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TRACE ELEMENTS DISTRIBUTION IN ENVIRONMENTAL COMPARTMENTS

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ABSTRACT

Trace elements term defines the presence of low concentrations metals at environment. Some of them are considered biologically essential, as Co, Cu and Mn. Others can cause detriment to environment and human health, as Pb, Cd, Hg, As, Ti and U. A large number of them have radioactive isotopes, implying the evaluation of risks for human health should be done considering the precepts of environmental radiological protection.

The ecosystem pollution with trace elements generates changes at the geochemistry cycle of these elements and in environmental quality. Soils have single characteristics when compared with another components of biosphere (air, water and biota), cause they introduce themselves not only as a drain towards contaminants, but also as natural buffer that control the transport of chemical elements and other substances for atmosphere, hydrosphere and biota.

The main purpose of environmental monitoring program is to evaluate the levels of contaminants in the various compartments of the environment: natural or anthropogenic, and to assess the contribution of a potential contaminant source on the environment. Elemental Composition for the collected samples was determined by inductively coupled plasma mass spectroscopy. The main objective of this work was to evaluate the map baseline of concentration of interest trace elements in environmental samples of water, sediment and soil from Environmental Monitoring Program of Instituto de Radioproteção e Dosimetria (IRD). The samples were analyzed using an inductively coupled plasma mass spectrometer (ICP-MS) at IRD. From the knowledge of trace elements concentrations, could be evaluated the environmental quality parameters at the studied ecosystems. The data allowed evaluating some relevant aspects of the study of trace elements in soil and aquatic systems, with emphasis at the distribution, concentration and identification of main anthropic sources of contamination at environment.

1. INTRODUCTION

The term trace elements have been used to define low concentrations of cationic metals and oxyanions present in soils, plants and natural waters, like less than 100 $mg.kg^{-1}$. Much of these elements are present at concentrations much lower than this (Hooda, 2010). Most of the important trace elements for human health and environment are metals as cadmium, chromium, cobalt, cooper, gold, lead, manganese, mercury, molybdenum, nickel, palladium, platinum, rhodium, silver, thallium, tin, vanadium and zinc. Some of them are biologically essentials but, in special conditions, they can cause negative impacts to terrestrial and aquatic ecosystems being contaminants or pollutants of soils and waters (L. R. G. Guilherme, 2005).

Elements such as uranium, lead and others have radioactive isotopes. This condition implies the necessity of do the hazard evaluation for human health under the radiological protection precepts. Thus, the risk to environment and health can be minimized by the expose reduction of these elements.

Studies on environmental pollution in a given local often need of reliable data from the natural level of trace elements. The natural background is determined by local composition of prevailing rock type in the soil. The distribution of trace elements in the environmental compartments is mainly controlled by weathering and mass transport. From soil, trace elements are transported for others environmental compartments. Aquatic systems pollution with trace elements induces some changes in geochemistry cycle. Also, soil pollution needs special attention. They have unique characteristics when compared with other components of biosphere (water, air and biota), acting as natural buffers and controlling the transit of chemical elements and other substances for atmosphere, hydrosphere and biota (Kabata-Pendias, 2001). The natural processes that contribute for the appearance of trace elements in aquatic systems are weathering of rocks and leaching on soil profile. Anthropogenic sources are responsible for addition of 1.16 million ton of metals by year in aquatic and terrestrial ecosystems. The main anthropogenic activities are mining, industries and municipal effluents generations (L. R. G. Guilherme, 2005).

Environmental monitoring programs (EMP) are common tools to control the state of pollution in specific areas, as well as to address possible remediation strategies. The EMP allows clarifying whether environmental pollutants are derived from anthropogenic activities or natural processes.

