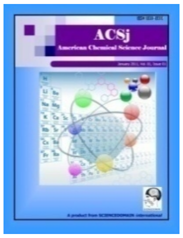

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Determination of Trace-metals in Sediments and Plants on Canal of Jandiá and Igarape of Fortaleza in Macapá-AP-Brazil

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Authors' contributions

This work was carried out in collaboration between all authors. Authors KNRS, RMB and CBR designed the study, wrote the protocol, involved in writing the first draft, participated in experiments and data collection. Authors CCL, FSB, AMF and JCTC managed the literature search, analyses of the study and manuscript preparation. Author AMF, FSB and CBRS performed the statistical analysis and also aided in data interpretation and was actively involved in reading the manuscript. All authors read and approved the final manuscript.

Original Research Article

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ABSTRACT

Aims: Determine the concentration of trace-metals (Na, K, Mg, Ca, Pb and Zn) in sediments and plant *Cenchrus echinatus* L. species on Canal of Jandiá and Igarape of Fortaleza in the municipality of Macapa, Amapa, Brazil.
Study Design: The sediment samples were collected (0.3kg) at 05 points on Canal of Jandiá and Igarape of Fortaleza, totaling 10 sampling points, where each point contained

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a distance of 200m between them, which was determined with the aid of equipment Garmin GPS model. The samples of plants of the *Cenchrus echinatus* L. species (0.2kg) were used to determine the concentration of metals and submitted to calcination and filtration process, and analyzes carried out in atomic absorption spectrophotometer model 6300 Shimadzu AAS.
Place and Duration of Study/Methodology: The study and analyses were carried out at the Department of Biological Sciences and Health, in Laboratory of Atomic Absorption and Bioprospecting (LAAB), Laboratory of General and Analytical Chemistry of Federal University of Amapá and Department of Aquaculture and Fisheries (Embrapa) between January to October of 2011.
Results: The statistical significance was calculated using a two-tailed Student t test and Mann-Whitney U test with 95% confidence interval. In Igarape of Fortaleza, the values of trace-metals in sediments for K ranged from 0.2mg/L to 6.1mg/L, Ca from 5.5mg/L to 18.1mg/L, Mg from 1.4mg/L to 1.6mg/L, Pb from 0.13mg/L to 4.2 mg/L and Zn from 1.3mg/L to 2.1mg/L. In the Canal of Jandiá, measured values of Na ranged from 0.0 to 9.4mg/L, Ca from 5.3mg/L to 18.4mg/L, Pb from 0.4mg/L to 1.6mg/L and Zn from 1.6mg/L to 2.7mg/L. Trace-metals not detected were Na, in Igarape of Fortaleza, and K, in the Canal of Jandiá. The results obtained in the determination of trace-metals (Na, K, Mg, Ca, Pb and Zn) in plants of the *Cenchrus echinatus* L. species in the Canal of Jandiá, showed that the measured values of Na ranged from 0.0 to 9.4mg/L, Ca from 5.9mg/L to 1.1mg/L, Pb from 0.4mg/L to 1.6mg/L and Zn from 0.2mg/L to 2.07mg/L. In Igarape of Fortaleza, the trace-metal of Ca ranged from 8.07mg/L to 26.2mg/L, Mg from 1.3mg/L to 1.4mg/L, Pb from 0.06mg/L to 0.1mg/L and Zn from 0.4mg/L to 0.5mg/L. Trace-metals not detected were Na, in Igarape of Fortaleza and Mg and in the Canal of Jandiá. The ion K had no variation in measurements in Igarape of Fortaleza.
Conclusion: The metals Pb and Zn exceeded the reference values of CONAMA nº344/2004 resolution, which undertake plants and sediments. For the other elements the concentrations were found within recommended limit. However, they require special attentions since the concentration of the metals at some points are close recommended limits.

Keywords: Sediments; macrophytes; trace-metals; spectrophotometry.

