

## **TOXIC ELEMENTS IN SEDIMENT FROM TWO WATER BODIES NEAR BRAZILIAN MULTIPURPOSE REACTOR – RMB INSTALLATION AREA**

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### **ABSTRACT**

Aquatic ecosystems are directly affected by contaminants, such as, toxic elements that do not remain in sediment in a insoluble form. Anthropogenic and natural actions influence sediment dynamics that could lead to a potential contaminant accumulation. Therefore, to evaluate possible environmental impacts is, in many cases, mandatory. Environmental impact assessment studies are a licensing tool that seeks to control degradation activities, taking into account the legal and regulatory provisions and technical standards applicable to the case. The present study aims to evaluate the sediment quality in the area of influence of the Brazilian Multipurpose Nuclear Reactor (RMB) to be installed in the contiguous area of the Experimental Center of Aramar of the Technological Center of the Navy in São Paulo (CTMSP), located in the city of Iperó - SP. The potentially toxic elements As, Cd and Hg were analyzed by Graphite Furnace Atomic Absorption Spectrometry (GFAAS) and Cr, Cu, Ni and Zn by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES). Results were compared with Canadian Council of Ministers of the Environment (CCME) guideline values (TEL and PEL) and the maximum permitted values of Resolution 454/12. These toxic elements (As, Cd, Hg, Cr, Cu, Ni and Zn) were found below maximum allowed concentrations from national and international legislation. This study provides support for RMB post-completion evaluations, in order to prevent these elements to exceed tolerated levels, ensuring ecological, social and economic values.

### **1. INTRODUCTION**

According to Quinágua [1], sediment is a layer of particulate material, deposited in the bottom of natural water bodies. Guimarães [2] also states that the material which composes sediment is the result of continuous weathering and erosion processes of mineral and rocky surfaces, being carried along by wind, ice and water from terrestrial surfaces, and natural chemical and biological processes of aquatic ecosystems and deposition of organic matter. Responsible for providing nutrient sources to organisms living at the interface (sediment-water), sediments present ecological, social and economic value. From the ecological point of view, it is important to emphasize that sediment is a energy resource for the biotic compartment and the key component for studying the ecological integrity of these environments [3].

Ecological integrity can be damaged by anthropogenic action, such as, solid waste discharge and untreated industrial and sanitary wastewater into the waterways. This could influence sediments natural dynamics, due to the potential accumulation of contaminants, metals and trace elements that can be released into the water column. Contaminants transport and destination in sediments usually involves processes that depend on physical and / or chemical properties, as well as the type of water body in which the sediments remain [4].

These physical, chemical and biological processes can affect ecosystems structure and functioning, altering metals bioavailability. The most important processes are bioaccumulation and biomagnification, where benthic organisms are exposed to contaminants at the interface water-sediment. According to U.S.EPA - United States Environmental Protective Agency [4] bioaccumulation is the accumulation of contaminants in the tissue of organisms through any route, including breathing, ingestion or direct contact with contaminated water, sediment, pore water or dredging material. Biomagnification is the result of the bioaccumulation process, whereby the concentrations of bioaccumulated chemical elements increase as the element passes through the

trophic levels [4]. In this way, sediment is one of the most important tools to the evaluation of environmental impact in aquatic ecosystems.

In Brazil, the Law nº 6.938/81 [5] provides National Environmental Policy, which defines the competence of the Federal Executive Power to contribute with the licensing of nuclear installations. Nuclear activities in Brazil are submitted to the environmental licensing process, by the Brazilian Institute of Environment and Renewable Natural Resources (IBAMA), as well as in the nuclear point of view, by the National Commission of Nuclear Energy (CNEN). These activities require a broad planning and practice of environmental management, since they exert possible impacts on the worker, community and the environment, so, it is necessary to establish constraints and requirements to be met in order to minimize the negative impacts resulting from them, as well as to maximize their positive impacts.

Hence, the present work aims to evaluate toxic elements (As, Cd, Hg, Cr, Cu, Ni and Zn) in the sediment of two water courses, around RMB direct influence area (Municipality of Iperó - SP).

## 2. MATERIALS & METHODS

### 2.1. Study Area

Fig. 1 shows RMB installation area, located in the municipality of Iperó - São Paulo (23° 23 '33.5"S 47° 7' 12.4"W).

