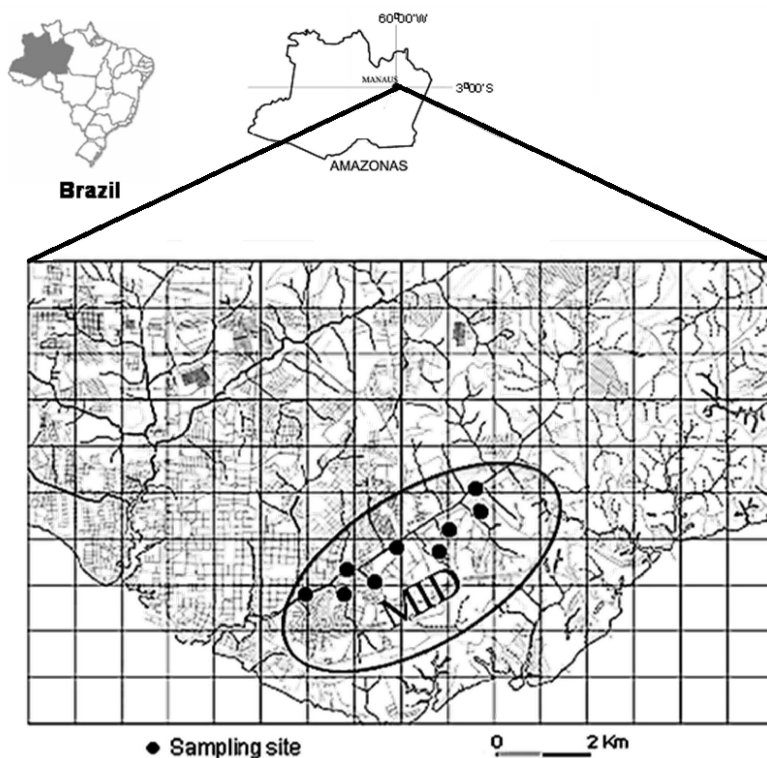


Figure 1 – Map showing the sampling sites along the Igarapé do Quarenta stream.

Data obtained from this study showed to be particularly suited for a lot of reasons like, heavy metal relatively high concentration, varying environmental conditions, localities, and so on. Furthermore, Crane (2003) claimed that settled sediment samples are more appropriate for assessing the general risk of contamination from sediment-bound chemicals, such as, heavy metal and organic substances. Therefore, given to their accessibility and representativeness, nine sites were selected for sediment sampling in a nearly 8 km long stretch at MID (Figure 1). The samples were collected from February to March 1999 (rainny season) using an Eckman dredger sampler. Each sample was collected from the upper 2.0 cm layer of the sediment. They were immediately placed on ice and were kept at 4 °C in the laboratory until being processed and analyzed.

Samples were dried at room temperature as well as put through a 2,000 μ m-meshed sieve. The metal analyses were performed in this fraction because metals are usually found within the small grains (Dassenakis et al., 2003). This fraction also homogenizes easily, and thus, it reproduces metal measurements more clearly (Forstner and Salomons, 1980).

2.1. Sequential extraction method

The different extraction procedures are not always selective because chemical reagents may themselves alter the indigenous speciation of a trace element. In the choice of extractants, less powerful leaching solution will probably be more selective for specific fractions than more severe reagents, which may attack in other forms, although the overall efficiency of extraction may be lower. Also to be taken into consideration are factors such as readsorption processes, the time required to carry out the experiments, the temperature effect and the ratio between the solid mass and the extractant solution volume (Das et al., 1995 and references therein). Therefore, we have chosen the extraction procedure described in Table 1, which seems to be more adequate to access the distribution of metals in the MID region.

Table 1 - Different-valued pH solutions.