1. INTRODUCTION

The ionic composition in surface and deep waters is a consequence of hydrological, mineralogical, rainfall and anthropogenic effects of a region in an integrated manner. Unpolluted waters should presumably reflect the concentrations of trace-elements of rocks and soils [1]. The accumulation of sediments (metals and other components), in aquatic ecosystems, depending on environmental conditions, can be dissolved in water and become bioavailable. From these conditions, aquatic biota may be affected, resulting in bioaccumulation of these sediments along the food chain and can reach the human being, affecting their health [2,3].

In order to understand the bioavailability of metals in an aquatic ecosystem, materials plant origin and sediments close water supply areas should be quantified, especially when released into the water body, where metals are adsorbed by organic or inorganic particles, and are incorporated into the soil by process of sedimentation, resulting in high levels of metals in these locations. Therefore, the analysis of sediments is very importance to assess the intensity of pollution in aquatic ecosystems [4]. The metals present in the sediment should consider the concentration in aquatic plants and vegetation around water supply areas to be studied. Thus, there is a complete characterization of the study site. The macrophytes are considered important components of the aquatic ecosystem, not only as a food source for animals, but also as an accumulator of heavy metals, may act as efficient biological filters by the fact of concentrating a large amount of substances, as heavy metals, which are considered as indicators of environmental pollution [2,5].

Samuel [6] conducted studies of metals (Zn, Fe, Pb, Cu, Mn, Cr, Na, Mg, Ca and K) in water samples, sediments and fish from the dam Itapaji, southwestern Nigeria, in two seasons (dry and rainy), during two years. The metals were determined using standard analytical methods. The concentrations of metals in sediment samples were higher than those of fish samples, while the concentrations of fish samples were higher than that of water samples. Fagbote and Olanipekun [7] determined the concentrations of heavy metals in water (surface and groundwater) and in aquatic macrophyte (*Ceratophyllum demersum*), in the area of deposit of bitumen Agbabu, Nigeria. In the period from 2008 to 2009, have made the sampling during the dry and rainy seasons, and compared the values with standard recommendations.

The study was aimed at quantifying the trace-metals (Na, K, Mg, Ca, Pb and Zn) present in sediments and plants of the *Cenchrus echinatus* L. species on Canal of Jandiá and Igarape of Fortaleza in the Municipality of Macapa-AP, it also involves comparing the results with the values established by Resolution of the National Environmental Council/Brazil (CONAMA n°344/2004) that establishes general guidelines and minimum procedures for the evaluation of material to be dredged in Brazilian territorial water [8].

2. MATERIALS AND METHODS

2.1 Location of the Study Area and Data Collection

The study was carried out in two different locations, one located at the Canal of Jandia in the Northern zone of the municipality of Macapa-AP, which was opened in order to serve as a drain water of hangover that were dammed [9], and the other located in Igarape of Fortaleza in the South Zone of the municipality of Macapa-AP, west of the municipality of Santana-AP See Fig. 1.

The sediment samples were collected (0.3kg) at 5 points of the Canal of Jandiá and Igarape of Fortaleza, totaling 10 sampling points, where each point contained a distance of 200m between them, which was determined with the aid of equipment Garmin GPS model, which indicated the altitude, longitude and terrain elevation see Fig. 2. The sediments were collected with the aid of collector Polyvinyl Chloride (PVC) tube, and then the material was removed and placed in polyethylene pots previously sterilized.

Plant samples of *Cenchrus echinatus* L. species (0.2kg) were collected to determine the concentration of trace-metals (Na, K, Mg, Ca, Pb and Zn). The collections of plants were performed with use of gardening supplies, and thereafter stored. Then, the materials collected were transported to the laboratories of Atomic Absorption and Bioprospecting (LAAB) and General and Analytical Chemistry of the Federal University of Amapá. The collection period covered of month of January to October 2011. Plant samples were subjected to calcination process (550°C) and slow filtration (filter paper blue band), and analysis of metal-traces were performed in an atomic absorption spectrophotometer model 6300 Shimadzu AAS.

