METAL AND TRACE ELEMENT SEDIMENT ASSESSMENT FROM SALTO GRANDE RESERVOIR, SÃO PAULO STATE, BRAZIL, BY INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS

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ABSTRACT

The Salto Grande Reservoir is used for electric generation, irrigation, fish farming, recreation and water supply for the region's cities. The reservoir belongs to the city of Americana, located in on the eastern region of São Paulo State, Brazil. It belongs to the Piracicaba River Hydrographic Basin, the second most important economic and populated region and one of the most polluted areas in the State. This basin is located in a highly industrialized and agricultural region. Due to urban, industrial and agricultural activities as well as sewage wastes the water and sediments of this reservoir and surroundings are extremely contaminated, mainly by metals, according to CETESB (Environmental Control Agency of the São Paulo State). In order to obtain better information about its sediment contamination the present study reports results of the concentration of some major (Ca, Fe, K and Na), trace (As, Ba, Br, Co, Cr, Cs, Hf, Rb, Sb, Se, Ta, Th, U, Zn and rare earth (Ce, Eu, La, Lu, Nd, Sc, Sm, Tb and Yb)) elements in sediments and Cd, Cr, Cu, Ni and Pb concentration in sediments and water from the Salto Grande Reservoir. Multielementar analysis was carried out by Instrumental Neutron Activation Analysis (INAA). Multielemental concentrations in the sediment samples were compared to NASC (North American Shale Composite) values. The concentration values for metals As, Cd, Cr, Cu, Pb, Ni and Zn were compared to the Canadian Council of Minister of the Environment (CCME) oriented values (TEL and PEL) and adopted by CETESB,

1. INTRODUCTION

The Salto Grande reservoir is located in Americana County and occupies an area of 13 km^2. It belongs to the Piracicaba River Hydrographic Basin, the second most important economic and populated region. It is also one of the most polluted areas in São Paulo State. This basin is located in a highly industrialized and agricultural region. The reservoir was built during 1940 and 1949 with the main purpose of electric generation, but nowadays it is used for irrigation, fish farming, recreation and water supply for the region.

The reservoir has an average depth of 8.00 m and a maximum depth of 19.80 m. Its length is 17 km and the maximum volume is 106 x 10^6 m^3, with a mean retention time of 30 days. This system serves as a receptor of residues produced by the Paulínia and Campinas cities [1]. Due to this sediment and waters from Salto Grande reservoir are highly affected mainly by heavy

metals, which presents high toxicity for the biota, according to the results obtained by CETESB (Companhia Ambiental do Estado de São Paulo) in its monitoring program [2]. Some metals are considered essential to human health and survival of several organisms (micronutrients) but others such Cd, Pb, Cu, Cr, Hg, Ni and Zn are considered contaminants when present in high concentrations, presenting toxicity for different life forms [3-6]. Metals are found in different chemical forms (elemental, dissolved, adsorbed to solid particles, etc) and are distributed in several environmental compartments (soil, water, air, sediment and live organisms) which strongly interact with each other. In general, the mixture and deposition of chemical substances in aquatic environments settles and accumulates in bottom sediments. Consequently, bottom sediments can be a sink as well as a source of contaminants in the water body depending on local physico-chemical conditions [1,3,4,7,8].

Natural processes responsible for the formation of bottom sediments are altered by anthropogenic activities. Analysis of sediments provides information of environmental significance and their chemical composition characterization is needed to understand the anthropogenic load on water bodies. Nuclear and related analytical techniques such as Neutron Activation Analysis (NAA) and X-Ray Fluorescence spectrometry (XRF) have proven to be very useful for elemental characterization, and gamma spectrometry for radionuclides determination in such kind of samples. Although these are non-destrutive techniques, they require sample preparation prior to analysis so as not contribute significantly to the overall uncertainty in the measurement process [9].

