

METAL AND TRACE ELEMENT SEDIMENT ASSESSMENT FROM RIBEIRA DO IGUAPE RIVER, SÃO PAULO STATE, BRAZIL, BY INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS

Francisco J. V. de Castro¹, Déborah I. T. Fávaro², Gilson A. Quinaglia¹, Robson L. Franklin³, Francisco J. Ferreira³

¹ CETESB – Companhia Ambiental do Estado de São Paulo
ELTA – Setor de Análises Toxicológicas
Av. Professor Frederico Hermann Jr., 345
05459-900 São Paulo, SP
franciscovc@cetesbnet.sp.gov.br
gilsonn@cetesbnet.sp.gov.br

² Instituto de Pesquisas Energéticas e Nucleares (IPEN / CNEN - SP)
Laboratório de Análise por Ativação Neutrônica (LAN-CRPQ)
Av. Professor Lineu Prestes, 2242 – Cidade Universitária - SP
05508-000 São Paulo, SP
defavaro@ipen.br

³ CETESB – Companhia Ambiental do Estado de São Paulo
ELAI – Setor de Química Inorgânica
Av. Professor Frederico Hermann Jr., 345
05459-900 São Paulo, SP
robsonf@cetesbnet.sp.gov.br
franciscoj@cetesbnet.sp.gov.br

ABSTRACT

The watershed region of the Ribeira do Iguape River and the estuarine complex of the Paranaguá-Iguape-Cananéia and the various river basins located between this region and the Atlantic Ocean, is known as the Ribeira Valley. The Ribeira do Iguape River runs a total length of approximately 470 km, being the main source of fresh water in the Estuarine Complex of the Iguape-Cananéia-Paranaguá (Lagamar). The Ribeira do Iguape River is the last major river in the State of Sao Paulo that has not been altered by dams. During virtually the entire 20th century, the region of the Ribeira Valley was the scene of constant environmental degradation resulting from the intense exploration and refining of lead, zinc and silver ores that were processed in the mines of the region, in a rudimentary way and without any control over environmental impacts. Since 1996, all such activities ceased, however, leaving behind a huge amount of environmental liabilities. This study aims to investigate the presence and concentration levels of metals and semi-metals arsenic (As), cadmium (Cd) and lead (Pb) in the sediment and water of aquatic systems of Ribeira do Iguape River and its tributaries, for an environmental assessment and monitoring of the region. The determination of these elements was carried out by GF AAS technique for water samples and ICP OES for the sediment samples. This study also assessed the occurrence of some major (Ca, Fe, K and Na), trace (As, Ba, Br, Co, Cs, Hf, Rb, Sb, Sc, Se, Ta, Th, U, Zn) and rare earth elements (La, Ce, Eu, Nd, Sm, Lu, Tb and Yb) by Neutron Activation Analysis (NAA). Validation of both methodologies, according to precision and accuracy, was done by reference material analyses. The results obtained for As, Cd and Pb were compared to the Canadian Environmental oriented values (TEL and PEL). The results obtained for multielemental analyses in the sediment samples were compared to UCC values (Upper Continental Crust).

1. INTRODUCTION

The watershed region of the Ribeira do Iguape River and the estuarine complex of the Paranaguá-Iguape-Cananéia and the various river basins located between this region and the Atlantic Ocean is known as the Ribeira Valley. It covers an area of 2,830,666 hectares (28,206 km²) in the southern state of Sao Paulo and east of the state of Paraná. It covers 1,119,133 hectares in the state of Parana and 1,711,533 hectares in the state of São Paulo, representing respectively 39.5% and 60.5% in relation to the total area of the basin [1]. The Ribeira do Iguape River is the main source of freshwater-Estuarine Complex of Iguape, Cananéia and Paranaguá, known as Lagamar, a region of great environmental importance that extends for 200 km of coastline from north of the Ecological Station Juréia-Itatins in São Paulo to Pontal Sul, Parana State, Brazil. It is a very complex ecosystem, which includes a set of lagoons, inlets, bays, estuaries, salt marshes and islands [2].

The Ribeira do Iguape River basin belongs to the UGRHI -11 (Water Resources Management), Ribeira do Iguape / South Coast, and is managed by CETESB (Environmental Company of São Paulo, Brazil) which keeps monitoring environmental sampling points of water and sediments, performing biological assays, toxicological, ecotoxicological, chemical and physical tests, with determinations of heavy metals and metalloids in the various compartments of the aquatic system. [3]

Recent years, has seen an increase of research on metals present in sediments, not as a sink or a location of deposition of metal species, but as an active agent that plays a key role in the interaction of these species with the biota of aquatic life. Therefore, the analysis of sediments from rivers, lakes and oceans has become important in environmental assessment. The definition of chemical and physical characteristics of the sediment provides adequate parameters to assess the degree of contamination of the watershed and the impact of contaminated sediments on aquatic biota [4]. In this context, it is only possible to assess the toxic effect of metallic elements in aquatic ecosystems through an integrated assessment, using data for the analysis of water, sediment and biomarkers.