The main objective of this work was to estimate the baseline of concentration of interest trace elements in environmental samples of water and soil from Environmental Monitoring Program of Instituto de Radioproteção e Dosimetria (IRD). The samples were analyzed using an inductively coupled plasma mass spectrometer (ICP-MS) at IRD. Some parameters of environmental quality in the studied ecosystems were evaluated from the knowledge of the elementary concentrations. The data allowed understanding some relevant aspects of the study of trace elements in soil and aquatic systems, with emphasis on the distribution, concentration and identification of the main sources of contamination in the environment

1.1. Study Area

The Instituto de Radioproteção e Dosimetria - IRD from the Comissão Nacional de Energia Nuclear (CNEN), addresses national needs in assessing and analyzing public and workforce radiation dose and risk; developing and operating national security radiation emergency preparedness and consequence assessment; ensuring the quality and the traceability of radiation measurements and managing education programs to help supply scientists, engineers and technicians to meet future science and technology needs (IRD, 2017).
It´s situated at Barra da Tijuca area in the state of Rio de Janeiro, Brazil. It is located near from Jacarepaguá Lagoon in the City of Rio de Janeiro,

Figure 1: Localization of IRD

The IRD laboratories produce small quantities of chemical and radioactive wastes. In order to preventing or minimizing the generation of hazardous wastes, the wastes are managed. The strategy for managing waste practiced by IRD aims to maximize safety and minimize environmental impact. That way, sanitary wastewater produced at IRD is sent to the Sewage Treatment Unit where is undergoes biological treatment before it is discharged to the environment. Evaluations of chemical, radiological and biological contents are done.

The radioactive waste generated in the laboratory activities are collected, processed and stored in the small facility waiting the construction of a national repository for disposal of radioactive waste. After collection and preliminary treatment, others hazardous wastes are sent to a company contracted which is licensed by the competent environmental agency for purpose of transportation, recycle, treat, store or dispose of the waste. Discharges liquid effluents into the environment are small to ensure that environmental impact and public exposure is minimized.

1.2. Radiological Environmental Monitoring Program (REMP)

Since 2002 the Institute has maintained a radiological environmental monitoring program (REMP), as integrating part of the environmental radiologic control applied. The monitoring program was then designed considering the following main objectives (Melo, Rochedo, Souza, Ferreira, & Peres, 2005):

- to assessment of the adequacy of controls on the release of radioactive effluents to the environment;
- to verify the compliance the operation of the Institute with the applicable national regulatory requirements and standards;
- to determine trends and to evaluate how the environment and public are affected by the Institute activities;
- to identify potential environmental problems and evaluate the need for remediation actions or measures to mitigate the problems.

The REMP includes collect and analyses of soil, sediment, surface and ground water, vegetation samples. The gamma radiation levels near to the IRD facilities and neighboring environment are determined using thermoluminescent dosimeter.

Besides the radiochemical analyzes and gamma spectrometry, the concentrations of a number of trace elements were analyzed in soil, sediment and surface e ground water samples collected. The main results obtained by the program up to now, no environmental and non-radiological and radiological impact could be observed (Melo, Rochedo, Souza, Ferreira, & Peres, 2005).

An environmental monitoring program is an important item of a correct operation of any plant, housing or commercial unit. It can lead to good practices in order to identify environmental impacts.

1.3. Jacarepaguá Lagoon and IRD location

The Lagoon Complex of Jacarepaguá is a piece of Baixada de Jacarepaguá hydrographic basin. It presents a brackish water mirror of around 11.2 km^2, within 13 km extension approximately, and a soil composition of quartz sand, fine and medium, covered by eolian deposits. To the west is located the Jacarepaguá Lagoon, object of this study. The water of these lagoons is connected with the sea by the Joatinga channel, like figure 1. The main sub-basins responsible for sewage charging in the lagoon are Zona dos Canais, Camorim and Caçambé River, Guerenguê River and Passarinhos River, constituted by about 39 rivers in more than 100km^2.