Most of major, minor and trace elements determination in sediments are made by destructive analytical techniques such as inductively coupled plasma atomic emission spectrometry (ICP OES) or mass spectrometry (ICP-MS), monoelemental technique as atomic absorption spectrometry, some electrochemical methods, isotopic dilution mass spectrometry (ID-MS), fluorimetric and spectrophotometric methods are also used.[10]

The purpose of the present study was to perform a multielemental characterization in a sediment from Salto Grande reservoir by Instrumental Neutron Activation Analysis (INAA). The determination and distribution of the metals Cd, Cr, Cu, Ni and Pb in sediment and water samples were also made. The sediment toxicity for the *Vibrio fischeri bacteria* and for the local benthonic community was evaluated. The results obtained by INAA were compared to the North American Shale Composite (NASC) values and the Enrichment Factor (EF) was calculated. For metal and semi-metals As, Cd, Cr, Cu, Pb, Ni and Zn the concentration values were compared to the TEL and PEL oriented values from Environmental Canada and adopted by CETESB for sediment quality monitoring.

2. MATERIAL AND METHODS

2.1. Study location

The Salto Grande reservoir is located in the eastern region of São Paulo state, in the Americana County and belongs to the UGRHI 5 (Unidade de Gerenciamento de Recursos Hídricos do Estado de São Paulo). Figure 1 shows the location of Salto Grande reservoir in the UGRHI 5.
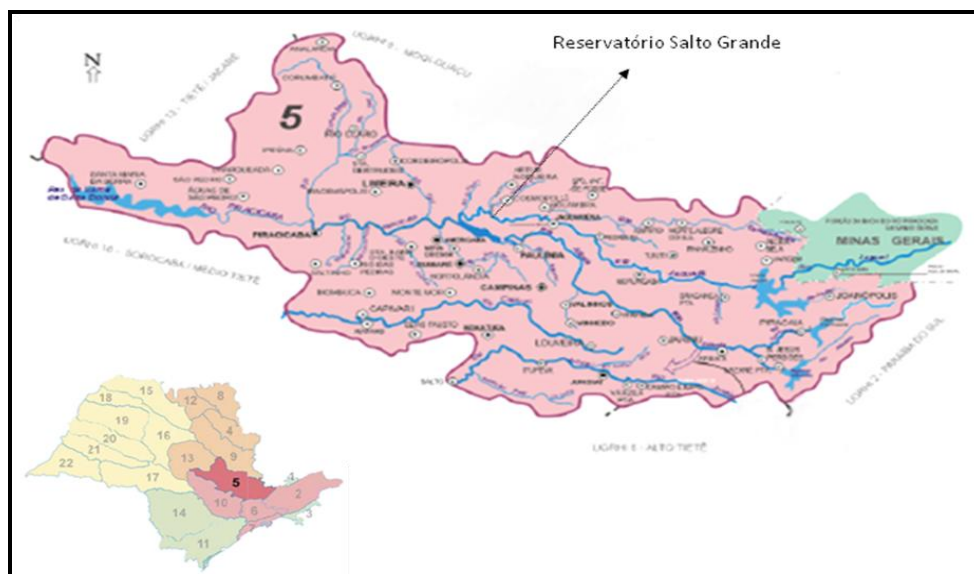
Figure 1. Salto Grande reservoir in the UGRHI 5 (CETESB, 2009)

2.2. Sampling and sample preparation

Sediment and water sampling from Salto Grande reservoir were carried out on June 1st, 2011 by the Setores de Amostragem (ELCA) and Comunidades Aquáticas (ELHC) from CETESB (Companhia Ambiental do Estado de São Paulo). The sampling point was the same used for sample collection (ATSG2800) for CETESB in its environment program for sediment quality. This point is located in the central region of the reservoir, in front of the Praia Azul beach (latitude 22º43'30"). Figure 2 shows the sampling point location. Water samples were collected with a stainless steel bucket and kept in appropriate recipients for metal determination, preserved with HNO_3 addition and kept in a refrigerator. Sediment samples were collected by using an Ekman sampler in appropriate recipients and kept refrigerated for metal determinations and acute toxicity for *V. Fisheri* bacteria. For the benthic community evaluation the samples were collected in triplicate, preserved in formaldehyde, kept in polyethylene bags and transported to the laboratory where they were washed in a 0.50 mm sieve, separated and the organisms identified.