Also important are chemical concentrations of metals and metalloids in aquatic species and biotopes, since these elements in addition to bioaccumulation are often magnified along the food chain. In other words, the organisms on the top of the food chain have higher concentrations than those below. [5]

Among the activities that cause environmental impact mining is extremely important to the economic and social development of many countries. The extraction and processing of ores when practiced without responsibility and without the principles of sustainable development has created serious environmental problems such as: deforestation, erosion, sedimentation, and production of huge amounts of mining waste products containing high levels of heavy metals which are disperse into the environment and contaminate air, water and soil, putting at risk not only the local biota but human health as well.

During virtually the entire 20th century, the Ribeira Valley region suffered constant environmental degradation resulting from intense exploration and refining of ores of lead, zinc and silver mines that were processed in the region, in a rudimentary fashion, and without any control over the environmental impacts. In 1996, all these activities were interrupted. However, they left the banks of the river unprotected and subject to environmental liabilities. These consisted of ore tailings with high levels of heavy metals, generating impacts on water quality and sediments of the Ribeira do Iguape River and its basin (Figure 1).

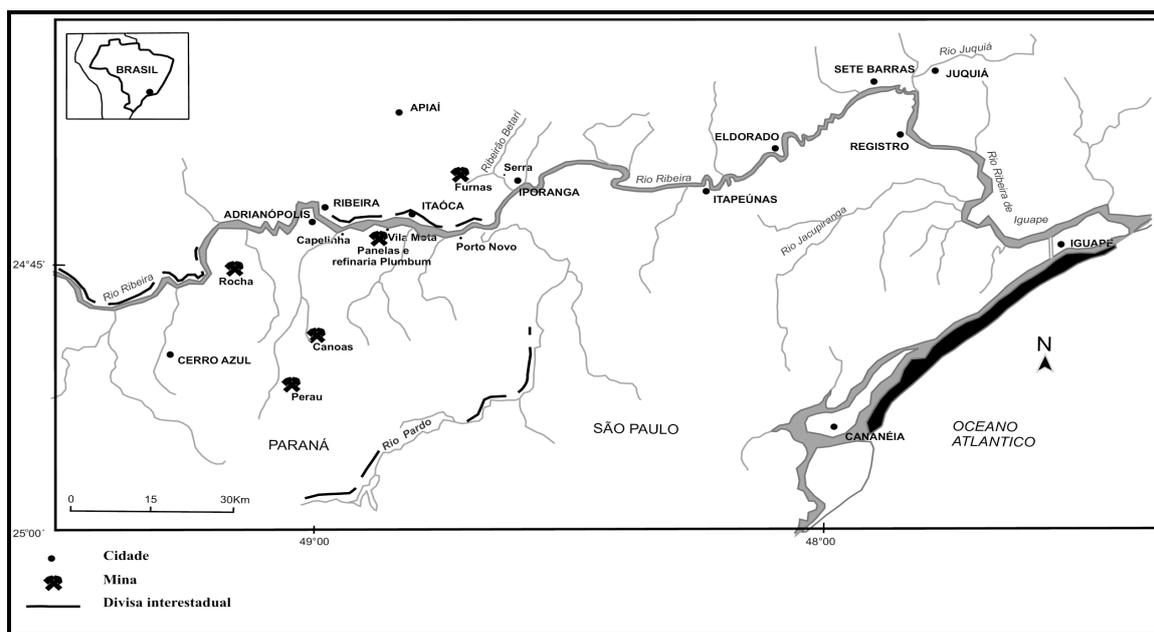


Figure 1. Ribeira do Iguape River Basin

This study aimed to investigate the presence and the concentration levels of As, Cd and Pb in water and sediments from Ribeira do Iguape River basin and its tributaries, making possible an environmental diagnosis of the region in regards to contamination of these elements. The determination of these elements in water samples was carried out by Graphite Furnace Atomic Absorption Spectrometry (GF AAS) while in the sediment samples by inductively coupled plasma atomic emission spectroscopy (ICP OES) analytical techniques. This study also characterized the sediment samples by instrumental neutron activation analysis (INAA) and the concentration of the following elements were quantified: major (Ca, Fe, K and Na), trace (As, Ba, Br, Co, Cs, Hf, Rb, Sb, Sc, Se, Ta, Th, U, Zn) and rare earth elements (La, Ce, Eu, Nd, Sm, Lu, Tb and Yb). The results for As, Cd and Pb were compared to oriented values TEL and PEL from Environmental Canada. The results obtained by INAA were compared to UCC (Upper Continental Crust) values.

2. MATERIALS AND METHODS

2.1. Sampling and sample preparation

2.1.1 Sampling

Water and sediment samples were collected in 05 (five) sampling points in the Ribeira do Iguape River. Table 1 shows the sampling points and their geographical positions. Water samples were collected in a simple way with the aid of a stainless steel bucket, transferring 250 mL volume collected in a polyethylene bottle, preserved with HNO₃. The sediment samples were collected using a Van Veen dragger and placed in stainless steel tray and transferred to 500 mL wide mouth polyethylene bottles, filled to their entire volume. The

samples were kept refrigerated in a cooler with ice and sent to the laboratory. The materials used in the collection are appropriate for each type of matrix, subject to the analytical standards and quality standards for cleanliness and preservation for the determination of trace metallic elements. Sampling points are shown in Figure 2.