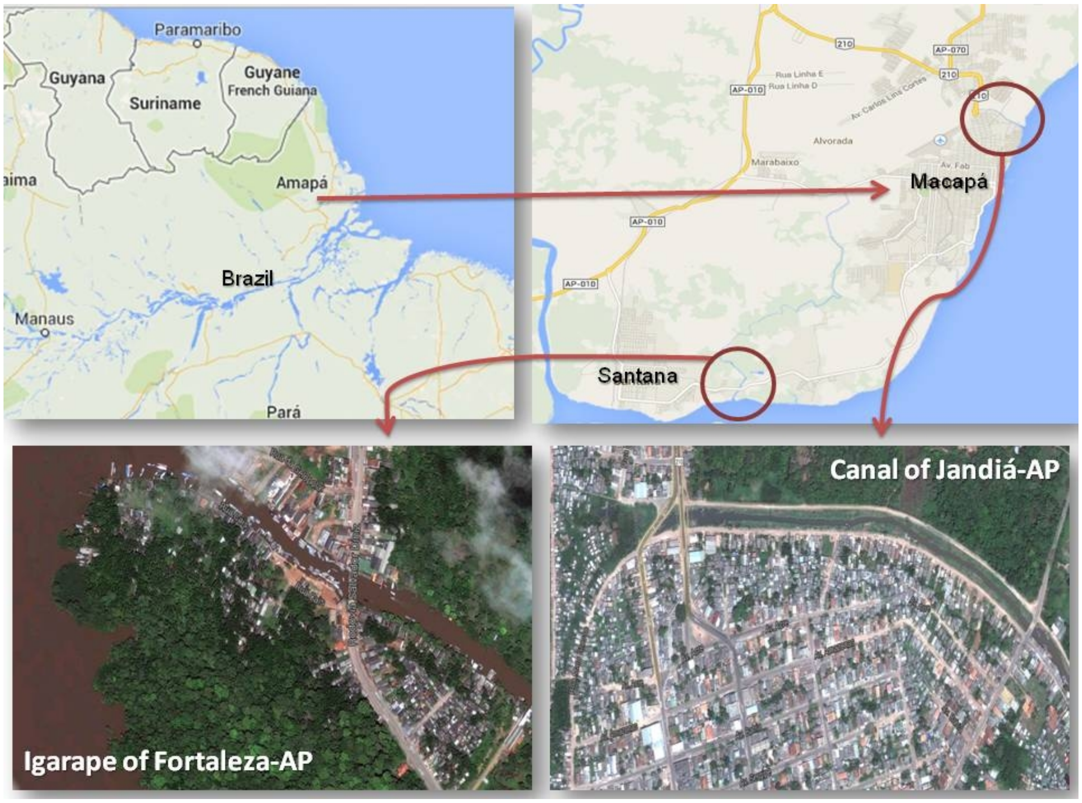

Fig. 1. Satellite image of Canal of Jandiá, Macapa-AP; Image of the Igarape of Fortaleza-AP
Source: Google, 2014

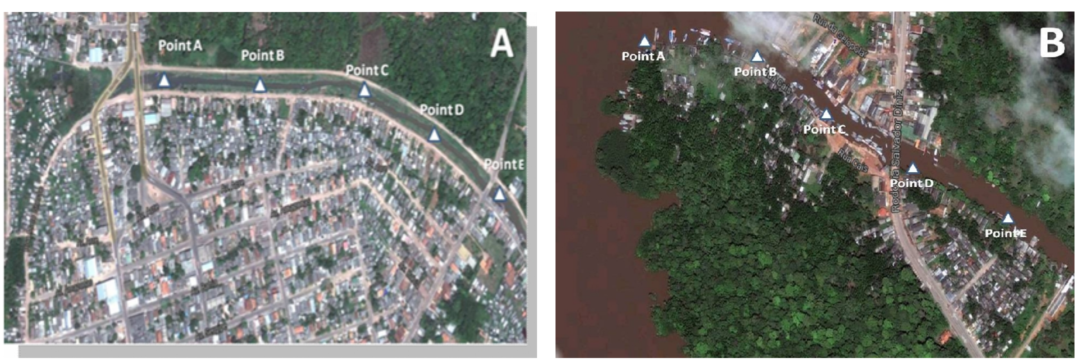

Fig. 2. Satellite image of the collection points - (A) Canal of Jandiá, Macapa-AP, (B) Igarape of Fortaleza-AP
Source: Google, 2014