The sediment samples were first passed through a 2 mm sieve, then dried at 40 ℃ in a ventilated oven until constant weight, ground in a mortar, passed through a 0.250 mm sieve and then homogenized before analysis. The total fraction of the sediment was analyzed (< 2 mm). The humidity (%) obtained for the dried sediment was 73.3 % at 40 ℃ until constant weight.

The granulometric analysis of the sediment samples was performed by CETESB according to the 7473 and 1664-B Standard Methods [11].
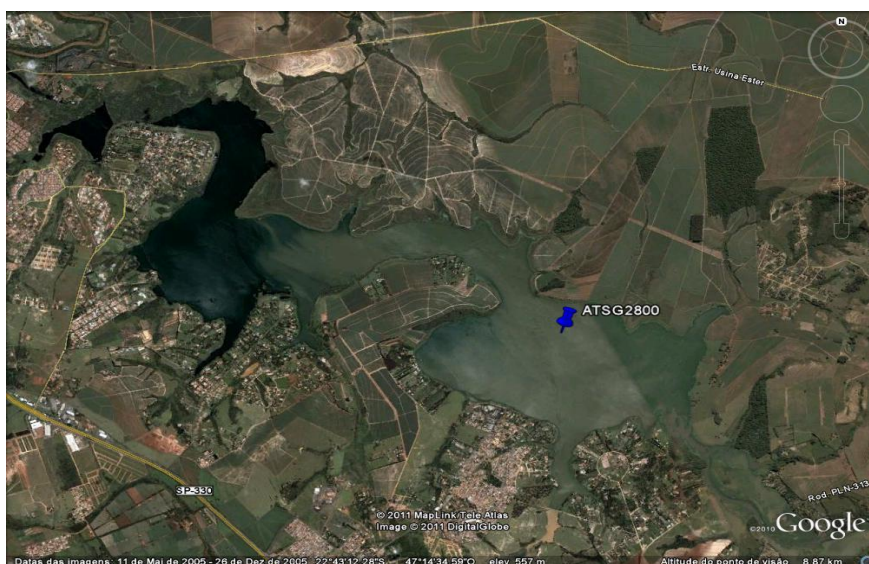
Figure 2. Sampling point location at Salto Grande reservoir

2.3. Instrumental Neutron Activation Analysis (INAA)

2.3.1. Instrumental Neutron Activation Analysis (INAA) – theoretical aspects

Activation methods are based on radioactivity measurements of that have been induced in samples by irradiation commonly with neutrons [12]. Neutron Activation Analysis is (NAA) is a sensitive analytical technique useful form 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 trough emission of one or more characteristic prompt gamma rays. About 70% of the elements have properties suitable for measurement by NAA [13]. 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 [12].

2.3.2. 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 5x 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 ^{57}Co and ^{60}Co, 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 errors propagation. The precision and accuracy of the method was verified by using the Z score according to Bode [14] 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 [15].

2.4. Water and Sediment sample microwave-assisted digestion

For metal determination in water and sediment samples by using ICP OES and GF AAS analytical techniques the previous digestion of the samples is required. In this study sample digestion was performed by microwave-assisted method following the SW-846-3051 – US EPA for sediments and SW-846-3015 – USEPA for water samples [16,17].

2.4.1. Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP OES)

This analytical technique shows multielemental capacity, can be sequential or simultaneous, high sensitivity and analytical versatility [5,6,18]. In this study the determination of the concentration of Cu, Cr and Ni was done in the water and sediment samples digested according to the procedure 2.4. The analytical procedure followed the 3120B Standard Methods [11]. The measurements of these metals were done in the Setor de Química Inorgânica (ELAI) from CETESB, ICP OES equipment Spectro model Flame Modulo.