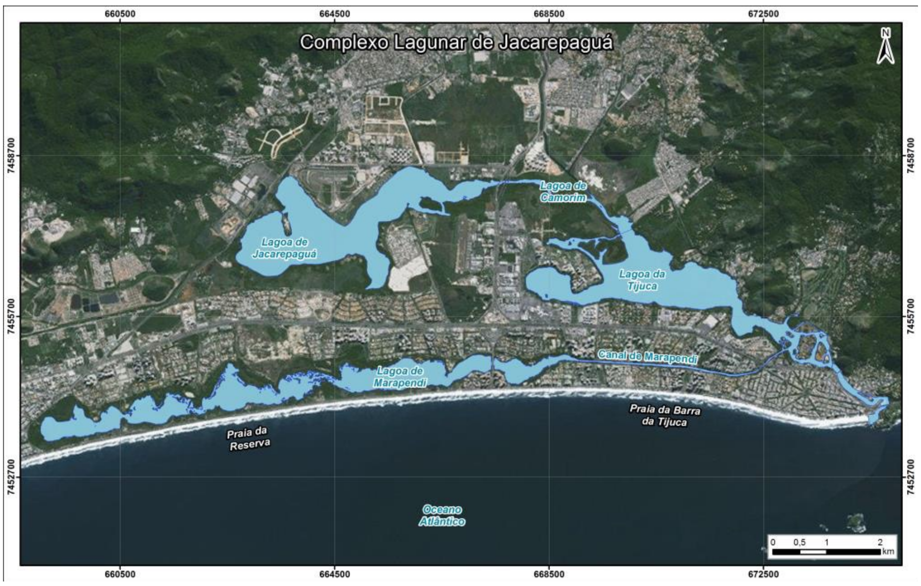

Figure 2: The Lagoon Complex of Jacarepaguá

1.4. The importance of this study

The hydrographic basin as a whole suffered during decades with messy occupation and discharge of sewage *in natura* in its lagoons and riverbeds, compromising the water quality. The majority of these discharges are from residences and some adjacent industries

(Masterplan, 2015). The neighborhoods of Barra da Tijuca, Recreio dos Bandeirantes, Camorim, Itanhanga and Jacarepaguá influence the lagoon directly.

Environmental laws and technical regulations were created to control the negative impacts due to the area development, such as:

- Among other regulations, the National Commission of Nuclear Energy requires compliance with the Standard 3.01/2011 " Basic Guidelines for Radiological Protection" (CNEN, 2014) and with the Standard 6.02/2014 "Licensing, Radioactive Installation" (Comissão Nacional de Energia Nuclear, 2014), both require an Environmental Radiological Monitoring Program, .
- The Resolution Nº 357/2005 from Conselho Nacional do Meio Ambiente (CONAMA) classifies the water bodies and gives the environmental guidelines for the classification. Furthermore, all commercial, industrial or housing units need to fulfill environmental rules (CONAMA, 2005). The Resolution nº 430/2011, from Conselho Nacional do Meio Ambiente (CONAMA), provides conditions and standards for liquid effluents in all the national territory (CONAMA, 2011). For soils, the resolution CONAMA 420/2009 stablishes criteria and guiding values for their quality (CONAMA, 2009).
- The Technical Regulation NT-202.R-10/1986 stablishes criteria and standards for liquid effluent discharges as integrant part of the System of Polluting Activities Licensing – SLAP in Rio de Janeiro (INEA, 1986).

2. METHODS

As case study it will be considered only surface and ground waters, sediment and soil samples. The samples of surface water and sediment were taken in Jacarepaguá Lagoon, to demonstrate that IRD facilities does not affect aquatic environment. Groundwater and soil samples were taken at the limits of IRD in order to observe if liquid discharges are affecting the quality standards of groundwater and soil (Peres, Reis, & Ribeiro, 2013).

Five sampling points were chosen from the REMP of IRD as showed in Table 1. The samplings were done once each six months, in 2013 and 2014 years for waters and in 2013 for soil and sediment.

Table 1: Collection points of REMP.

Point Number	Type of Sample	Location
1	Underground water	Property area of IRD
2	Underground water	Property area of IRD
3	Soil	Property area of IRD
4	Superficial water	Jacarepaguá Lagoon
5	Sediment	Jacarepaguá Lagoon

The filtered water sample in 0.45µm filter membrane was then immediately acidified to pH less than 2, using concentrated HNO_3, for better conservation. The samples of soil and sediment were dried, macerated, sifted and homogenized. After this step, an aliquot was passed thought a wet decomposition using microwave and concentrated HNO_3, H_2O_2 and HF as reagent mixture.