2.2 Determination of Trace-metals in Sediments Samples

The sediments were air dried for 48 hours, and then were sieved, and the weight determined on an analytical balance. The samples were sent to Empresa Brasileira de Pesquisa Agropecuária (EMBRAPA-AP) for the digestion, and then was returned to LAAB to be submitted to chemical analysis using the technique of atomic absorption spectrophotometry.

2.3 Determination of Trace-metals in Plant Samples

Plant samples were washed and disposed on filter paper to dry, and then the samples were triturated to a calcination procedure of vegetal material. The calcinations were carried out in the following manner:

1) The sample was placed in a porcelain capsule triturated, in which the material was flamed and taken the muffle with a temperature of 550ºC for 6 hours.
2) Prepared a solution of HCl (1mol/L) was added 20ml of this solution into each sample and then filtered and subsequently transferred to 100ml volumetric flask.
3) The analyzes of the material collected filtrate for determination of trace-metals were performed with the aid of atomic absorption spectrophotometer AAS-Model-6300 Shimadzu.

2.4 Statistical Analysis

The data are presented as mean±(SE). The Statistical analysis was performed using the free software R 3.02 (R Core Team, 2013). The statistical significance was calculated using a two-tailed Student t test and Mann-Whitney U test with 95% confidence interval.

3. RESULTS AND DISCUSSION

3.1 Determination of Trace-metals in Sediments

In Table 1 are shown the variation of the total extracted contents to metals (Na, K, Mg, Ca, Pb and Zn) in the sediments on Canal of Jandiá and Igarape of Fortaleza. In Canal of Jandiá, the values of Na ranged from 0.0 to 9.4mg/L, Ca from 5.3mg/L to 18.4mg/L, Pb from 0.4mg/L to 1.6mg/L and Zn from 1.6mg/L to 2.7mg/L. In Igarape of Fortaleza, the values of K ranged from 0.2mg/L to 6.1mg/L, Ca from 5.5mg/L to 18.1mg/L, Mg from 1.4mg/L to 1.6mg/L, Pb from 0.13mg/L to 4.2mg/L and Zn from 1.3mg/L to 2.1mg/L. Trace-metals not detected were Na, in Igarape of Fortaleza, and K, in Canal of Jandiá. The Mg had the lowest standard deviation for the metals found in Igarape of Fortaleza (±0.05) and in Canal of Jandiá (±0.01). Furthermore, the mean values of Mg were close, being 1.43mg/L in Igarape of Fortaleza and 1.4mg/L in Canal of Jandiá. The highest standard deviation was observed for the Ca, being (±1.4) for Igarape of Fortaleza and (±2.2) in Canal of Jandiá. Still on Table 1, the results for Pb and Zn are considered toxic to the environment with values above the recommended by CONAMA Resolution nº344/04, affirming that having contamination by these metals in sediments.

In accordance with McBride [10], Pb is considered one of the metals less mobile in the soil and can be complexed by the organic matter, into oxides and silicate minerals and precipitated as carbonate, hydroxide or phosphate in conditions of high pH values. The normal range of concentrations in sediments and plants for zinc is 10 to 300µg Zn/g and 15 to 200mg Zn/g, respectively [11,12]. Also Singh and Steinnes (1995) typical of this metal contamination in soil are found in the range of 10 to 300mg Zn/kg [13].