2.4.2. Graphite Furnace Atomic Absorption Spectrometry (GFAAS)

Graphite furnace atomic absorption spectrometry (GFAAS) is also known by various other acronyms, including electro thermal atomic absorption spectrometry (ETAAS). Briefly, the technique is based on the fact that free atoms will absorb light at frequencies or wavelengths characteristic of the element of interest (hence the name atomic absorption spectrometry). Within certain limits, the amount of light absorbed can be linearly correlated to the concentration of a present analyte. Free atoms of most elements can be produced from samples by the application of high temperatures. In GFAAS, samples are deposited in a small graphite tube, which can then be heated to vaporize and atomize the analyte.

The high specificity, selectivity, easy operation, low detection limits and low cost compared to other techniques are the major advantages of GFAAS [5,6,19]. In the present study, Cd and Pb determinations in water and sediment samples were performed according to the 3113 Standard Methods [11]. The measurements of these metals were done in the Setor de Química Inorgânica (ELAI) from CETESB, GFAAS equipment Perkin Elmer model AAnalyst600.

2.5. Acute toxicity tests with *Vibrio fischeri*

Among the various ecotoxicological tests available, the acute toxicity using the luminescent bacteria *Vibrio fischeri* has been widely used for determining toxicity in environmental samples in different parts of the world. This test is based on the measument of the luminescence produced by a culture of approximately one million cells of *Vibrio fischeri*. During its metabolism, bacteria use of the energy produced in the Krebs cycle to emit a 490 nm wavelength of blue-green light when in contact with toxic substances that can interfere with energy production. The bacteria decrease or cease light emission, which can be measured in a luminometer and the result expressed as percentage inhibition of luminescence, EC20 (concentration of test sample causing 20% decrease in light emission) or EC50 (concentration the tested sample causing 50% decrease in light output). As the observed effect is acute, the tests are performed over a short time, which in the case of *Vibrio fischeri* can be 5, 15 or 30 minutes of contact being 15 minute exposure the most commonly used. In spite of using a marine organism the test shows similar results for freshwater and sediment toxicity assessment. To perform this test in sediment samples it is necessary to extract the interstitial water. This extraction can be obtained, among other methods, by centrifugation of the sediment at a speed of 2000 x g for 30 minutes. The great advantage of this test is its simplicity and quickness, as well as a small sample size. [20, 21,22]

2.6. Benthic Community Evaluation

The benthic community corresponds to the set of organisms living all or part of their life cycle in sediments of aquatic environments. The macroinvertebrates (invertebrates selected network of 0.5 mm) that make up this community have been systematically used in biomonitoring networks in several countries, as they occur in all types of aquatic ecosystem; live in close association with the substrate, the final pollutant receptor; display wide range of tolerance to various degrees and types of pollution, have low locomotion capacity, and are continually subject to aquatic environmental changes allowing for long-term evaluation of regular, intermittent and diffuse pollutant discharges as well as subject to variable pollutant concentrations. The sediment samples collected are washed in mesh net of 0.5 mm and organisms retained are screened and sorted by species. According to the level of environmental pollution, a replacement process in the community will take place in which the most sensitive populations tend to diminish and even disappear, while species with higher resistance will persist in the environment and expand their populations. With increasing pollution, the more resistant will also tend to diminish and even disappear. The evaluation of the variety of species and number of organisms of each species indicate the degree of degradation environment [2,23]. The benthic community evaluation was done in the Setor de Comunidades Aquáticas (ELHC) from CETESB.

3. RESULTS AND DISCUSSION

The granulometric analysis for the sediment sample collected at the Salto Grande Reservoir presented the following composition: 19.93% of silt (0.004 to 0.063 mm); 79.93 % of Clay (< 0.004 mm) and 0.09% of sand (> 0.063 mm). The composition of silt + clay correspond to the 99.86% of the sediment sample. This means a great adsorption capacity of metals. In other words, 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.

