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MANGROVE LEAVES (*RHIZOPHORA MANGLE*) AS ENVIRONMENTAL CONTAMINATION BIOMONITORS.

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ABSTRACT

Sometimes, plants growing in contaminated sediments by trace metals can not avoid absorption of these metals, but only to limit its translocation, so that the accumulated metals in their tissues will have different levels of concentrations. Some trace metals (copper, zinc, manganese, among others) are essential for plants, although they are toxic at high concentrations, damaging its growth, production or quality. The aim of this work from is to verify the presence of metals such as copper, manganese and iron in mangrove leaves (*Rhizophora mangle*) collected in some beaches of the Northeast of Brazil (such as: Maceió, São José da Coroa Grande, Japaratinga, Croa do Goré, Ponta das Pedras). Leaves' metals content (extracted by adding acids) were determined by a fast sequential atomic absorption spectrometer (SpectrAA-220FS/VARIAN). The results showed that there are more Fe and Mn in mangrove leaves than in other metals comparing with all study areas (Fe > Mn > Co > Zn > Cu).

1. INTRODUCTION

Mangroves are vital for maintaining the population of fish, molluscs, crustaceans and other species, hence their importance as a source of pollutants when exposed to uptake of soluble metals in polluted waters [1]. Results of effective pollution can be determined in living organisms and one of the most suitable organisms for this purpose are plants. [2].

Geological characteristics of the area, hydrochemical parameters and anthropogenic contamination influence the concentrations of heavy metals in water and its accumulation in plants. In addition, factors such as light, oxygen content, temperature, nutrients, among others, can influence the accumulation of metals in young plants, resulting in large fluctuations of results [3]. Plants growing in sediments contaminated by trace metals cannot avoid absorption of these metals, but only confine their translocations, so that the accumulated metals in their tissues will have different levels of concentrations [4, 5].

The survival strategy of plants growing in contaminated soils is based on its ability to tolerate and not to annul the toxicity of metal [4, 6]. Tolerant species generally accumulate higher concentrations of trace metals in roots relating to the aerial parts of plants [7- 9]. Tolerant plants differ in their absorption characteristics, and may vary from each species and metal, and may be considered: as accumulators, excluders or indicators [4]. The excluders do not regulate the absorption of metals, but merely transport it from the root to the leaf. In excluders species, root uptake and transport are more or less balanced, and metals can be accumulated in the roots or may retain extremely high levels of metals without suffering adverse consequences.

There are cases where plants have more than 100mg/kg of Cd and 1000mg/kg of Ni and Cu or Zn and Mn of dry matter when growing in sediment rich in metals, being called hyperaccumulators [10, 11]. It also can occur metal nutrients transfer from senescent leaves to mature leaves, in order to be reused, and there is transference of trace metals from mature leaves to senescent leaves, so that they can be eliminated.

Some trace metals (copper, zinc, manganese, among others) are essential to plants, although they are toxic at high concentrations. The critical level of metals in the leaves is the one that decreases the growth, production and/or quality. [12]. The determination of the critical levels if the plants elements is not performed only to the essential elements for some kinds of species, because plants roots do not seem to have a mechanism skilled enough to avoid the absorption of non-essential elements, which can also be absorbed in excess, being accumulated in high concentrations. The critical level of toxicity can be determined as the concentration of the nutrient that reduces 10% of the plant production [13]. The determination of toxic levels are mainly related to changes in sediments characteristics, indicating the need for further studies.

Copper is required for chlorophyll formation, catalyzes various processes in plant metabolism and is necessary to promote several reactions, large amounts of copper may be toxic, because the excess of copper decreases the activity of iron and causes deficiency symptoms such as: yellowing of leaves (chlorosis) due to non-translocation in the plant. Metals such as iron, manganese and aluminum affect the availability of copper for plant growth. Zinc helps the substances that act on the growth and in the enzyme systems, and it is essential for the activation of certain metabolic reactions that are required for the production of chlorophyll and carbohydrates formation. Zinc is not translocated within the plant, therefore the deficiency symptoms first appear in the leaves and are characterized by: shortening the leaves and other plant parts in some species [14].