Solution	pH	Sedimentation fraction
Na ₃ PO ₄	10.05 ± 0.02	Organics
NH ₄ OH/CH ₃ COOH	7.80 ± 0.40	Exchangeable
NaCl	6.27 ± 0.03	Exchangeable
MgCl ₂	5.93 ± 0.04	Exchangeable
NH ₄ CH ₃ COO/CH ₃ COOH	4.88 ± 0.05	Exchangeable
Na ₂ EDTA	4.56 ± 0.13	Carbonates, Fe occluded (amorphous)
HNO ₃	3.27 ± 0.04	Sulfides
NaCH ₃ COO/CH ₃ COOH	2.78 ± 0.01	Carbonates
HCl	2.57 ± 0.01	Mineral matrix (easily soluble)
HNO ₃ /HClO ₄ /HF	<1.0	Residual

One grams of < 2,000 µm sediment samples were submitted in replicate (n = 5) to a modified sequential extraction procedure as described below:

- I. Step 1: A 15 mL Na₃PO₄ solution was added into a 100 mL centrifuge tube and shaken for 2 h at room temperature. The extractant was separated from the solid residue by centrifugation at 2,000 rpm for 30 minutes.
- II. Step 2: A 15 mL NH₄OH/CH₃COOH solution was added in the centrifuge tube to the residue of Step 1, and the extraction was performed as described above.
- III. Next, this same procedure was used for the other extracting solutions shown in Table 1.

An untreated sediment portion of 0,100 g was digested at 150 °C for 2 hours in a Teflon vessel by the following concentrated acid sequence: HNO₃ (5 mL), HClO₄ (15 mL), and HF (15 mL).

The contents of Fe, Zn, Cu, Cr and Pb present in the extracted and digested solutions were determined by using FAAS (Perkin Elmer, model ASS 3300), air/acetylene flame, standard calibration procedures and standard reagent certificates (SpecSol) with concentrations at 1.000±0.003 mg g⁻¹. For all elements, the readings were made only with calibration curves presenting $r^2 \geq 0.99$. The figure of merit for heavy metal analyses were obtained by linear correlation and residual standard deviation (RSD) < 9% for n=5. For quality control, analytical blanks and certified standard solutions of all elements were prepared and analyzed using the same procedures and reagents. The limits of detection (LOD) was calculated as under, LOD (3 x s/m), where s is the standard deviation of 10 measurements of the blank and m is the slope of the calibration graph obtained for each case, the LODs (µg g⁻¹); Fe (0.07), Zn (0.005), Cu (0.01), Cr (0.07) and Pb (1.1). The quantification limit found by (10xs/s) were Fe (0.90), Zn (0.01), Cu (0.02), Cr (0.07) and Pb (1.1)

The laboratory analytical performance was evaluated through the Certified Reference Material BCR-701 analysis to check accuracy and the recovery percentages obtained for the metals analyzed were in all cases between 85 and 105% (Sahuquillo et al., 1999).

3. RESULTS AND DISCUSSION

Chemical analyses show that the contents of Pb, Cd and Cr in the whole sediment samples to be less than the LOD. However, Table 2 shows that the residual fraction only presents Fe, Zn and Cu associated with the crystalline mineral structure. The $\Delta = \text{Whole samples} - \text{residual fraction}$ suggests that Fe, Zn and Cu comprise different sources as those inherent of anthropogenic activities. As sediments are a potential secondary source of metals and released back into water columns along with changing environmental conditions, the Δ values indicate high contamination metal risk for IQ40 aquatic ecosystem. For Zn our findings corroborate with the results found by (Souza and Santana, 2014). These authors observed that exist a remarkable difference between the concentration of Zn in the exchangeable and residual fraction.

Additionally, sediments are the sink for particle-sorbed contaminants in aquatic systems and can serve as a reservoir of toxic contaminants that continually threaten the health and viability of aquatic biota. The concentration of heavy metals, such as Zn, Cu,

and Fe, in the sediment can be several orders of magnitude greater than in the overlying water. Metals found in the sediment directly threaten detrital and deposit-feeding benthic organisms, and could possibly be a long-term source of contamination higher up the food chain (Pulatsü and Topçu, 2015). It is an unfortunate consequence of industrialization that releases to environment their undesirable toxic wastes and effluents (Chen and White, 2004).