Table 1. Sampling points in the Ribeira do Iguape River and its tributaries

Sampling points	Location	Geographical Position (GPS)	Depth (m)
Point 3	Ribeira River*, Itaóca - PR, downstream Plumbum refinery	S 24°39'23.70'' W 48°49'54.80''	2.0
Point 5	Betari River, Iporanga- SP, downstream Furnas River	S 24°33'8.93'' W 48°40'38.64''	3.0
Point 6	Ribeira do Iguape River, Iporanga - SP, downstream of the confluence of the river Betari	S 24°35'4.80'' W 48°35'25''	2.5
Point 7	Ribeira do Iguape River, Eldorado city, SP	S 24°31'34.90'' W 48°6'7.10''	2.0
Point 8	Ribeira do Iguape River, Registro - SP, downstream of the Juquiá River	S 24°26'24.50'' W 47°49'37.20''	2.0

*Ribeira do Iguape River is called Ribeira River in the Paraná State.

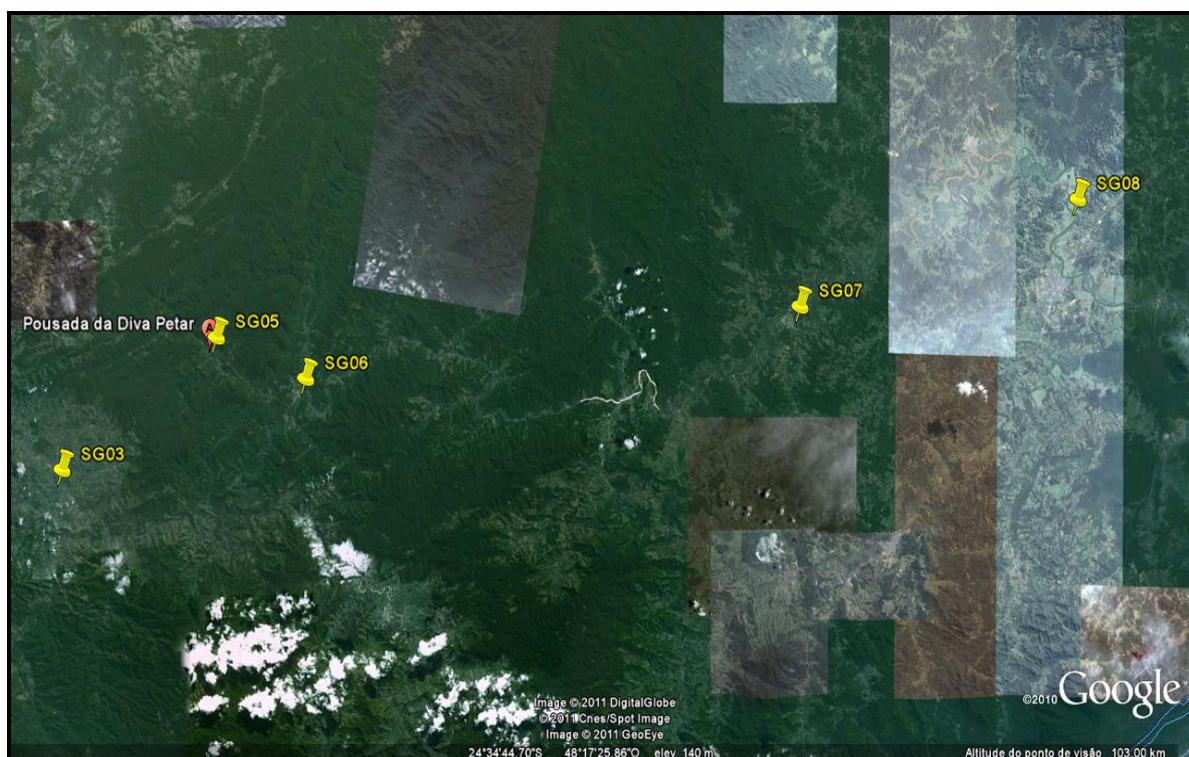


Figure 2. Location of the sampling points in the Ribeira do Iguape River and its tributaries

2.1.2. Sample preparation

Firstly, the water samples were filtered through acetate membrane with 0.45 micron porosity and collected in 50 mL volumetric flask. Following, 25 mL of the filtered samples were transferred to Teflon vials, 2.5 mL of conc. HNO₃ P.A. was added and the digestion of the samples according to SW-846-3015A - U.S. EPA procedure in a microwave oven was applied [6].

The sediment samples were previously passed a 2 mm sieve to remove the coarse fraction and dried at 40⁰ C in a ventilated oven until constant weight. The dried sample was macerated in an agate mortar and passed through a sieve of 0.063 mm (230 mesh) to obtain homogeneity of the sample. In this condition sediment samples were ready for chemical analysis. Since the determination in solid samples by ICP OES requires digestion of material, 0.5 g of the sieved material was transferred to Teflon bottles and 10 mL of concentrated nitric acid P.A. was added. In this study sample digestion was performed by a microwave-assisted method following the SW-846-3051 – US EPA for sediments [7]. After digestion the sample was transferred under filtration to 50 mL volumetric flask and completed the final volume with ultrapure water.

2.2. Sediment sample granulometric analysis

The granulometric analysis of the sediment samples was performed by CETESB (Limeira) according to the 7473 and 1664-B Standard Methods [8]. The results are presented in Table 2. The granulometric classification was based on the following criteria: silt (particles from 0.004 to 0.063mm), Clay (< 0.004 mm) and sand (> 0.063mm).