It was not shown that cobalt is essential for the growth of higher plants, but bacteria associated with vegetables require this nutrient for atmospheric nitrogen fixation. Molybdenum is necessary for the formation of the enzyme nitrate reductase, which reduces the ammonium nitrate in most plant species. Molybdenum is also essential to convert inorganic phosphorus into organic forms [14].

Manganese acts mainly as part of the enzymatic system in plants, activates several important metabolic reactions, has a direct effect on photosynthesis helping in the synthesis of chlorophyll, accelerates germination and maturity and increases the availability of phosphorus and calcium. Its deficiency symptoms appear, first, in young leaves, with yellowing between the veins; these deficiencies are often associated with high pH. They also occur as a result of an imbalance with other nutrients, such as calcium, magnesium and iron. An extremely acid pH can cause toxicity of manganese, aluminum and iron to the cultures.

In an estuary, the free connection with the open sea is a continuous mixture between the rivers and the sea. The estuary is considered a transition region between the fresh and salty water. When the rivers leach the soil leading to the estuarine environment, materials required by plant, dilution of seawater, it becomes beneficial. This dilution becomes hazardous when the water contains the waste from domestic and industrial sewage [15, 16].

The atmosphere in the presence of trace metals contributes to contamination of the aquatic environment due to rain precipitation. Studies indicate that it is the main contributor to the presence of these metals in the waters of the open sea [17, 18]. In estuaries , the concentration of trace metals is higher than in the sea, because all these phenomena (soil erosion, water currents, and atmospheric "input") influence the increase of these elements.

The input of nutrient salts in the vegetation is controlled through the root system, which has at its roots, adaptations and osmorregulators structures, allowing withstand variations in salinity of the medium thus avoiding excessive sweating [19].

The determination of metallic trace elements in plants is carried out because they act as a bioindicator (part of an organism or community of organisms that contain information about the quality of the environment) and this is already well established [3, 20]. Excess concentrations of heavy metals such as cadmium, copper, zinc, lead or mercury are relevant for being environmental pollutants that induce physiological changes in plants. These changes include growth retardation, damage to the membrane and changes in enzyme activity or induce oxidative stress.

The aim of this work is to verify the presence of metals such as copper, manganese and iron in mangrove leaves collected in some beaches of the Northeast of Brazil (such as: Maceió, São José da Coroa Grande, Japaratinga, Croa do Goré, Ponta das Pedras).

2. METHODS

A number of 20 leaves per branch were collected in 5 branches of five plants, the mean height of trees within a radius of 50m for each species present in the mangrove, so that there is a representative sample [2]. The leaves were selected in an intermediate size (mature, and not so new or senescent) for Red Mangrove (*Rhizophora mangle*). Sterile plastic bags were used to transport the samples to the laboratory. The leaf samples are washed in ultrapure water several times, dried in an oven at a temperature of 50^{o}C and then ground in a porcelain mortar, and then separated by thin granulometry series of sieves to obtain particles smaller than 0.065 mm in which, then, retained the heavy metal substrates in this study. A method used to digestion was to take 0.1 g of the sample in the presence of 10 ml of water, 5 ml of nitric acid and 4 ml of hydrofluoric acid and 1 mL of hydrochloric acid. After digestion, the samples were transferred to a flask and 50 mL. An atomic absorption spectrophotometer (AAS) was used to determine the contents of the elements in the samples [23].

3. RESULTS

The results of mangrove leaves obtained are shown in the Table 1. The quality control of analytical results were evaluated by analyzing certified reference material and these results are presented in Table 2.

Table 1. Results for trace elements in Mangrove leaves, *Rhizophora mangle*.