RMB will be a nuclear research reactor, whose purpose is the manufacture of radioisotopes, which are the basis for radiopharmaceuticals treatments in nuclear medicine and for the production of radioactive sources used in industrial, agricultural and environmental applications. In addition, to irradiation tests of nuclear fuels and structural materials, used in power reactors, as well as conducting scientific research with neutron beams in several areas of knowledge [6].



**Figure 1 - RMB deployment area.**

Its influence area is part of the Tietê/Sorocaba Water Resources Management Unit (UGRHI-10), specifically in the Middle Sorocaba sub-basin, the main watercourse in the region is the Sorocaba River, with its tributaries, does Ferro Stream, Iperó and Ipanema River.

According to Decree N° 8468/76 [7], that approved the Regulation Law N° 997/76, to provide the prevention and control of environmental pollution, UGRHI 10 is classified as Class 2, waters destined for domestic supply, after conventional treatment, irrigation of vegetables or fruit plants and recreation of primary contact (swimming, water skiing and diving).

Nearby RMB area is located the National Forest (FLONA) of Ipanema, among the municipalities of Iperó, Araçoiaba da Serra and Capela do Alto. Ipanema FLONA is a Sustainable Use Conservation Unit managed by the Brazilian Institute of Environment and Renewable Natural Resources - IBAMA [8].

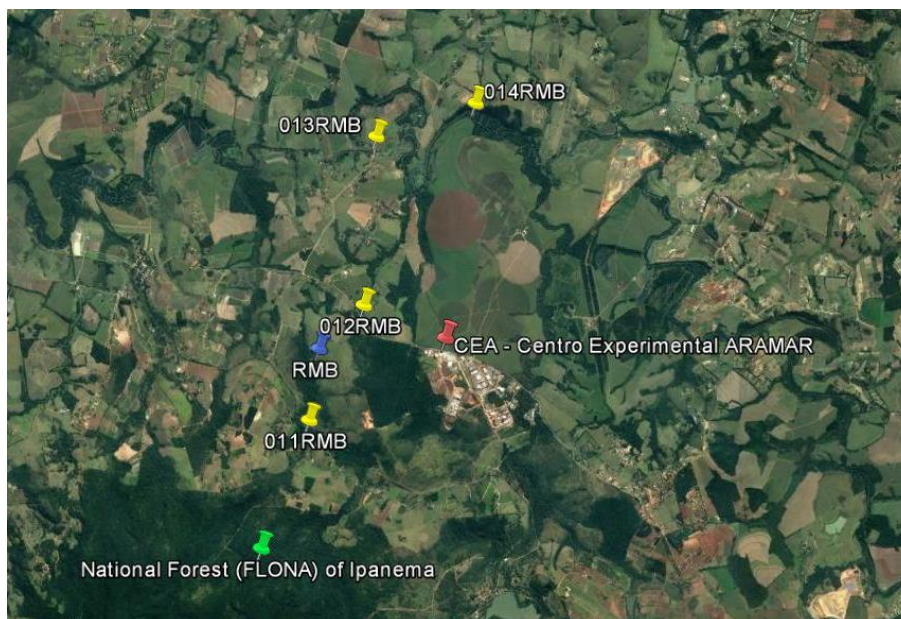
## 2.2. Collection of sediment samples and pre-treatments

Sediment samples were collected from two water bodies in four seasons (April; June; August and December 2015), using a dredger at the points presented in Table 1 and Fig. 2.

**Table 1 - Location of samples collection points**

IDENTIFICATION OF POINTS	LOCATION	GEOGRAPHICAL COORDINATES UTM
011RMB	do Ferro Stream, downstream of the development	23°24'17"S 47°37'29"W
012RMB	do Ferro Stream, upstream of the development	23°23'19"S 47°37'01"W
013RMB	Sorocaba River, downstream of the point of discharge of the do Ferro Stream	23°21'56"S 47°36'54"W
014RMB	Sorocaba River, upstream from the point of discharge of the do Ferro Stream, after the Ipanema River	23°21'55"S 47°35'34"W

Source: Centro Experimental de Aramar (CEA - CTMSP)



**Figure 2 - Location of samples collection points**

Collection and sampling procedures followed the National Guide on Collection and Preservation of Samples [9]. Samples were collected and conditioned in polyethylene pots, previously decontaminated, properly identified and maintained at 4°C, in order to preserve the analytes of interest.

All samples were treated, stored and analyzed at Centro de Química e Meio Ambiente (CQMA) IPEN/CNEN-SP.