It is noted that the Mg and Pb showed high values for Igarape of Fortaleza ($p<0.05$), whereas Zn presented greater values to Canal of Jandiá ($p<0.05$). The Point A of Igarape of Fortaleza is located in the margins of Amazon River, and nearby this point are located navigations of boats, where constant leaking engine oil of the boats occurs, which affects the large quantity of Pb and Zn liberated to the environment, and therefore contaminating the sediments. Already in the Canal of Jandiá, the point D showed a higher concentration of Zn, this being located in a impacted by disordered urban occupation area, which is littered with disposed metallic scrap, batteries, in addition to the contribution of sewage released on Canal by the very people around, and in other regions.

In order to obtain comparative data, it is necessary to establish a reference value. However the reference value indicates the concentration of a substance that the soil naturally would present in areas not impacted anthropogenically. These objective values primarily serve as a basis for judgment about the quality of the soil. Furthermore, the reference value aids in the establishment of maximum permissible values [8,14].

Table 1. Variation in concentration of metals in sediments for the Igarape of Fortaleza and Canal of Jandiá

Metals	Canal of Jandiá		Igarape of Fortaleza		Reference values [8]
	Mean±SD	Range	Mean±SD	Range	
Na^{NA}	2.9±1.9	0-9.4	NA	NA	ND▲
K*	NA	NA	0.22±1.1	0.2-6.1	ND▲
Ca*	15.3±2.2	5.3-18.4	9.8±1.4	5.5-18.1	ND▲
Mg^{ns}	1.4±0.01	1.3-1.4	1.43±0.05	1.4-1.6	0.1mg/L
Pb^{ns}	0.8±0.2	0.4-1.6	1.07±0.7	0.13-4.2	0.01mg/l
Zn**	2.3±0.2	1.6-2.7	1.4±0.1	1.3-2.1	0.18 mg/L

*ns=Non significant, * =Significant at 0.05, ** =Significant at 0.01, NA not applicable.▲ND Non determined by CONAMA nº344/2004*

3.2 Determination of trace-metals (Na, K, Mg, Ca, Pb and Zn) in plants of *Cenchrus echinatus L.* species

Table 2 shows the determined values of the mean, standard deviation and parameters of CONAMA Resolution nº344/04 for the plant *Cenchrus echinatus* L. species. The results obtained on Canal of Jandiá showed that the measured values of Na ranged from 0.0 to 9.4mg/L, Ca from 5.9mg/L to 1.1mg/L, Pb from 0.4mg/L to 1.6mg/L and Zn from 0.2mg/L to 2.07mg/L. In Igarape of Fortaleza, the trace-metal of Ca ranged from 8.07mg/L to 26.2mg/L, Mg from 1.3mg/L to 1.4mg/L, Pb from 0.06mg/L to 0.1mg/L and Zn from 0.4mg/L to 0.5mg/L. Trace-metals not detected were Na in Igarape of Fortaleza and Mg in Canal of Jandiá. The K metal had no variation in measurements in Igarape of Fortaleza. The values of standard deviation (±0.01) of the Mg metal were the same in both study areas, with of the mean values in Igarape of Fortaleza (1.34mg/L) and Canal of Jandiá (1.3mg/L). The Ca had the highest values of standard deviation, being ±9.1 in Igarape of Fortaleza and ±3.5 on Canal of Jandiá ($p<0.05$). It is observed that the absorption of Ca and Mg by plants in Igarape of Fortaleza and Canal of Jandiá are within of limits described, being calcium and magnesium elements realty in phloem, and disarrangements are due to their deficiency that may be located, and in root which is the organ most severely affected [15].

In Table 2, the content of Pb and K in the samples of plants in Canal of Jandiá and Igarape of Fortaleza showed relatively high values. The Pb is found in replacing the K silicates or carbonates, replacing Ca, because it presents similar to the group of alkaline earth metals chemical characteristics, which determines ability to move such elements. This implies environmental impact that is being caused by the surrounding population, without ceasing to emphasizing that the area of Igarape of Fortaleza is a port area and of Canal of Jandiá is a housing area, where residents themselves contaminate their environment, favoring the absorption of these elements by plants [16].