Elements (mg/kg)	Japaratinga	Maceió	S. J. da Coroa Grande	Ponta das Pedras	Croa do Goré
Cu	0.092 ± 0.002	0.112 ± 0.0004	0.077 ± 0.014	0.190 ± 0.002	0.106 ± 0.011
Mn	0.466 ± 0.016	0.702 ± 0.0001	0.394 ± 0.006	0.294 ± 0.002	0.678 ± 0.004
Co	0.416 ± 0.020	0.611 ± 0.0045	0.631 ± 0.028	0.577 ± 0.021	0.623 ± 0.009
Zn	0.265 ± 0.024	0.186 ± 0.0095	0.231 ± 0.013	1.32 ± 0.002	0.302 ± 0.008
Fe	1.80 ± 0.190	2.12 ± 0.0001	2.13 ± 0.189	7.80 ± 0.0001	8.80 ± 0.0001

Table 2. Results obtained in the certified reference material (*Seaweed fucus sp*)

Elements	Confidence interval	Recommended Value (mg/kg)	Results obtained (mg/kg)	Error (%)
Fe	1221 - 1291	1256	1281.97	1.0
Mn	53.7 - 58.5	56.1	54.47	2.8
Cu	4.77 – 5.33	5.05	4.98	2.2
Co	0.766 – 1.01	0.876	1.00	3.0

4. DISCUSSION

Only in Ponta das Pedras (Alagoas) and Croa do Goré (Aracaju) beaches the highest foliar Values for Fe were higher than on the others beaches. A value that differs from the others was also the value found for Zn in evaluated samples from the Ponta das Pedras (Alagoas). However in general amounts of macronutrients and micronutrients found in mangrove leaves do not show huge differences between the beaches studied.

According to the work done by Fruehauf [24] the average values in *Rhizophora* sheets, to Zn was 5.09 mg/kg and to Cu was 2.10 mg/kg, in the estuaries of Santos and São Vicente (composed by the Canal Cosipa (a channel), Rios Mariana and Cascalho (both rivers). The region of the estuaries of Santos and São Vicente is a region highly affected by ports and industries that contribute to high air pollution. It is observed that the values obtained in this work for Brazil's northeastern beaches are smaller than these.

Other studies show much higher values for Fe and Mn in mangrove leaves than the values obtained in this work. According to Lacerda et al. [25], there is some variability in Fe and Mn content in different mangroves. Lacerda [26] said that the absorption of Fe and Mn is governed by its concentration in the sediment, as these elements are sensitive for redox conditions and in such an anoxic conditions environment they remain in dissolved form thereby facilitating plant uptake. Lacerda et al. [25] has observed correlations between the concentration of these two metals in the leaves and in the soil to the different species (and the lower Fe content in *R. mangle*) does not seem to reflect differences in the concentration of metal in sediments where each specie is dominant; this difference can be associated with the salts exclusion mechanism that *R. mangle* show that could affect the metal uptake and reduce absorption by plant roots [25]. Lacerda et al. [27] studied the distribution of trace metals (among which Fe and Mn) in the rhizospheres of *Rhizophora* and *Avicennia* and their results suggested that higher concentrations of trace metals found in the leaves of *Avicennia* comparing with leaves of *Rhizophora* is resulting of the greater availability of these metals and absorption by the *Avicennia*. The authors concluded that less variations in chemical conditions in the sediment guarantee greater stability for complexed metals that precipitate in the rhizosphere, as found in *Rhizophora*, reducing the concentration of exchangeable forms of metals and their availability to plants.

For leaves of R. mangle studied by Ramos (2007) [28], in Rio Cubatão, Cu values were around 1.18 mg/kg and 4.57 mg Zn/kg; values higher than those found in this work. However, it is necessary to point out that in Rio Cubatao, there are landfill contribution, residential sewage, batteries and metallurgical foundry industry wastewater in the region.

The values of the metal content considered excessive or toxic (20 to 100 for Cu and 100 to 400 for Zn) [29] and those considered normal for vegetable (5 to 30 when analyzing Cu and 27 to 150 after the Zn analysis) however are much higher than the values shown in this work.

Mn values of 15-20 mg/kg in plant tissue results in a good development for the plant values found in plant tissue of other crops such as coffee and sugarcane; soy and orange have 100 mg/kg of Fe. The Mn values are under 1mg/kg in mangrove leaves studied in this work, while the Fe values do not exceed 9 mg/kg.

5. CONCLUSIONS

The adequacy of the results indicates that the proposed methodology can be used for leaves tissue analyses. We conclude that, at the moment, mangrove leaves of Brazilian northeastern beaches studied are without trace metals contamination.

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