2009 International Nuclear Atlantic Conference - INAC 2009
Rio de Janeiro, RJ, Brazil, September 27 to October 2, 2009
ASSOCIAÇÃO BRASILEIRA DE ENERGIA NUCLEAR – ABEN
ISBN: **978-85-99141-03-8**

ASSESSMENT OF SEDIMENTS FROM TIETÊ RIVER – TOXICITY, AND TRACE ELEMENTS - FROM SALESÓPOLIS TO SUZANO COUNTIES, SÃO PAULO, BRAZIL

Gabriel F. Alegre[1], Sueli Borrely[1], Thuany M. Nascimento[2], Deborah I.T. Favaro[2]

[1] Centro de Tecnologia das Radiações, CTR, IPEN/CNEN - SP
Av. Professor Lineu Prestes 2242
05508-000 São Paulo, SP
gabrielfonseca@usp.br

[2] Laboratório de Análise por Ativação Neutrônica, CRPQ, IPEN/CNEN - SP,
Av. Professor Lineu Prestes 2242
05508-000 São Paulo, SP
defavaro@ipen.br

ABSTRACT

In the present study, sediment samples from the Tietê River were evaluated for toxicity and trace metals (5 sampling sites). The studied region includes Salesópolis to Suzano and surroundings, a highly industrialized area. The study involved toxicity evaluation (sediment, elutriate and pore-water) and the distribution of some major, trace and rare earth elements on sediments. Multielemental analysis was carried out by instrumental neutron activation analysis (INAA) and total mercury by cold vapor atomic absorption technique (CV AAS). The concentration values obtained for the metals As, Cr, Hg and Zn in the sediment samples were compared to the Canadian Council of Minister of the Environment (CCME) oriented values (TEL and PEL). Regarding toxicity, whole sediments and elutriate fractions were evaluated using chronic assays for *Ceriodaphnia dubia*, while the pore water was carried out for *Vibrio fischeri* toxicity assays. These assays followed Brazilian Standardized Methods (ABNT). Whole sediments and elutriate evidenced negative biological effects, even at Salesópolis county, the control site (less impacted area). The worst effects were obtained at Mogi das Cruzes and Suzano counties (sampling stations 3 and 4). The elutriate fractions collected at the same stations showed acute toxicity in two of three samples (*C. dubia*). When pore water was evaluated, a toxicity gradient which increased as the river flowed through Mogi das Cruzes county was obtained. Regarding toxic metal contents in the sediment samples points 3 and 4 exceeded the TEL oriented values for As, Cr, Hg and Zn and point 4 also exceeded the PEL values for all these elements.

1. INTRODUCTION

Substantial part of São Paulo Metropolitan Region (SPMR) is included at Tietê Hydrographic Basin (Alto Tietê). Tietê River flows from Salesópolis to Rasgão's Dam, totalizing 5.985 km² draining basin area. The region includes 35 municipalities: part is an agriculture area and most is urban area. The region is important for water supply once superficial waters come

from the interior region to the cities. This area accounts for 5 reservoirs of water but the occupation is seriously affecting the water quality. The general uses for water at this region are: public and industrial supplies, irrigation, generation of energy, transport, dilution of pollutants (SABESP)[1].

As a result of occupation, important amount of water resources from Alto Tietê Basin is contaminated. According to Waters and Energy Department, DAEE, Ponte Nova Reservoir, located at Salesópolis, supply 3.4 thousand liters per second of water. Close to this reservoir there are industrialized cities: Mogi das Cruzes and Suzano with lots of environmental negative interferences and effluents as well. Mogi das Cruzes has no sewage treatment station and the sewage from this city is partially treated at Suzano Waste Water Treatment Plant [2].

CETESB is the Environmental Control Agency of Sao Paulo State, which is in charge of water quality and sediments monitoring. Due to a so large space and complex occupation their efforts are most devoted to that areas which are water suppliers. Although chemical and physic and chemistry parameters are often measured, nowadays genotoxicity and toxicity is part of their hard job.

Baudo et al [3] pointed out the importance of keeping water toxicity measurements once it is the unique way to confirm if the contaminant is able to interact with living organisms. Ecotoxicity data have been presented in order to confirm that fixing standard values for chemical contaminants most of the combination between contaminants may result in negative effects to the biota.