Table 2. Granulometric composition of the sediment samples

Sample	Sand (%)	Silt (%)	Clay (%)	Textural classification [9]
Point 3	49.14	41.88	8.99	Highly silt sand
Point 5	79.40	17.55	3.05	Moderate silt sand
Point 6	78.09	19.04	2.87	Moderate silt sand
Point 7	49.81	39.47	10.73	Highly silt sand
Point 8	36.30	47.61	16.09	Highly silt sand

2.3. Analytical methodologies applied

In the present study 3 analytical techniques were used: for water (GF AAS) and sediment samples (INAA and ICP OES) for the determination of metals, major and trace elements.

2.3.1. Instrumental Neutron Activation Analysis (INAA)

Activation methods are based on radioactivity measurements of that have been induced in samples by irradiation commonly with neutrons [10]. Neutron Activation Analysis is (NAA) is a sensitive analytical technique useful for performing both qualitative and quantitative multi-element analysis of major, minor and trace elements in samples from almost every conceivable field of scientific or technical interest. For many elements and applications, NAA offers sensitivities that are superior to those attainable by other methods, on the order of parts per billion or better. The application of purely instrumental procedures is commonly called Instrumental Neutron Activation Analysis (INAA). When a neutron interacts with a nucleus via non-elastic collision, a compound nucleus forms in an excited state. The compound nucleus will almost instantaneously de-excite into a more stable configuration through emission of one or more characteristic prompt gamma rays. About 70% of the elements have properties suitable for measurement by NAA [11]. Using the comparative technique, sample plus one or more standards are irradiated simultaneously with thermal neutrons (with energy about 0.04 eV). The samples may be solid, liquid or gases, and the standards should approximate the samples as closely as possible both physically and chemically. Care is taken to be sure the samples and standards are exposed to the same neutron flux. The time of irradiation is dependent upon a variety of factors and often is determined empirically; generally vary from several minutes to several hours. Often these procedures are nondestructive and for this reason are applied to the analysis of art objects, coins, forensic and environmental samples, and archaeological specimens [10].

2.3.1.1 Experimental procedure

For the multielemental analysis, approximately 150 mg of sediment (in triplicate) and reference materials were accurately weighed and sealed in pre-cleaned double polyethylene bags, for irradiation. Single and multi-element synthetic standards were prepared by pipetting convenient aliquots of standard solutions (SPEX CERTIPREP) onto small sheets of Whatman No.41 filter paper. Sediment samples, reference materials and synthetic standards were irradiated for 8 hours, under a thermal neutron flux of 1 to 5×10^{12} n cm⁻² s⁻¹ in the IEA-R1 nuclear research reactor at IPEN. Two series of counting were made: the first, after one week decay and the second, after 15-20 days. Gamma spectrometry was performed using a Canberra gamma X hyperpure Ge detector and associated electronics, with a resolution of 0.88 keV and 1.90 keV for ⁵⁷Co and ⁶⁰Co, respectively. The elements determined by using this methodology were As, Ba, Br, Co, Cr, Cs, Fe, Hf, Na, Rb, Sb, Sc, Ta, Th, U, Zn and the rare earths Ce, Eu, La, Lu, Nd, Sm, Tb and Yb. The analysis of the data was made by using in-house gamma ray software, VISPECT program to identify the gamma-ray peaks and by an ESPECTRO program to calculate the concentrations. The uncertainties of the results were calculated by error propagation. The precision and accuracy of the method was verified by using the Z score according to Bode [12] for Soil 5 (IAEA), Lake Sediment SL1 (IAEA) and BEN Basalt-IWG-GIT reference materials analyses. Details of the analytical methodology is described at Larizzatti et al [13].

2.3.2. Graphite furnace atomic absorption spectrometry (GF AAS)

The atomic absorption spectrometry with graphite furnace electrothermal heating (GF ET AAS) is an instrumental analytical technique based on the extent of absorption of radiant energy from a specific source of electromagnetic radiation by atoms in the ground state. The atoms in a ground state are subject to heating in a graphite furnace of the spectrometer. The amount of radiant energy absorbed is transformed in concentrations of analyte in the sample. This analytical technique is highly sensitive, requires only small sample volume and sample pre-treatment and can be applied to a variety of samples [14].

2.3.2.1 Experimental procedure (GF AAS)

As, Cd and Pb measurements in water samples were performed in the laboratory of ELAI - Department of Inorganic Chemistry from CETESB, according to Standard Methods 3113 [8], using a GF AAS (AAAnalyst model 600), from Perkin Elmer. After water sample preparation, as described in 2.1.2., an aliquot (600 μ L) is placed in a 2 mL plastic recipient in the autosampler carousel of the apparatus for analytical determination. Measurements were performed in duplicate, limited to a deviation $\leq 20\%$ and the concentration values were obtained by comparison with an analytical calibration curve. A calibration blank and a reagent blank were also measured, whose concentrations should be less than the detection limit (DL) of the method to verify the quality of reagents and methodological procedures, respectively. The precision and accuracy of the method were evaluated by checking the recovery (%) of analyte present in the Certified Reference Material used as a quality control sample.