The precision and accuracy of the INAA analytical methodology was verified by reference materials analysis and Z value calculation was made according to Bode [24]. 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 1 shows the results obtained by INAA, mean (triplicate) and standard deviation, NASC (North American Shale Composite) values [25], Enrichment Factors, TEL and PEL oriented values from Environment Canada [26]. These both TEL and PEL values were established by the CCME and adopted by CETESB for sediment quality monitoring program. 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 [2,26]. The value obtained for As was lower than TEL and Cr and Zn between TEL and PEL oriented values. There is no oriented value for the other elements analyzed.

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 [24,27]:

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

Fe, Al and Sc are generally used as reference elements for normalization purposes [24]. In the present study Sc was chosen as a reference element and NASC values as reference values for sediments [28]. According to Zhang and Liu [29], 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.

The elements that presented EF > 1.5 were **As, Br, La, Nd** and **Sm.** As a result, a strong anthropogenic influence was observed for these elements, probably due to the domestic and industrial effluents from the rivers that flow into the reservoir. For the other elements analyzed by INAA the $0.5 < EF < 1.5$ were obtained indicating that these concentrations are probably due entirely to crustal or natural weathering origins.

Table 1. Results for the elements determined by INAA (mg kg^{-1}): mean (triplicate) (dry basis), standard deviation, NASC, EF, TEL and PEL values

Element	Concentration (mg kg^{-1})	NASC [25]	EF	TEL [26]	PEL [26]
As	3.8 ± 0.7	2.0	1.52	5.9	17
Ba	491 ± 81	636	0.62		
Br	6.5 ± 0.3	0.69	7.56		
Ca (%)	0.40 ± 0.03	2.59	0.12		
Ce	135 ± 17	73.0	1.48		
Co	19.1 ± 0.6	28.0	0.55		
Cr	81.1 ± 9.8	125.0	0.52	37.3	90.0
Cs	5.5 ± 0.2	5.2	0.85		
Eu	2.26 ± 0.03	1.24	1.46		
Fe (%)	6.3 ± 0.2	4	1.26		
Hf	3.44 ± 0.16	6.3	0.44		
K (%)	1.14 ± 0.03	3.29	0.28		
La	85 ± 2	32.0	2.13		
Lu	0.46 ± 0.03	0.48	0.77		
Na	693 ± 24	7500	0.07		
Nd	69 ± 9	27.4	2.02		
Rb	82 ± 5	125	0.53		
Sb	0.72 ± 0.04	2.09	0.28		
Sc	18.7 ± 1.1	15.0	1.00		
Sm	11.2 ± 0.1	5.7	1.58		
Ta	1.4 ± 0.1	1.1	1.00		
Tb	1.1 ± 0.2	0.85	1.04		
Th	19.4 ± 1.5	12.0	1.30		
U	4.4 ± 0.2	2.7	1.31		
Yb	2.6 ± 0.2	3.1	0.67		
Zn	157 ± 6	85	1.49	123	315

Figure 3 presents the concentration values for the elements analyzed normalized by NASC values. In Figure 3 it can be seen that there was enrichment for most of REE (La, Ce, Eu, Nd, Sm, Tb), U and Th. For Ba, Rb, Co, Cr and Yb depletion in regards to NASC values was observed.