All samples were diluted with ultra-purified water, according the necessities, in order to obtain representative and repeatable results. After that, the concentrations of trace elements of interest were measured using an ICP-MS Perkin Elmer, Elan 6000 model, showed in Figure 3. Calibration curves were prepared using Perkin Elmer Mix Standards, at concentrations from 0.001 $\mu g.L^{-1}$ to 0.02 $\mu g.L^{-1}$ in HNO_3 2%, with addition of internal standards, including blank. As inner standard, was used In/Tl 0.02 $\mu g.L^{-1}$ mixture, to improve the intensity resolutions and provides any correction in the measures if necessary.

In this study, it will be presented the results for Arsenic (As), Cadmium (Cd), Chromium (Cr), Copper (Cu), Lead (Pb), Manganese (Mn), Nickel (Ni), Thorium (Th), Uranium (U) and Zinc (Zn), because they represent toxic potentials for human health.

Figure 3: ICP-MS Elan 6000 model, Perkin Elmer, used for the analysis

3. RESULTS AND DISCUSSION

Figure 4 shows the trace elements concentrations for underground water samples collected at Point 1 of REMP of IRD. Samples collected in April of 2013 presented Mn concentrations of 146 $\mu g.L^{-1}$. Although this value is above of other concentration values founded for further elements, it is under investigation level of 400 $\mu g.L^{-1}$ determined in CONAMA 420/2009 Resolution. However, according the pretended use, the underground water may be used in irrigation activities, seeing that the concentration value for Mn is under the Maximum Allowed Value (MAV) of 200 $\mu g.L^{-1}$ stablished in CONAMA 369/2008 Resolution (2008). Other kinds of use are unappropriated, because they exceed the MAV for human consumption (100 $\mu g.L^{-1}$), recreation (100 $\mu g.L^{-1}$) and animal watering (50 $\mu g.L^{-1}$). It is worth mentioning that, according CONAMA 369/2008 Resolution, in this concentration of 146 $\mu g.L^{-1}$, if used for human consumption, the Mn could be cause just organoleptic effects, changing the water flavor. For the other analyzed trace elements, the concentrations are below the standard values. The CONAMA Resolutions do not stablish standards for Thorium and Uranium concentrations. These concentrations must be obtained from the environmental radiological impact assessment and in accordance to authorized levels for the release of liquid radioactive effluents into the environment.

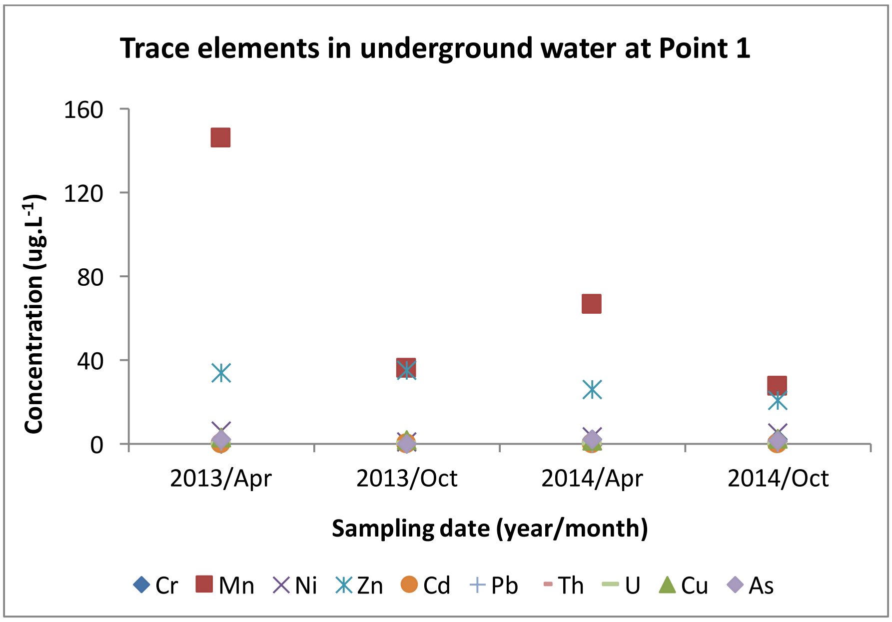

Figure 4: Trace element concentrations in underground water, collected at point 1 (inside IRD)