2.3.3 Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP OES)

Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP OES) is a widely used analytical technique which can identify and quantify trace elements in samples of environmental interest as sediments, wastewater and natural soils, domestic and industrial sludge, biological samples, including other. In this analytical technique the sample should be in the form of a solution and converted into an aerosol mist. The aerosol is guided into the argon plasma and the atoms or ions of the elements are excited by this plasma source, the highest temperature occurring at the transition to the high-energy electrons. Immediately, the electrons undergo excited state relaxation and return to ground state accompanied by emission of light (photons), with its radiation characteristics. These radiations are directed to the monochromator or polychromator which decomposes and separates them by wavelength. The selected radiation is then directed to a detector and is converted into electronic signals. in terms of concentrations. This is a robust technique that offers the possibility of rapid sequential or simultaneous determination of multielements. The sequential optical instruments, despite the simplicity, take more time and have higher sample consumption [14].

2.3.3.1 Experimental procedure

For metal determination in sediment by using ICP OES analytical technique a previous digestion of the samples is needed. In this study sample digestion was performed by a microwave-assisted method following the SW-846-3051 – US EPA for sediments [7]. About 500 mg of sediment sample (duplicate) and 500 mg of the WQB-3 and 1646^a reference materials were weighed directly in Teflon tubes and 10 mL of conc HNO₃ was added. After the digestion procedure the sample was filtered and transferred to a volumetric flask and the final volume was completed to 50 mL. The measurements were carried out using the ICP OES SPECTRO FLAME MODULAS, CETESB (Companhia de Tecnologia de Saneamento Ambiental) equipment. Methodology validation in terms of precision and accuracy was verified by means of reference materials analyses (WQB-3 (NRCC, Canada) and Estuarine Sediment (NIST SRM 1646^a). These materials present certified/information values for the concentration of the elements analyzed by using the digestion procedure 3051 from US EPA.

3. RESULTS AND DISCUSSION

The granulometric composition of the sediment samples collected along the Ribeira do Iguape River was: points 03, 07 and 08 presented the highest proportion of silt and clay fraction (50.9, 50.2 and 63.7%, respectively). The finer the sediment, the greater its ability to retain chemicals including metals, due to high surface area, providing the capacity to interact with various molecules and ions. Points 05 and 06 presented a higher proportion of sand (79.4 and 78.1%) with lower proportion of silt (17.6 and 19.0%), respectively. These 2 sampling points presented the lowest clay proportion, 3.0 and 2.9%, respectively. (Table 2)

The precision and accuracy of the INAA analytical methodology was verified by reference materials analysis and Z value calculation was made according to Bode [12]. If $|Z| < 3$, the individual result of the control sample (reference material) lies on the 99% confidence interval of the target value. For the reference materials analyzed in the present study all the results were in the interval range of $|Z| < 3$, indicating good precision and accuracy of the INAA technique.

Table 3 shows the results obtained by INAA, mean (duplicate) and standard deviation and UCC (Upper Continental Crust) values [15]. As in Brazil we still do not have reference values for sediments these reference values are commonly used. In the present study the sediment concentration was compared to UCC values.

The results obtained by INAA for **As**, **Sb** and **Zn** showed very high concentrations in all sampling points, mainly at point 05 and much higher than UCC reference values. The REE (Ce, Eu, La, Lu, Nd, Sm, Tb and Yb) and Br, Co, Cr, Hf, Fe, Sc, Th and U showed enrichment in relation to UCC values, in all sampling points mainly at points 07 and 08. This can be partially explained by the granulometric composition of the samples from these points that presented a higher proportion of the silt+clay fraction (50.2 and 63.7%, respectively). As already said, the finer the sediment, the greater its ability to retain chemicals including metals. The other elements analyzed, in general, presented concentration values at the same order of magnitude or lower than UCC values.

Table 3. Results for the elements determined by INAA (mg kg⁻¹): mean (duplicate), standard deviation, and UCC values [15]