Table 2 presents the concentrations for Cd and Pb obtained by GF AAS and Cr, Cu and Ni by ICP OES for the sediment sample, besides TEL and PEL oriented values from CCME [26]. For Cd and Pb the concentration obtained were below the TEL values, however Cr and Cu showed a concentrations higher than TEL but lower than PEL oriented values. Ni presented concentration value higher than PEL value. This is indicative of probable level of occurrence of adverse effects on the biological community for this element.
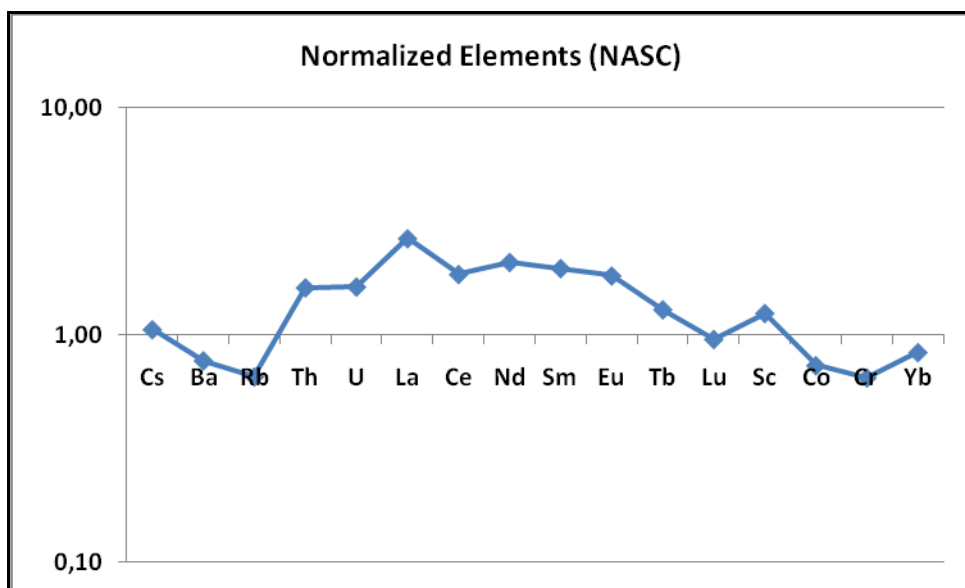
Figure 3. Normalized elements (NASC) for the sediment sample from Salto Grande reservoir

Table 3 presents Cd and Pb results obtained by GFAAS and Cr, Cu and Ni by ICP OES for the water sample collected at the same point. As can be seen, all the concentrations were below the quantification limits for these elements in their respective analytical technique.

The results show that, despite the presence of these metals in the sediment at concentrations that may be hazardous to aquatic biota, especially for Ni in conditions of probable occurrence of adverse effects on the biological community, they were not available for the water body. It seems that the sediment of the reservoir is working as a sink for these metals in the water body, but it can cause a risk for the organisms that are directly in contact with the sediment compartment.

Table 2. Results for the elements determined by GFAAS and ICP OES (mg kg^{-1}) in the sediment sample: mean (dry basis), TEL and PEL values

Elements	Concentration (mg kg^{-1})	TEL [26]	PEL [26]
Cd[1]	0.24	**0.6**	**3.5**
Cr[2]	74.6	**37.3**	**90.0**
Cu[2]	46.8	**35.7**	**197.0**
Ni[2]	36.3	**18.0**	**35.9**
Pb[1]	29.4	**35.0**	**91.3**

(1)GF AAS; (2)ICP OES

Table 3. Results for the elements determined in the water sample by GFAAS and ICP OES (mgL^{-1})

Element	Concentration (mg L^{-1})
Cd[1]	< 0.0002
Cr[2]	< 0.02
Cu[2]	< 0.01
Ni[2]	< 0.02
Pb[1]	< 0.005

(1)GF AAS; (2)ICP OES

The benthic community evaluation performed in the sediment sample showed low diversity of organisms and 5 different species were found. Four species belongs to the Oligochaeta class and one to the Chironomidae family. Table 4 presents the number of organisms found in each sample replicate, the density (number of individuals/m^2 of the sediment) and the relative abundance of each species. Results show low relative abundance of tolerant species (*Dero* and *Chironomus*) (31.22%), dominance of *Opystocysta* (50.05%) and absence of sensitive species in this environment. The Ephemeroptera, Odonata and Trichoptera families and Chironomidae-Tanytarsini *Stempellina* are considered sensitive species and *Limnodrilus hoffmeisteri*, *Dero*, *Pristina*, *Pristinella* and *Chironomus* as tolerant [2,23]. The evaluation of results indicates the diagnostic of environment quality for the biological community. The sediment sample evaluated in the present study was classified as regular quality.