Pretreatment was based on pre-drying samples for around 16 h at 60°C, using an oven with mechanical circulation of air. After this procedure, samples were sprayed in agate mortar, homogenized and packed in plastic containers for further analysis.

### 2.3. Digestion of Sediment Samples

To measure toxic elements in sediment samples a prior digestion is performed. EPA Method 3051A was adopted in this study [10]. Microwave assisted digestion was chosen for its efficiency, fastness and low contamination probability, compared to digestion by heating plate and digester block. This procedure is to transfer about 0.50 g of the previously treated sample to Teflon® flasks, which will be assisted in a closed system, with monitored pressure in the DGT-100 Plus Analytical Microwave. A 3:1 ratio of HNO<sub>3</sub>: HCl was added. At the end of programming and samples cooling, the digested samples were filtered, swollen with Type I deionized water in a 50 mL volumetric flask and transferred to Falcon flasks.

As quality control, analysis were performed in the total fraction (particles <2mm), in triplicate accompanied by blank and addition of reference material (RM) NIST 8704 - Buffalo River Sediment [11]. The acceptable recovery value was between 75 and 125%.

### 2.4. Chemical analysis

As, Cd and Hg were determined by Atomic Absorption Spectrometry with Graphite Furnace Atomization (GFAAS). An AAnalyst - Perkin Elmer, model HGA 400 equipment was used.

The amounts of Cr, Cu, Ni and Zn were determined by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES), a Spectrometer ARCOS Spectro® was used.

Table 2 presents limits of quantification - LQ of the analyzed elements ICP-OES and GFAAS.

**Table 2 - Limits of quantification of analyzed elements**

Element	As	Cd	Hg	Cr	Cu	Ni	Zn
LQ (mg kg <sup>-1</sup> )	0.49	0.11	0.11	11.9	17.9	11.9	11.7

## 3. RESULTS AND DISCUSSION

Sediment Quality Values Guidelines (SQVG) are used on sediment samples evaluation. SQVG aim to protect aquatic life and environment. CONAMA Resolution N° 454/12 [12] establishes general guidelines and referential procedures to material management to be dredged in water under national jurisdiction, and adopts guiding values relied on *Canadian Council of Ministers of the Environment* established limits [13]. Both guidelines were used in this study.

Table 3 shows guideline values adopted in the present study. *TEL-Threshold Effect Level* is associated to the lower probability of adverse effects to the biota. These values were adopted in Brazilian legislation as Level 1. Also, *PEL - Probable Effect Level* is the value where adverse effects are likely to occur to biota. These are equivalents to Brazilian legislation Level 2 [12].

**Table 3 – Guideline values for metals in freshwater sediments**

ELEMENTS	TEL mg kg <sup>-1</sup>	PEL mg kg <sup>-1</sup>
As	5.9	17
Cd	0.6	3.5
Hg	0.17	0.486
Cr	37.3	90
Cu	35.7	197
Ni	18	36
Zn	123	315

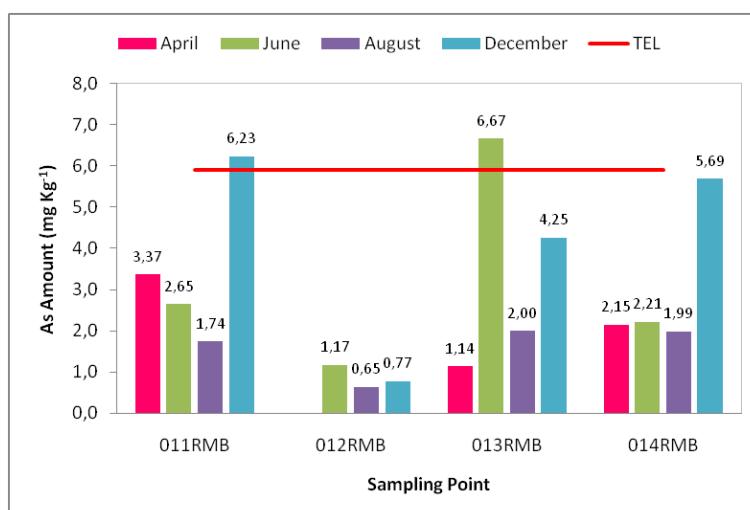
For Cd, the majority of results were below the analytical method limit of quantification (LQ), except to 013RMB ( $0.5 \pm 0.1$  mg kg<sup>-1</sup>) and 014RMB ( $0.4 \pm 0.2$  mg kg<sup>-1</sup>) in June, and to point 014RMB in April ( $0.14 \pm 0.01$  mg kg<sup>-1</sup>). These values were above TEL (0.6 mg kg<sup>-1</sup>).