Elements	Sampling Points					UCC
	03	05	06	07	08	
As	6.2 ± 0.4	139 ± 4.3	6.9 ± 0.4	9.2 ± 0.3	8.7 ± 0.3	2
Ba	1121 ± 32	444 ± 14	773 ± 40	774 ± 29	773 ± 29	668
Br	3.7 ± 0.2	3.3 ± 0.2	1.6 ± 0.3	6.1 ± 0.3	5.1 ± 0.3	1.60
Ca (%)	2.4 ± 0.1	2.1 ± 0.1	2.0 ± 0.1	1.5 ± 0.0	1.5 ± 0.0	2.95
Ce	111.7 ± 3.3	67.0 ± 2.0	94.1 ± 4.1	115.8 ± 3.5	144.4 ± 4.4	65.7
Co	18.5 ± 0.3	21.3 ± 0.3	18.6 ± 0.4	20.6 ± 0.3	22.3 ± 0.3	11.6
Cr	67.5 ± 1.9	57.5 ± 1.9	73.0 ± 2.4	77.8 ± 2.5	85.5 ± 2.7	35
Cs	3.4 ± 0.2	3.3 ± 0.2	4.2 ± 0.3	5.2 ± 0.2	6.3 ± 0.3	5.8
Eu	1.52 ± 0.05	0.94 ± 0.04	1.23 ± 0.05	1.50 ± 0.04	1.84 ± 0.05	0.95
Fe (%)	4.54 ± 0.03	4.72 ± 0.03	4.46 ± 0.04	5.01 ± 0.04	5.33 ± 0.04	3.09
Hf	16.2 ± 0.4	6.9 ± 0.2	12.9 ± 0.6	14.9 ± 0.3	19.1 ± 0.5	5.80
K (%)	2.2 ± 0.2	1.2 ± 0.1	2.3 ± 0.4	2.2 ± 0.3	2.3 ± 0.4	2.87
La	55.6 ± 0.6	32.1 ± 0.3	45.7 ± 0.7	56.2 ± 0.7	69.2 ± 0.9	32.30
Lu	0.36 ± 0.02	0.35 ± 0.02	0.38 ± 0.03	0.42 ± 0.02	0.55 ± 0.03	0.27
Na	8035 ± 119	3184 ± 48	7995 ± 172	7012 ± 110	5678 ± 89	2.57 (%)
Nd	49 ± 5	27 ± 3	53 ± 2	33 ± 1	45 ± 4	25.90
Rb	104 ± 3	62 ± 2	101 ± 4	108 ± 3	123 ± 4	110
Sb	0.8 ± 0.1	6.7 ± 0.4	0.8 ± 0.1	1.2 ± 0.1	1.2 ± 0.1	0.31
Sc	12.5 ± 0.2	13.0 ± 0.2	12.3 ± 0.3	15.0 ± 0.3	16.7 ± 0.3	7
Sm	7.7 ± 0.1	5.4 ± 0.1	6.7 ± 0.2	8.3 ± 0.1	9.8 ± 0.2	4.70
Ta	1.7 ± 0.2	1.1 ± 0.1	1.2 ± 0.1	1.7 ± 0.1	1.7 ± 0.1	1.50
Tb	0.8 ± 0.1	0.7 ± 0.1	0.7 ± 0.1	0.8 ± 0.1	1.4 ± 0.1	0.50
Th	11.8 ± 0.2	7.5 ± 0.2	12.4 ± 0.4	15.1 ± 0.3	16.9 ± 0.4	10.30
U	2.4 ± 0.1	1.6 ± 0.1	2.6 ± 0.2	3.1 ± 0.2	4.2 ± 0.2	2.50
Yb	2.1 ± 0.1	2.1 ± 0.1	2.2 ± 0.1	2.3 ± 0.1	3.4 ± 0.2	1.50
Zn	91 ± 3	692 ± 20	109 ± 5	123 ± 5	122 ± 3	52

The Enrichment factor (**EF**), defined as a double ratio normalized to a reference element (**RE**), is an index used as a tool to evaluate the extent of metal pollution in a given environment [16,17]:

$$EF = ([M]/[RE]_{sed}) / ([M]/[RE]_{ref}) \quad (1)$$

Fe, Al and Sc are generally used as reference elements for normalization purposes [16]. In the present study Sc was chosen as a reference element and UCC values as reference values for sediments [15]. According to Zhang and Liu [18], if 0.5 < EF < 1.5, the elemental concentration is probably due entirely to crustal or natural weathering origins; values above 1.5 indicate anthropogenic contributions. The higher the EF value, the more severe the anthropogenic contribution.

Table 4 shows the results obtained for the EF calculated using the UCC values as reference values. There is still no regional reference value for comparison in Brazil and as such the UCC values are commonly used.

Table 4. EF values calculated for sediment samples using UCC as reference values

Elements	Sampling Points				
	03	05	06	07	08
	Enrichment Factor				
As	1.7	37.4	2.0	2.1	1.8
Ba	0.9	0.4	0.7	0.5	0.5
Br	1.3	1.1	0.6	1.8	1.3
Ca (%)	0.5	0.4	0.4	0.2	0.2
Ce	1.0	0.5	0.8	0.8	0.9
Co	0.9	1.0	0.9	0.8	0.8
Cr	1.1	0.9	1.2	1.0	1.0
Cs	0.3	0.3	0.4	0.4	0.5
Eu	0.9	0.5	0.7	0.7	0.8
Fe (%)	0.8	0.8	0.8	0.8	0.7
Hf	1.6	0.6	1.3	1.2	1.4
K (%)	0.4	0.2	0.5	0.4	0.3
La	1.0	0.5	0.8	0.8	0.9
Lu	0.7	0.7	0.8	0.7	0.9
Na (%)	0.2	0.1	0.2	0.1	0.1
Nd	1.0	0.6	1.2	0.6	0.7
Rb	0.5	0.3	0.5	0.5	0.5
Sb	1.4	11.6	1.6	1.8	1.6
Sc	1.0	1.0	1.0	1.0	1.0
Sm	0.9	0.6	0.8	0.8	0.9
Ta	0.6	0.4	0.5	0.5	0.5
Tb	0.9	0.7	0.8	0.8	1.1
Th	0.6	0.4	0.7	0.7	0.7
U	0.5	0.3	0.6	0.6	0.7
Yb	0.8	0.8	0.8	0.7	1.0
Zn	1.0	7.2	1.2	1.1	1.0

EF > 1.5 –highlighted

From Table 4 it can be seen that an **EF > 1.5** was found for As in all sampling points (from 1.7 to 37.4); Sb at points 05, 06, 07 and 08 (from 1.6 to 11.6); Hf at point 03 (1.6) and Zn in point 05 (7.2). Point 05 presented the higher EF values for As, Sb and Zn. Values above 1.5 indicate anthropogenic contributions and the higher the EF value, the more severe the anthropogenic contribution.