For underground water samples collected at Point 2 (Figure 5), all concentration values of analyzed trace elements were maintained below the stablished values of CONAMA Resolutions nº 420/2009 and nº 369/2008. Thus, there are no restrictions for the use of this water as human consumption, irrigation and recreation. However, there is a restriction for using as animal watering, because the Mn concentration founded was 54 $\mu g.L^{-1}$, a lightly superior to the MAV of 50 $\mu g.L^{-1}$. Though, for an accurate classification and evaluation, the analysis of other parameters is necessary.

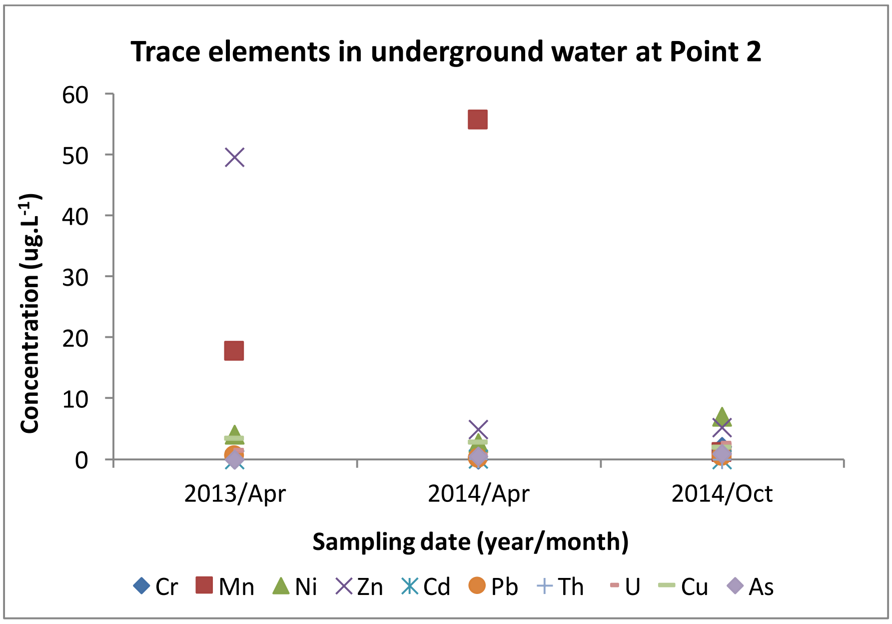

Figure 5: Trace element concentrations in underground water, collected in point 2 (inside IRD).

As presented in Figure 6, the analysis of soil collected at Point 3 showed concentrations of 74.5 $mg.kg^{-1}$ of Cr and 43.7 $mg.kg^{-1}$ of Ni, for samples collected in Abril, 2013. It can be observed that Cr concentration is so close to Prevention Values (PV) of CONAMA Resolution nº 420/2009, 75 $mg.kg^{-1}$. For Ni, the concentration is above the PV, which is 30 $mg.kg^{-1}$. The Ni concentration in the soil above the prevention value is not related to eventual releases of IRD effluents. It is important to mention that the VP is the concentration of the limit value of determined substance in soil, such that it is capable to sustain its main functions, although don´t implies in potential risks, direct or indirect, to human health, considering an standardize exposition scene.

