

# METAL, MAJOR AND TRACE ELEMENTS ASSESSMENT OF TIETÊ RIVER SEDIMENTS, SÃO PAULO, BRAZIL

ALEGRE, G. F.<sup>1</sup>, BORRELY, S. I.<sup>1</sup>, Oliveira, S.M.B.<sup>2</sup>, Vukan, W.<sup>3</sup>, Vieira, A. S.<sup>3</sup>, FAVARO, D. I. T.<sup>3</sup>

<sup>1</sup>Radiation Technology Center, Instituto de Pesquisas Energéticas e Nucleares (IPEN / CNEN - SP), Av. Prof. Lineu Prestes 2242, CEP 05508-000, São Paulo, Brazil.

<sup>2</sup>Geosciences Institute, University of São Paulo, P.O. Box 11348, São Paulo, Brazil.

<sup>3</sup>Neutron Activation Analysis Laboratory (LAN/ CRPq), Instituto de Pesquisas Energéticas e Nucleares (IPEN / CNEN - SP), defavaro@ipen.br



## INTRODUCTION

Cutting São Paulo State, Tietê is the most important river flowing to the South of Brazil. As a consequence of river usages the water quality is not good even very close to the spring. The Upper Region of the Tietê River, USTR, includes the Salesópolis County up to the Ração Storage Dam, an agricultural area. At Salesópolis there is an important water reservoir called Ponte Nova. The following municipalities Biritiba-Mirim, Mogi das Cruzes and Suzano are urban areas, with diverse industrial production.

Negative impacts to the river are evidenced by water oxygen depletion, excessive organic matter in water and sediment and related contaminants organic and inorganic.

There is a general consensus that the sediment from water bodies plays a fundamental role in the transport dynamics, accumulation and availability of pollutants. In the sediment quality triad, considered one of the best approaches for the study of anthropogenic contaminated aquatic systems, the chemical and biological data (bioassays and benthic community analysis) are combined to show the degradation of each site.

The objectives of the present study were :

- to quantify some metals, major and trace elements, contained at field-collected sediments from Upper Side of the Tietê River (USTR) by using XRF and NAA analytical techniques, collected in 3 sampling campaigns.
- to compare the results to Upper Continental Crust (UCC) values. The enrichment factor in relation to UCC values using Sc as a normalizer element was also calculated.
- to compare Cd, Hg and Pb concentrations to TEL and PEL oriented values from Environment Canada and CONAMA 344 resolution from the Brazilian Council of Environment.
- to assess the biological effects (ecotoxicity) of sediments in order to evaluate the potency for biological damages of determined contaminants on that environmental matrix. Amphipods, as benthonic organisms, are dependents on sediments the reason why *Hyaella azteca* was exposed to these sediments samples.

## MATERIALS AND METHODS

### Sampling and sample preparation

Sampling locations: The site of USTR is represented by the following counties and correspondent sample identification: Ponte Nova's Reservoir in Salesópolis (P0) and in the watercourse Biritiba-Mirim (P1 and P2), Mogi das Cruzes (P3) and Suzano (P4), (Figure 1).

Sampling campaigns: March/2008 (2<sup>nd</sup>), September/2008 (3<sup>rd</sup>), February/2009 (4<sup>th</sup>).

Sediment preparation: dried at 45°C in a ventilated oven until constant weight. After this step, were passed through a 2 mm sieve, ground in a mortar, once again passed through a 200 mesh sieve and then homogenized before analysis. The total fraction (< 2 mm) was analyzed.

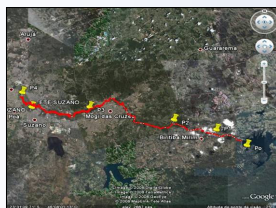


Figure 1. Sampling sites location at the Tietê River

### Analytical techniques applied

XRF : determination of major elements  
 NAA: determination of some major and trace elements : 8 hs irradiation, under a thermal neutron flux of 10<sup>12</sup> n cm<sup>-2</sup> s<sup>-1</sup> in the IEA-R1 nuclear research reactor at IPEN  
 AAS: GF AAS (Cd and Pb) and CV AAS (Hg): sample digestion was performed by microwave-assisted method following the SW-846-3051 - US EPA for sediments .

### Ecotoxicological assays

The toxicity assays were carried out with *H. azteca* raised in the laboratory (LEBA/CTR). Natural water and polymer net were used for living organisms maintenance. During the sediment assays the polymer net is replaced by studied sediments, as in the natural environment.

## RESULTS AND DISCUSSION

The Enrichment Factor calculated for the NAA results showed: (EF > 1.5 indicates anthropogenic contribution)

- EF >1.5 for the elements As, Br, Hf, Mn, Rb, Ta, Th, Ti, U, Zn and REE.
- Point 0 for the elements Br, Hf, Th, Ti, and Yb;
- Point 01 for the elements As, Br, Cr, Hf, Ta, Th, U and REE;
- Point 02 for the elements Br, Hf, Rb, Ta, Th, Ti, U, and REE
- Point 03 and 04, for the elements As, Br, Sb, U and Zn.
- Therefore anthropogenic contributions can be observed throughout the Tietê River from P0 (springs) to P4 (Suzano county) mainly due to the EF values obtained for As, Br, Sb and Zn at points 03 and 04 and REE, Hf, Ta, Ti, Th and U at P1 and P2. The highest EF was found for Hf (1.0 to 21.9), Th (0.8 to 27.2), U (1.0 to 14.4) and REE at P2.