For Hg, all results were below LQ, as well as TEL (0.17 mg kg<sup>-1</sup>).

Although Cd and Hg presented values lower than guideline values, their monitoring is of paramount importance, due to their bioaccumulative characteristics.

Since the studied water bodies are classified as Class 2, applied to irrigation of vegetables or fruit plants and recreation (swimming, water skiing and diving), this can have direct and indirect contact with the community.

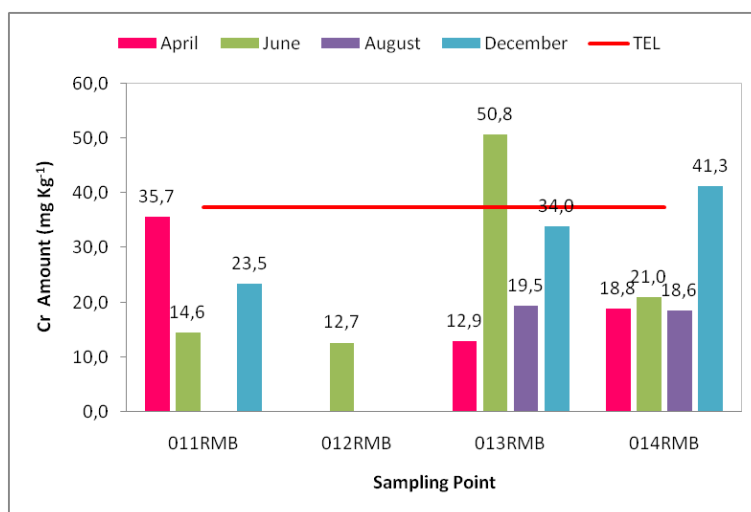
For As, values ranged from 0.65 to 6.67 mg kg<sup>-1</sup>, details are presented in Fig. 4. Point 012RMB in April was the only to present values below LQ, no results exceeded the PEL value, but points 013RMB in June and 011RMB in December exceeded TEL.

**Figure 4 – Results of As concentrations.**

Arsenic is usually found in inorganic forms of As (III) and As (V) in natural waters. As (III), most common form is H<sub>3</sub>AsO<sub>3</sub>, that will prevail under anaerobic and reducing conditions, flooded soils or sediments. As (V) will exist as H<sub>2</sub>AsO<sub>4</sub> and HAsO<sub>4</sub><sup>2-</sup>, under aerobic and oxidizing conditions, generally remain bound to minerals, such as iron hydroxide and alumina, limiting their mobility and bioavailability [1,14,15,16]

Common methods to evaluate contaminants bioaccumulative potential are study of partition coefficients. K<sub>PW</sub>, or the As particle-water partition coefficient is lower than K<sub>SW</sub>, the sediment-water partition coefficient (L kg<sup>-1</sup>), so arsenic mobilization is more likely in the sediment [17].

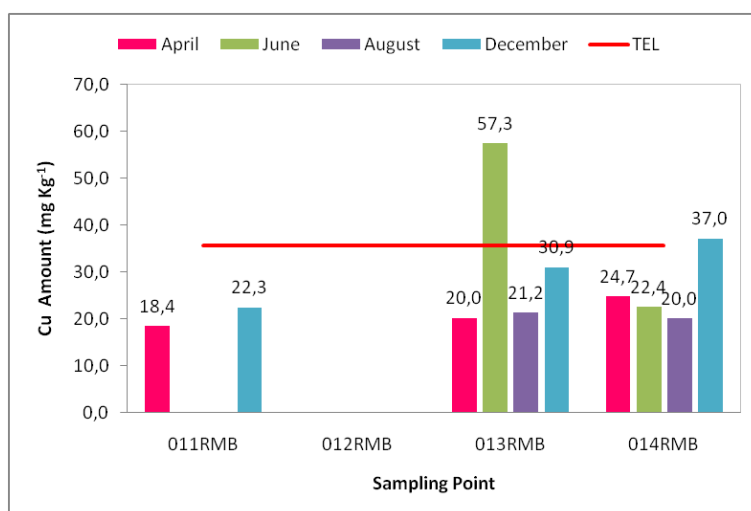
Fig. 5 shows Cr results that ranged from 12.7 to 50.8 mg kg<sup>-1</sup>, except to 011RMB in April and to 012RMB in April, August and December, found to be below the LQ. 013RMB in June and 014RMB in December exceeded TEL.