Table 2 – Heavy metals concentrations in whole sediment samples and residual fraction. Replicates = 5.

Site	Whole sample			Residual fraction		
	Fe	Zn	Cu	Fe	Zn	Cu
1	172±7	1.40±0.07	0.78±0.03	56.4±0.0	0.012±0.001	0.31±0.10
2	130±2	1.49±0.01	1.19±0.09	41.4±0.9	0.015±0.002	0.31±0.03
3	114±8	1.21±0.07	0.68±0.03	15.4±0.3	0.012±0.008	0.54±0.01
4	94±6	2.36±0.07	0.44±0.04	13.8±0.8	0.009±0.002	0.46±0.02
5	122±4	1.19±0.03	0.41±0.05	20.7±0.9	0.011±0.010	0.46±0.03
6	67±2	1.42±0.08	0.35±0.08	13.8±0.2	0.01±0.005	1.06±0.09
7	102±1	1.83±0.10	0.36±0.05	42.6±0.4	0.01±0.002	0.69±0.07
8	41±7	1.86±0.08	0.36±0.06	16.1±0.7	0.01±0.007	0.64±0.06
9	81±2	1.86±0.06	0.41±0.09	18.4±0.4	0.01±0.008	0.54±0.09
Average	102.5±38	1.62±38	0.55±0.28	41.9±47.5	0.011±0.002	0.55±0.22

For understanding the assumptions about the distribution of Zn, Fe, and Cu in relationship sequential extraction, we obtained box plots with the concentration values. A box plot has the distinct advantage of allowing the reader to understand the distribution of the data in a much more complete way than a single value can give. A box plot gives the median value, the 25th to 75th percentile (interquartile range), and the outliers. Box lengths represent the interquartile range, the horizontal lines within the boxes the median value. The Figure 2 shows a variation of Fe, Zn and Cu in the fractions obtained by sequential extraction. The Box plots present for Zn, Cu and Fe outliers. In a data distribution derived from anthropogenic processes, there may appear to be outliers in the context of the main mass of the data. The asymmetric distributions is another characteristic attributed to the anthropogenic activity.

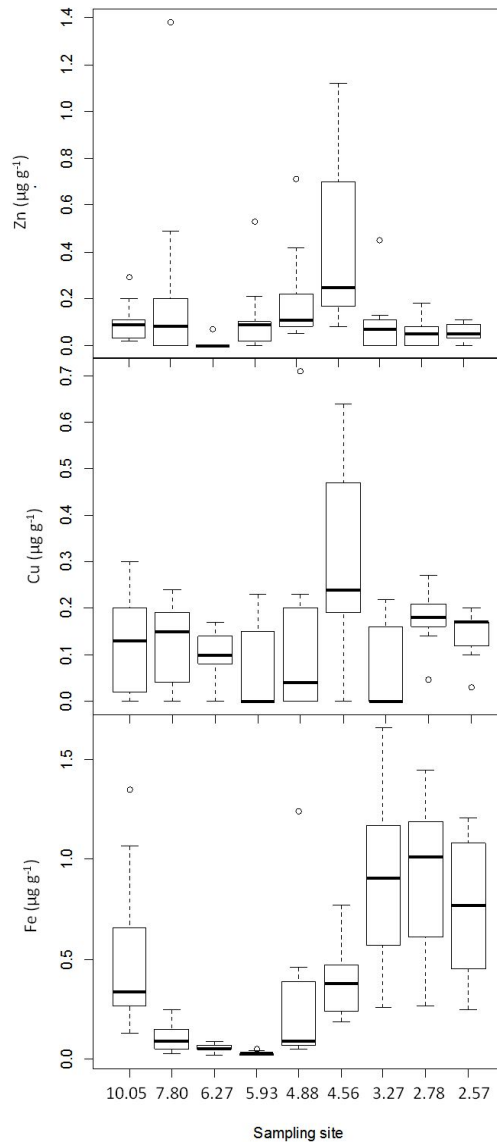


Figure 2 – Box plots showing the variation of the concentration of Fe, Cu and Zn released by sequential extraction.