Table 1. XRF results (µg) for sediment samples collected in the 2<sup>nd</sup> and 3<sup>rd</sup> campaigns and Continental Crust Values (UCC) (P0-P04).

Sample	2 <sup>nd</sup> Campaign										3 <sup>rd</sup> Campaign									
	P0	P1	P2	P3	P4	P1	P2	P3	P4	P1	P2	P3	P4	P1	P2	P3	P4			
As	10.1	10.1	10.1	10.1	10.1	10.1	10.1	10.1	10.1	10.1	10.1	10.1	10.1	10.1	10.1	10.1	10.1			

Table 3. Results for Cd and Pb by GF AAS, Hg by CV AAS in sediment samples (log kg), PEL and TEL values, CONAMA values, Regional Reference Values (RRV).

Sample	Hg (log kg)	Pb (log kg)	TEL (log kg)	PEL (log kg)
P0	44.3	44.1	12000.265	12000.265
P1	56.0	41.2	16000.418	16000.418
P2	43.9	45.2	12000.265	12000.265
P3	489.10	571.39	60000.000	60000.000
P4	219.20	181.74	12000.265	12000.265

Table 2. Results (mean ± s.d) (log kg) for some metals and trace elements in sediments determined by NAA (total concentration), and UCC values and Regional Reference Values (RRV) (Upper Tietê River) (total concentration).

Element	2 <sup>nd</sup> Campaign										3 <sup>rd</sup> Campaign									
	P0	P1	P2	P3	P4	P1	P2	P3	P4	P1	P2	P3	P4	P1	P2	P3	P4			
As	10.1	10.1	10.1	10.1	10.1	10.1	10.1	10.1	10.1	10.1	10.1	10.1	10.1	10.1	10.1	10.1	10.1			

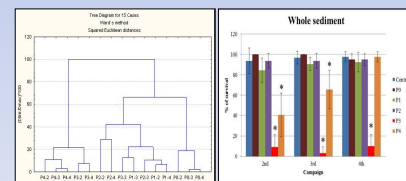


Fig. 1. Dendrogram comparing the similarity of the sediment samples at the sampling points (sites) in the three sampling campaigns.

Fig. 3. Survival percentage of *H. azteca* during exposure to whole sediment.

Cd, Hg and Pb results were compared to the oriented values (TEL and PEL) from Canadian Council of Minister of the Environment and CONAMA resolution: level 1 (TEL values) and level 2 (PEL values):

- Hg exceeded the TEL values (0.17 mg kg<sup>-1</sup>) at P3 and P4 in all sampling campaigns and PEL at P4 (2<sup>nd</sup>);
- Cd exceeded the TEL at P3 and P4 from the 1<sup>st</sup> campaign and P4 in the 2<sup>nd</sup> one. P0, P1 and P2: < TEL.
- Pb higher than TEL (35 mg kg<sup>-1</sup>) in all sampling campaigns. P0, P1 and P2: lower than TEL.

### Cluster Analysis

Cluster Analysis applied to the chemical data (all elements) showed three different groups:

- Group 1: P3 and P4 from all sampling campaigns formed a separate group, except for P3-3 that joined the group of samples from P1 and P2;
- Group 2: formed by P2 and P1 (all sampling campaigns);
- Group 3: formed by P0 (all sampling campaigns)

### Ecotoxicological Assays

Survival of *H. azteca* was lower when the organisms were exposed to sediments sampled at P3 and P4, mainly in the second and third campaigns. Toxicity results are in accordance with chemical determinations since P3 and P4 data for heavy metals are much higher when compared to the other sites. The tests measured interactive toxic effects of complex contaminant mixtures in sediment. P3 and P4 sampling sites are relatively close to the industrial area of Suzano County and Sao Paulo Metropolitan Region.

## CONCLUSIONS

- P0, located near the springs of the Tietê River, in general, showed the lowest concentration values for all elements determined in the sediment samples analyzed.
- P1 and P2 showed strong contamination by the elements of REE, Hf, Ta, Ti, Th and U probably due to the influence of an ore mining operation nearby (VCN mining).
- P3 and P4 showed high contamination levels for As, Br, Cd, Hg, Pb, Sb and Zn, probably due to industrial effluents and sewage discharges.
- Toxicity results are in accordance with chemical determinations at P3 and P4. The *H. azteca* survival rate was lower when the organisms were exposed to sediments sampled at P3 and P4. P3 and P4 exceeded TEL values for Cd, Hg and Pb in sediments. P4 presented values between TEL and PEL and the ecotoxicological assays with *H. azteca* proved the occurrence of adverse effects on the biological community.
- The assessment of metals, trace and major elements together with ecotoxicological assays with *H. azteca* organism allowed a more complete contamination evaluation of the Tietê River.