**Figure 5 – Results of Cr concentrations.**

Chromium has different oxidation states, the most common forms are Cr (II), (III) and (VI), and its toxicity depends on the oxidation state. Cr (VI) is more toxic than Cr (III) [18,19]. According to FIT – Ficha Informação Toxicológica [18], about 40% of chromium metal is available on its hexavalent form and most of it comes from anthropic activities, such as, industrial oxidation in mining, wood preservatives, organic syntheses and some types of fertilizers. In water, chromium is not soluble and deposit in sediments, with Cr<sup>+6</sup> reduction to Cr<sup>+3</sup>, depending on water oxy-reduction conditions, as well as, the organic matter amount in the sediment [1,18,19].

For Cu values ranged from 18.4 to 57.3 mg kg<sup>-1</sup>, as shown in Fig. 6. 011RMB point in June and August and 012RMB in all months were below LQ. Points that exceeded TEL value were 013RMB in June and 014RMB in December

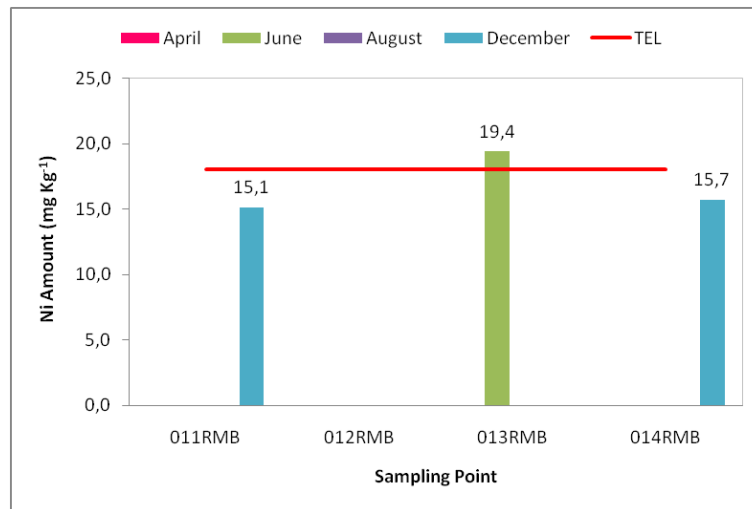


**Figure 6 – Results of Cu in sediment.**

Cu inputs also came from anthropogenic sources, such as, mining, smelting, coal burning as a source of energy, municipal waste incineration, and agricultural poisons. Its bioavailability in aquatic systems is influenced by processes, like complexation to organic and inorganic binders, adsorption to metal oxides, clay and suspended particulate matter and resuspension at the water-sediment interface [1,19,20].



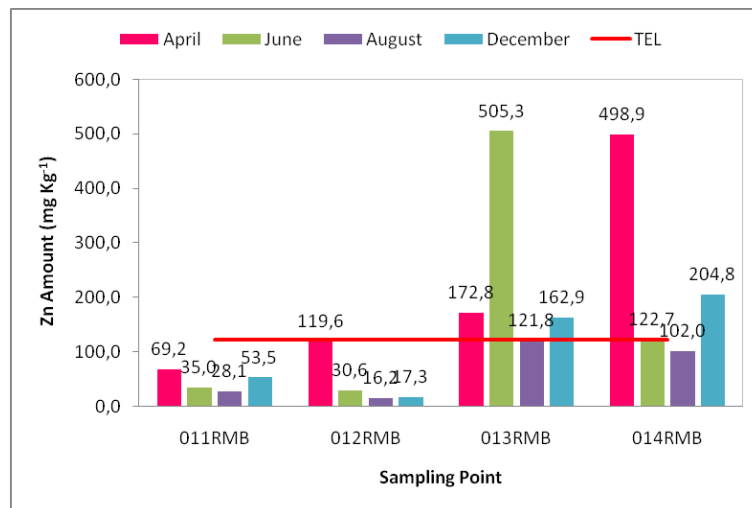
In most samples and most collection campaigns, Ni was below the LQ. Except to 011RMB with 15.1 mg kg<sup>-1</sup> and 014RMB, 15.7 mg kg<sup>-1</sup>, in December. To point 013RMB in June Ni results exceeded TEL, with 19.4 mg kg<sup>-1</sup> (Fig. 7).