Table 4. Number of organisms per replicate, density and relative abundance

Organisms	Replicate 1	Replicate 2	Replicate 3	Density (ind/m^2)	Relative abundance (%)
Aulodrilus	72	94	34	3378.67	18.37
Dero	181	108	49	5709.95	31.04
Stephensoniana	3	0	1	67.57	0.37
Opystocysta	293	84	168	9206.87	50.05
Chironomus	1	0	1	33.79	0.18

The *Vibrio fischeri* acute toxicity test performed with the interstitial water of the sediment sample, extracted by centrifugation, did not present toxic effect for the bacteria, which reinforces the hypothesis that these metals present in the sediments are not available for the water body.

4. CONCLUSIONS

The determination of metals and trace elements by way of Instrumental Neutron Activation Analysis (INAA) proved to be highly appropriate and can be an extremely important tool for sediment monitoring as its sensitivity, precision and accuracy are very reliable.

The sediment sample from the Salto Grande reservoir analyzed by INAA presented an enrichment for the elements Ce, Eu, La, Nd, Sc, Sm, Ta, Th and U in relation to NASC values. The elements Ba, Rb, Co, Cr and Yb were depleted in relation to NASC values.

The results obtained for metals in the sediment sample by ICP OES (Cr, Cu and Ni) and GF AAS (Cd and Pb) and INAA (Zn) analytical techniques showed that the concentrations of Cr, Cu, Ni and Zn are between TEL and PEL oriented values from CCME, indicating the probable occurrence of toxic effects to biota. The concentrations levels of Cd and Pb were lower than TEL values.

The benthic community evaluation performed in the sediment sample showed low diversity of organisms and 5 different species were found. The results evaluation classified the sediment sample as regular quality for the biological community.

The *Vibrio fischeri* acute toxicity test performed with the interstitial water of the sediment sample, did not present toxic effects on the bacteria. This reinforces the hypothesis that these metals present in the sediments are not available in the water body.

These results are preliminary results and other sampling campaigns must be undertaken in order to obtain further data for a more complete evaluation of the sediment and water monitoring quality of the Salto Grande reservoir.

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REFERENCES

1. L. G. Espíndola, M. A. Leite, C. B. Dornfeld (Ed.), *Reservatório de Salto Grande (Americana, SP): caracterização, impactos e propostas de manejo*. RiMa, São Carlos, SP, Brazil, 484p. (2004).
2. 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.
3. C. B. Dornfeld, Utilização de análises limnológicas, bioensaios de toxicidade e macroinvertebrados bentônicos para o diagnóstico ambiental do reservatório de Salto Grande (Americana, SP). 211f. Dissertação (Mestrado em Ciências da Engenharia Ambiental)-Escola de Engenharia de São Carlos, Universidade de São Paulo, São Carlos, SP, Brazil, http://www.teses.usp.br/teses/disponiveis/18/18139/tde-14072005-153541/ (2002). Accessed in August 2009.
4. G. A. Quináglia, Caracterização dos níveis basais de concentração de metais nos sedimentos do sistema estuarino da Baixada Santista. 239 f. Tese (Doutorado em Química)-Instituto de Química, Universidade de São Paulo, São Paulo, SP, (2006).

5. G. F. Nordberg, et. al. (Ed.), *Handbook on the toxicology of metals*. 3rd Ed. Elsevier, Amsterdam, Netherlands, 995p. (2007).

6. B. Sarkar (Ed.), *Heavy Metals in the Environment*. M. Dekker, New York, USA, 725p. (2002).

7. L. Bervoets, L. Int Panis, R. Verheyen, Trace metal levels in water, sediments and *Chironomus gr. thumni*, from different water courses in Flanders (Belgium). *Chemosphere*, [S.l.], **v, 29**, n. 8, pp. 1591-1601 (1994).