The elements Ca, Cs, K, Na and Rb presented **EF < 0.5** in all sampling points. All the other elements analyzed showed **0.5 < EF < 1.5** indicating that the elemental concentration is probably due entirely to crustal or natural weathering origins.

Tables 5 and 6 show the results obtained for the elements As, Cd and Pb in water by GF AAS and in sediment samples by ICP OES, respectively. The oriented values TEL and PEL are also shown. These oriented values were established by the CCME [19] and adopted by CETESB for sediment quality monitoring programs. TEL (Threshold Effect Level) is the limit below which no adverse effects on the biological community is observed and PEL, the probable level of occurrence of adverse effects on the biological community.

Table 5. Results for elements determined in water samples by GF AAS (mg L⁻¹)

Elements	Sampling Points				
	03	05	06	07	08
As	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005
Cd	< 0.0002	< 0.0002	< 0.0002	< 0.0002	< 0.0002
Pb	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005

Table 6. Results (mg kg⁻¹) for elements determined in sediment samples by ICP OES, TEL and PEL values (mg kg⁻¹)

Elements	Sampling Points					TEL	PEL
	03	05	06	07	08		
As	5.72	72.1	9.91	9.62	7.18	5.9	17.0
Cd	< 0.05	0.71	0.07	0.07	0.08	0.6	3.5
Pb	42.7	474	33.2	41.8	43.8	35.0	91.3

The elements **As**, **Cd** and **Pb** presented very low concentrations in all sampling points and below the detection limits (DL) of GF AAS analytical technique for water samples (Table 5). On the other hand, the concentration values for these elements in sediment samples were much higher. The results for **As** surpassed the TEL limit in points 06, 07 and 08 and PEL in point 05. **Cd** surpassed the TEL value only in point 05. The results for **Pb** exceeded the TEL in points 03, 07 and 08 and PEL at point 05. As can be seen point 05 exceeded the TEL limits for the three elements and PEL for **As** and **Pb**. It should be noted that the concentration values for these elements were much higher than PEL levels indicating the probability of the occurrence of adverse effects on the biological community.

Point 5 is located near the old Furnas mine that started its operation in 1919. The main ore of this mine was composed of galena (lead sulfide: 87% **Pb** and 13% **S**), argentifera (lead ore with high level of **Cu**), pyrite (iron disulfide: 53.4% **S** and 46.6% **Fe**), sphalerite (zinc sulfide: 67% **Zn** and 33% **S**) associated to arsenopyrite (Fe sulfoarsenieto: 46% **As**, 19.7% **S** and 34.3% **Fe**), chalcopyrite (**Cu** and **Fe** disulfide: 34.5% **Cu**, 30.5% **Fe** and 35% **S**) and estibnita (amonium trisulfide: 71.4% **Sb** and 28.6% **S**). This mine is located on the banks of the Furnas River, a tributary of the Betari River which in turn is a tributary of the Ribeira do Iguape River (Iporanga – SP).

The results for **As**, **Cd** and **Pb** by ICP OES and **As**, **Sb** and **Zn** by INAA in sediment samples at point 5 showed a high contamination level for these elements and can be classified as very poor quality for **As** (> 25.5 mg.kg⁻¹), **Pb** (> 137.0 mg.kg⁻¹) and **Zn** (> 473.0 mg.kg⁻¹) and good quality for **Cd** (0.6<**Cd**<2.1 mg kg⁻¹) according to the TEL and PEL oriented values and adopted by CETESB [3]. The high concentration for **Sb** at point 5 maybe related to sulfides associated to calcareous minerals explored in the region. The high concentration of metals

reflects the past mining activities of the region, as well as local geological composition. Although all mining operations have long ceased the effects on the environment are still present and felt.

3. CONCLUSIONS

The analytical techniques (INAA and ICP OES) applied in the present study for sediment samples and GF AAS for water samples proved to be accurate and sensitive for the determinations of some major and trace elements and heavy metals.

The results obtained by INAA for **As**, **Sb** and **Zn** showed very high concentrations in all sampling points, mainly at point 05 and much higher than UCC reference values. The REE (Ce, Eu, La, Lu, Nd, Sm, Tb and Yb) and Br, Co, Cr, Hf, Fe, Sc, Th and U showed enrichment in relation to UCC values, in all sampling points mainly at points 07 and 08. The other elements analyzed, in general, presented concentration values at the same order of magnitude or lower than UCC values.

The Enrichment factor (**EF**), an index used as a tool to evaluate the extent of metal pollution in a given environment showed an **EF > 1.5** for **As** in all sampling points; **Sb** at points 05, 06, 07 and 08; **Hf** at point 03 and **Zn** at point 05. Point 05 presented the higher EF values for **As**, **Sb** and **Zn**. Values above 1.5 indicate an anthropogenic contribution. Most of the elements analyzed showed **0.5 < EF < 1.5** indicating that the elemental concentration is probably due to crustal or natural weathering origins.