**Figure 7 – Results of Ni in sediments.**

Main anthropogenic sources of nickel are fossil fuels, metal mining and casting processes. Ni is usually associated with iron and copper sulphides, and pH is the main factor responsible for their availability. Nickel is not accumulated on aquatic organisms in significant quantities [21].

Fig. 8 shows Zn results that ranged from 16.2 to 505.3 mg kg<sup>-1</sup>. 013RMB exceeded TEL in April, June and December and 014RMB in April and December.



**Figure 8 – Results of Zn in sediments.**

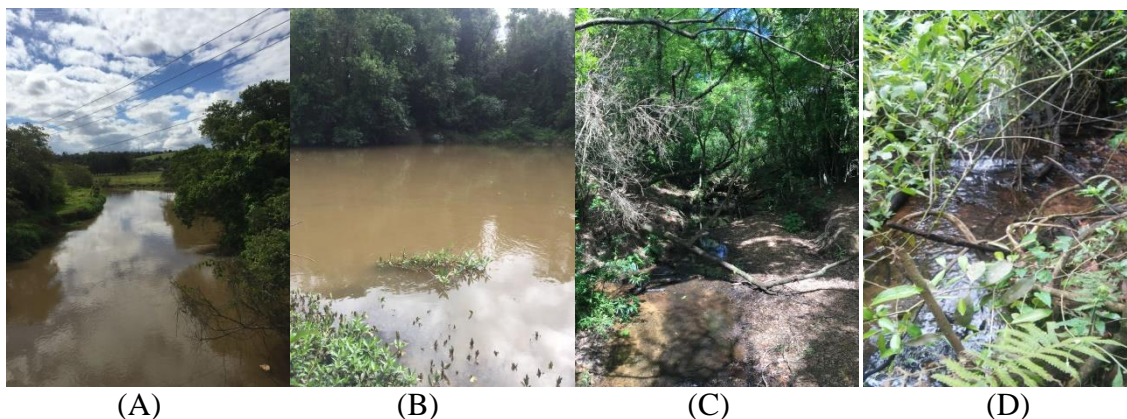
Zn is an element commonly found on Earth; however, the highest zinc emissions came from anthropogenic activities, e.g. metallurgical effluents, mining tailings, combustion process ash and zinc-based fertilizers. Brazilian soils have in most cases Zinc deficiency. Zn mobility is limited, under anaerobic conditions in presence of sulfides. Another factor that enriches the sediment compartment is the adsorption, dominant reaction of zinc in iron and manganese oxides, mineral clays and organic matter. This element is not concentrated in plants, presenting a low probability of biomagnification [19,22].

Analytical procedure quality control was performed with RM NIST 8704, that met the acceptability criteria (75% < Recovery < 125%), except to Cr that had a recovery of 74%. This RM has referenced values for metals

total dissection in fine fraction. However, our results expressed the environmentally available in total fraction with chemical digestion.

Do Ferro stream (points 011RMB and 012RMB) were born within the boundaries of FLONA Ipanema and passes through the area occupied by former mining company, and flows into the Sorocaba River. Today, the region is occupied by settled families that develop agricultural activities (Fig. 9).

Sorocaba River (points 013RMB and 014RMB) runs through important municipalities of São Paulo and flows into the Tietê River. That corresponds to area under accelerated urbanization and that suffers great anthropic pressure from industrial, agricultural and livestock activities, as well as having many tributaries, as shown in Fig. 9.



**Figure 9 – (A) Sorocaba River, downstream of the point of discharge of the do Ferro stream; (B) Sorocaba River, upstream from the point of discharge of do Ferro stream, after the River Ipanema; (C) do Ferro stream, downstream of the development; (D) do Ferro stream, upstream of the development.**

In general, both water bodies have punctual sources and diffuse pollution and due to their characteristics and metals features, these can accumulate in the bottom sediments.

#### 4. CONCLUSIONS

Among the evaluated samples, points located in the Sorocaba River show most of metals occurrences. Probably due to agricultural and industrial activities, as well as the influence of previously developed activities from the mining company in the region. This contributes a diffuse source of metal pollution into sediment. The results found out in the present study will be used, in the future, as pre installation conditions on RMB environmental monitoring program. This work is result from a major project that includes superficial and ground water monitoring, regarding both stable and radioactive compounds.

#### ACKNOWLEDGMENTS

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