Plants collected on Canal of Jandiá and Igarape of Fortaleza were classified with an average potential of concentration of Pb and Zn in their structures (roots and leaves), this indicates that this vegetation is susceptible to absorption of these elements. Highlight the *Cenchrus echinatus* which showed susceptibility to absorption of Pb and Zn in the areas studied.

Many chemical elements may present a threat to the balance of the food chain. Therefore, it is necessary to assess their contents available and investigate whether this occurring plant absorption. Thus, knowledge of the total elemental composition of metals in soil has little relevance in itself, so it is of fundamental importance for purposes of comparisons in studies of environmental contamination [17,18].

Table 2. Variation in concentration of metals in plants for the Canal of Jandiá and Igarape of Fortaleza

Metals	Canal of Jandiá		Igarape of Fortaleza		Reference values [8]
	Mean±SD	Range	Mean±SD	Range	
Na^{NA}	2.9±1.9	0-9.4	NA	NA	ND▲
K^{NA}	NA	NA	1.7	NA	ND▲
Ca*	9.5±3.5	5.9-1.1	17.2±9.1	8.07-26.2	ND▲
Mg^{ns}	1.3±0.01	1.3-1.4	1.34±0.01	1.3-1.4	0.1mg/L
Pb*	0.02±0.05	0.4-1.6	0.08±0.02	0.06-0.1	0.01mg/L
Zn*	1.1±0.9	0.2-2.07	1.4±0.03	0.4-0.5	0.18 mg/L

*ns=Non significant, * =Significant at 0.05, NA not applicable. ▲ND Non determined by CONAMA nº344/2004*

In soil, heavy metals often accumulate in the upper layer, which may thus become more accessible to microorganisms and plant roots [19,20]. Isen, Altundag and Keskin (2013) performed studies of concentration of heavy metals in roadside surface soil samples from D-100 highway in Sakarya, Turkey. In this study, the heavy metals (Ba, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Sr, V, and Zn) were determined for Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) in 24 soil samples and the analytical results were validated comparing with BCR-701 certified reference material [21-colocar referência]. Altundağ, Dündar and Keskin (2013) have conducted studies about trace metal (Cd, Co, Cr, Cu, Mn, Ni, Pb, Fe and Zn) levels in vehicle air and pollen filter dusts by the BCR extraction procedure, and the results obtained for recovery of all the elements were found in the range 95.4-101.3%, which are in agreement with data reported in the literature [22].

Some heavy metals, such as Pb element has no biological function, since other metals such as K and Zn are essential micronutrient for living beings. Although required in small amounts they are fundamental in the performance of various functions, but an excess these micronutrients may be toxic [10,23,24]. Thus, when arranged in the soil such residues may increase the concentration of these nutrients favoring plant development. Although total heavy metal analysis provides evidence of possible environmental contamination, knowledge of the concentration of free elements and their forms in soil solution are important for estimating its mobility and phytoavailability in the environment, since it is known that metal absorption by plants and the toxicity of these show great dependence with relationship the chemical species of the metal in solution and that responses correlate better with the concentration or activity of the free ion in solution.

4. CONCLUSION

The Mg, Pb and Zn metals exceeded the reference values recommended by CONAMA Resolution nº344/2004 [8], and these are undertake plants and sediments. The metals concentration levels require special attention at analyzed points. The availability of these elements considered toxic in sediments is a direct result of residues pollutants caused by the surrounding population, since there is a great deficiency in basic sanitation in these areas. Thus, the sediment Canal of Jandiá and Igarape of Fortaleza is a source of pollution to the river Amazon-Brazil, since these flows into this river. The heavy metal content of the sediment is transported by rain water, and this study shows that the contamination by heavy metals from sediment Canal of Jandiá and Igarape of Fortaleza can be dangerous for the Amazon River-Brazil.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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