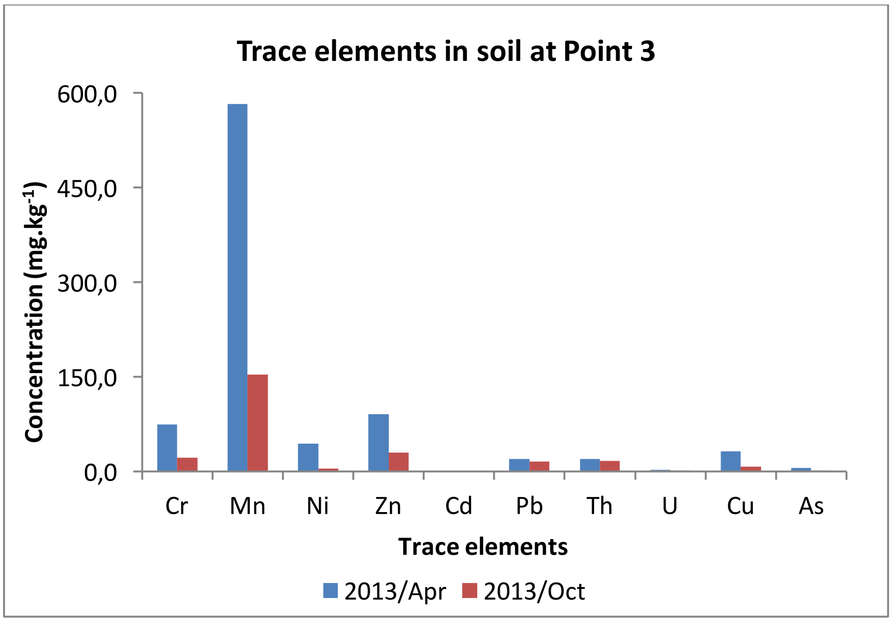

Figure 6: Trace element concentrations in soil, collected in point 3 (inside IRD)

At Jacarepaguá Lagoon, there were collected samples of superficial water (Point 4) and sediment (Point 5), whose trace elements concentrations were showed in Figures 7 and 8 respectively. In superficial water samples, by two consecutive samplings in 2014, the concentrations of As were above the maximum values stablished at CONAMA Resolution nº 357/2005 (10$\mu g.L^{-1}$), reaching around 22$\mu g.L^{-1}$. Arsenium is present in insecticides and herbicides, and it is possible that these concentrations come from the increasing in use of insecticides to combat mosquitoes that transmit diseases such as dengue fever, applied nearby Jacarepaguá Lagoon.

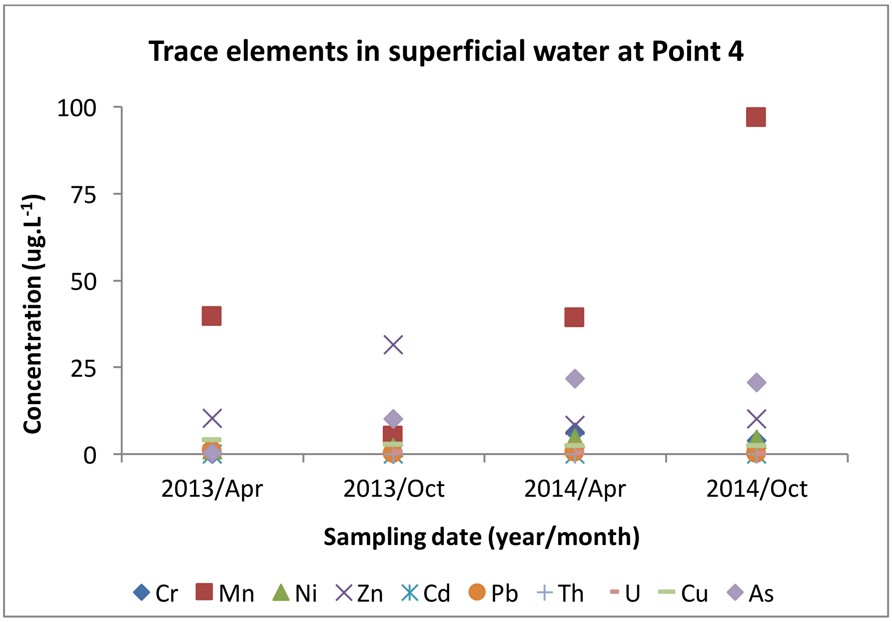

Figure 7: Trace element concentrations in superficial water, collected in point 4 (Jacarepaguá Lagoon).