In the other hand, the medians shows that the higher extraction of Fe occurs at pH at 2.78, and Zn and Cu at 4.56. Although, the box plots indicate that the release of Fe, Zn and Cu occur in all extractors. This finding suggests that the mobility these heavy metals to the aquatic biota and hence their introduction into the food chain did not depends the pH values. However, toxicity of an element is strongly dependent on its

chemical form (Ure *et al.*, 1995). For Bacon and Davidson (2008) the interpretation of data obtained by sequential extraction depends strongly on the metal pool could be considered as bioavailable in studies of plant uptake yet mobile or labile in leaching studies. Our findings show clearly the pH influence on the release of Zn, Fe and Cu. This information to the central Amazonia region is important because of the variations that occur during year. The Negro River basin is characterized by two distinct hydrological seasons: the dry period (September to February) and the wet period (rainy season from March to August), where the water level difference can reach up to 15 m (Da Silva *et al.*, 2009). In the rainy season, rivers tend to flood, covering the forest and surroundings areas, forming the so-called “igapós”, which act as an important source of labile organic carbon to the water bodies, thus markedly affecting the values pH and consequently the release of metals.

The sequential extraction proposed in this work indicates that the major efficiency of extraction has relation with following sediment fractions: sulfide-bound + organic matter (pH 2.0), carbonate-bound (pH 5.0) and amorphous iron oxides (pH 3.0) (Ure *et al.*, 1995). MID sewage is mainly a combination made up of domestic and industrial liquid and solids effluents, and therefore it is likely that H₂S and carbonates are formed by the decomposition of organic substances. These substances easily react with Zn, Cu and Fe according to their respective solubility products: ZnS ($\sim 10^{-23}$), CuS ($\sim 10^{-44}$), Cu₂S ($\sim 10^{-47}$), Fe₂S₃ ($\sim 10^{-36}$), FeS ($\sim 10^{-19}$).

5. CONCLUSION

Our results showed that the change in pH values can be used to evaluate the bioavailability of heavy metals in contaminated sediments. The sequential extraction proposed in this paper has the advantage of showing the pH value where the Zn, Cu and Fe are released into the environment. Although, our results showed that the release of these metals occur in all extractors used in this study. These findings motivated to continue studying other sediments contaminated with other heavy metals to check which pH will be greater within the bioavailability of the possible variations that occur in the aquatic ecosystem

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METAL DISTRIBUÍDO NOS SEDIMENTOS DA REGIÃO DO DISTRITO INDUSTRIAL DE MANAUS (DIM) (AM - BRAZIL)

RESUMO: Amostras de sedimentos de um grande Igarapé de Manaus (Igarapé do Quarenta - IQ40) foram coletadas em nove sites na Manaus Distrito Industrial (AM-Brasil), a fim de ser submetida a uma extração química sequencial para o particionamento de metais pesados (Cu, Co, Cr, Fe, Zn, Pb e Ni). As amostras foram tratadas com soluções de vários diferentes valores de pH, e a concentração dos metais foram determinadas por espectrometria de absorção atômica de chama (FAAS). Os resultados mostram a associação de Fe, Cu, Zn e com sulfetos, carbonatos e as frações orgânicas. A extração sequencial proposta a influência do pH sobre a biodisponibilidade de metais pesados em sedimentos contaminados. Além disso, a extração sequencial mostrou o valor de pH com maior liberação de Zn, Cu e Fe no sedimento IQ40.

PALAVRAS-CHAVE: Extração sequencial; metal pesado; sedimento de fundo; FAAS.