Very low concentrations for **As**, **Cd** and **Pb** were found for the water samples in all sampling points. On the other hand, the concentration values for these elements in sediment samples were much higher exceeding the TEL limit for **As** in the points 06, 07 and 08 and PEL in point 05. **Cd** surpassed the TEL value only in point 05. **Pb** exceeded the TEL in points 03, 07 and 08 and PEL at point 05. Point 05 exceeded the TEL limits for the three elements and PEL for As and Pb.

The high concentration of As and metals Cd, Pb, Sb and Zn reflect the past mining activities of the region, as well as local geological composition. Although all mining operations have long ceased the effects on the environment are still present and felt.

ACKNOWLEDGMENTS

The authors wish to thank professionals from Laboratório de Química Inorgânica e Radioatividade from CETESB (São Paulo and Limeira) for their help and support in this study.

1. REFERENCES

1. ISA – INSTITUTO SOCIOAMBIENTAL: *Diagnóstico Socioambiental do Vale do Ribeira*: Documento Síntese. São Paulo: Instituto Socioambiental, (1998).

2. J.P. Capobianco. *Análise da aplicabilidade do princípio da precaução no processo de licenciamento ambiental da UHE Tijuco Alto no Rio Ribeira de Iguape*, Campinas: Instituto de Economia/UNICAMP, 2000.
3. CETESB. “Relatório de qualidade das águas interiores do estado de São Paulo 2009”, <http://www.cetesb.sp.gov.br/agua/rios/publicações.asp> (2010). Accessed in May, 2011.
4. A. Mudroch, S.D. Macknight. *Handbook of Techniques for Aquatic Sediments Sampling*, CRC Press, second edition (1997).
5. T. J. Bomfim, C.E.C. Veiga. *Utilização de biomarcadores em peixes como ferramenta para avaliação de contaminação ambiental por mercúrio (Hg)*. *Revista Eletrônica O ecologia Brasiliensis*, 12 (4), 680-693 (2008).
6. _____, Microwave Assisted Acid Digestion of Aqueous samples and extracts, *Method 3015A*, <http://www.epa.gov/waste/hazard/testmethods/sw846/pdfs/3015a.pdf>, accessed in May 2009.
7. USEPA – United States Environmental Protection Agency, Microwave Assisted Acid Digestion of Sediment, Sludges, Soils and Oils, *Method 3051A*, <http://www.epa.gov/waste/hazard/testmethods/sw846/pdfs/3051a.pdf>, accessed in May 2009.
8. APHA – American Public Health Association, *Standard Methods for the Examination of Water and Wastewater*, 21th ed, New York, USA (2008).
9. B.W. Flemming. A revised textural classification of gravel free muddy sediments on the basis ternary diagrams. *Continental Shelf Research*, **20**, pp. 1125-113 (2000).
10. D. A. Skoog, F. J. Holler, T. A. Nieman, *Principles of Instrumental Analysis*, Fifth edition, Harcourt Brace & Company, Sea Harbor Drive, Orlando, Florida, 849p., (1998).
11. Archaeometry Laboratory – University of Missouri Research Reactor, Columbia - http://archaeometry.missouri.edu/naa_overview.html, August (2009).
12. Bode P (1996) Instrumental and organizational aspects of a neutron activation analysis laboratory, Interfaculty Reactor Institute, Delft, Netherlands, p. 147, 1996.
13. F, E, Larizzatti, D, I, T, Favaro, S, R, D, Moreira, B, P, Mazzilli, E, L, Piovano, Multielemental determination by instrumental neutron activation analysis and recent sedimentation rates using ²¹⁰Pb dating method at Laguna del Plata, Cordoba, Argentina, *Journal of Radioanalytical and Nuclear Chemistry*, **249**(1), pp. 263-268 (2001).
14. G.A.Quinágua. Caracterização dos níveis basais de concentração de metais nos sedimentos do sistema estuarino da Baixada Santista. 2006. 239 f. Tese (Doutorado em Química)-Instituto de Química, Universidade de São Paulo, São Paulo, SP, (2006).
15. K.H. Wedepohl. The composition of the continental crust. *Geochimica et Cosmochimica Acta* **59** (7), pp.1217-1232 (1995).
16. S. Audry, J. Schaefer, G. Blanc, J-M Jousneau. Fifty-year sedimentary record of heavy metal pollution (Cd, Zn, Cu, Pb) in the Lot River reservoirs (France). *Environ. Pollut*, **132**, pp.413-426 (2004).
17. F.C. Gomes, J.M. Godoy, M.L.D.P. Godoy, Z.L. Carvalho, R.T. Lopes, J.A. Sanchez-Cabeza, L.D. Lacerda, J.C. Wasserman. Metal concentrations, fluxes, inventories and chronologies in sediments from Sepetiba and Ribeira Bays: A comparative study. *Marine Pollution Bulletin*, **59**, pp.123-133 (2009).
18. J. Zhang & C.L. Liu. Riverine Composition and Estuarine Geochemistry of Particulate Metals in China – Weathering Features, Anthropogenic Impact and Chemical Fluxes. *Estuarine, Coastal and Shelf Science*, **54**, pp. 1051-1070 (2002).
19. CCME Canadian Environmental Quality Guidelines - Summary Tables, <http://www.ec.gc.ca/ceqg-rcqe/English/ceqg/sediment/default.cfm>, accessed in May 2009.