8. W. Salomons, W. M. Stigliani, (Ed.), *Biogeodynamics of pollutants in solils and sediments: risk assesment of delayed and non-linear responses*. Springer, Berlim, Germany, 353p. (1995).

9. IAEA - International Atomic Energy Agency, Collection and preparation of bottom sediment samples for analysis of radionuclides and trace elements, *IAEA_TECDOC-1360* (2003).

10. E. Bostelmann, Avaliação da concentração de metais em amostras de sedimento do reservatório Billings, braço Rio Grande, São Paulo, Brasil. Dissertação - Instituto de Pesquisas Energéticas e Nucleares/USP. São Paulo, SP, brazil. 130 p. (2006).

11. APHA – American Public Health Association, *Standard Methods for the Examination of Water and Wastwater, 21th ed*. New York, USA (2008).

12. D. A. Skoog, F. J. Holler, T. A. Nieman, *Principles of Instrumental Analysis*, Fifth edition, Hardcourt Brace & Company, Sea Harbor Drive, Orlando, Florida, USA, 849p. (1998).

13. ARCHAEOMETRY LABORATORY – University of Missouri Research Reactor, Columbia, http://archaeometry.missouri.edu/naa_overview.html, August (2009).

14. P. Bode, Instrumental and organizational aspects of a neutron activation analysis laboratory. *Interfaculty Reactor Institut*. Delft, Netherlands. 147 p. (1996).

15. 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 ^{210}Pb dating method at Laguna del Plata, Cordoba, Argentina. *Journal of Radioanalytical and Nuclear Chemistry*, **249(1),** pp. 263-268 (2001).

16. 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.

17. _____. 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.

18. E. B. S. Santos, et. al. *ICP-OES com vista axial e radial.* São Paulo, SP, Brazil (2002). Não paginado. Apostila da disciplina Análise Espectroquímica por Emissão Atômica do Instituto de Química da Universidade de São Paulo.

19. P. R. M. Correia, P. V. Oliveira, *Espectrofotometria de absorção atômica: aspectos gerais e aplicativos*. São Paulo, SP, Brazil (2005). 17f. Apostila integrante do curso Espectrofotometria de Absorção Atômica. Material particular.

20. AZUR ENVIRONMENTAL, *Microtox Omni^{TM} Software*. 1 CD-ROM (1999).

21. ENVIRONMENT CANADA, Environmental Protection Series. *Biological Test Method: Toxicity test using luminescent bacteria*. Canadá, 56p. Método Analítico (1992).

22. G. de A. Umbuzeiro, P. F. Rodrigues, O teste de toxicidade com bactérias luminescentes e o controle da poluição das águas. *O Mundo da Saúde,* **v. 28**, n.4, São Paulo, SP, Brazil, pp. 444-449 (2004).

23. CETESB. A fauna bentônica no complexo Billings (SP). CETESB, São Paulo, SP, Brazil (1997) http://www.cetesb.sp.gov.br/Agua/relatorios/relatorio_tecnico/07, Accessed in

August 2009.

24. 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*. **v. 59**. pp. 123-133 (2009).

25. S. R. Taylor, S. M. Mc Lennan, The continental crust: its composition and evolution. *Blackwell Scientific*, Palo Alto, Ca. pp. 25-27 (1985).

26. CCME, Canadian Environmental Quality Guidelines - Summary Tables, http://www,ec,gc,ca/ceqg-rcqe/English/ceqg/sediment/default,cfm, accessed in May 2009.

27. S. Audry, J. Schaefer, G. Blanc, U. J-M. Jousnnea, Fifty-year sedimentary record of heavy metal pollution (Cd, Zn, Cu, Pb) in the Lot River reservoirs (France). *Environ. Pollut*. **v. 132**, pp. 413-426 (2004).

28. K. H. Wedepohl, The composition of the continental crust. *Geochim. Coscochim. Acta*. **v. 59**, pp. 1217-1232 (1995).

29. 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*. **v. 54(6)**, pp. 1051–1070 (2002).