The CONAMA Resolution nº 454/2012 (2012) gives general guidelines for management of drag materials under national jurisdiction. The trace elements concentrations could be compared with Orientation Values (OV) of Resolution. Comparing the analyzed concentrations of the elements with their respective OV, it is possible to verify the sediment corresponds to level 1 (sediment from brackish water), not having obligation of physical, chemical or ecotoxicological characterization of the material. This way, complementary studies for the sediment drainage and direct disposition in soil are not necessary. However, the resolution does not stablish guidelines for concentrations of Mn. Upper concentrations of trace elements were described by Monken-Fernandes in 1991. In his study, Monken-Fernandes (1991) analyzed metal concentrations in 18 sampling points. In general, he found values more than 20 times higher for Mn, Zn, Ni and Cr, and 10 times higher for Cu and Pb. These higher concentrations were related to the release of industrial effluents in Tributaries Rivers and channels that flow in the Jacarepaguá Lagoon.

Almost three decades passed, some dragging procedures were realized at the Lagoon Complex, especially after 2010, during the preparation of Rio de Janeiro for World cup (2014) and The Olympic Games (2016). These processes could be contributed for the decrease of trace elements levels. Just the same, a future study will be conducted in the research, to define the relationship between the concentration of these elements with probable anthropic and natural contamination sources.

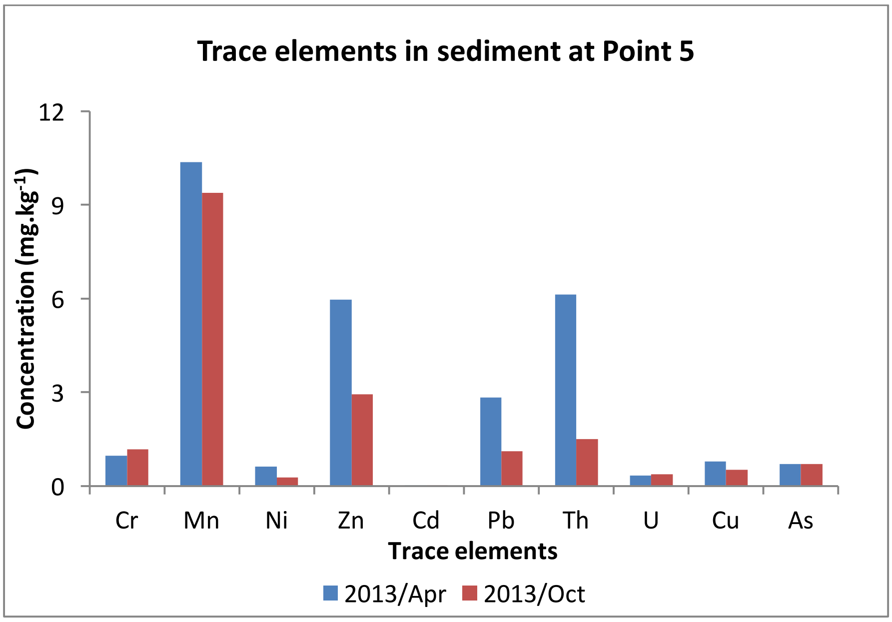

Figure 8: Trace element concentrations in sediment, collected in point 5 (Jacarepaguá Lagoon).

4. CONCLUSIONS

For all samples analyses, three of them (one of underground water, soil and superficial water) had some trace elements concentrations above the limits stablished for their corresponding resolutions. For Cd, Cu, Pb and Zn, all samples showed concentration values below the national standards. It´s important to emphasize the definition of quality standards for the samples studied contemplate other analytical parameters, according each resolution. However, these results give important information for environmental monitoring programs, helping their implementation and providing base values for future studies.

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