Concentrations of contaminants in sediment may be several orders of magnitude higher than in the overlying water. Nowadays sediment monitoring and studies are often recommended once sediment provides habitat for many aquatic organisms and is a major repository for many persistent chemical introduced to this system [4].

In the present study sediment samples from Tietê River were evaluated for toxicity and trace metals (5 sampling sites). It's involved two scientific areas: whole toxicity evaluation (sediment, elutriate and pore-water) and the distribution of some major elements: (Fe, K and Na), trace-elements (As, Ba, Br, Co, Cr, Cs, Hf, Hg, Rb, Sb, Sc, Ta, Tb, Th, U and Zn) and rare earth (Ce, Eu, La, Lu, Nd, Sm, Tb and Yb) on sediments. Multielemental analysis was carried out by instrumental neutron activation analysis (INAA). For total mercury determination cold vapor atomic absorption technique (CV AAS) was employed. Toxicity evaluation was carried out for *Vibrio ficheri* bacteria and the *Ceriodaphnia dubia* crustacean.

2. MATERIAL AND METHODS

2.1 Sampling sites

The study area covered the Salesópolis, Biritiba-Mirim, Mogi das Cruzes and Suzano counties, São Paulo State. Five sites were selected for sediment sampling and defined using Global Positioning System (GARMIN ®). The sampling sites were identified at Figure 1

(yellow markers) and Tietê River was represented by the red line. It is important to note the Ponte Nova Reservoir at the site was elected as P0.

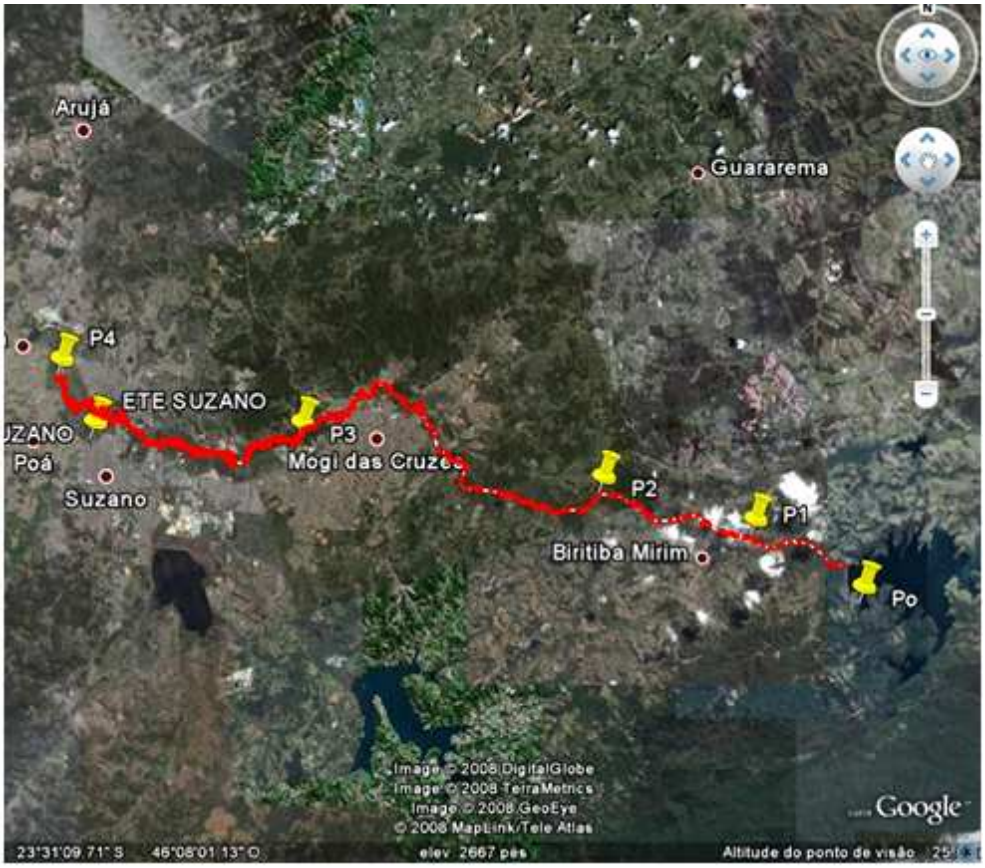

Figure 1 – Sampling sites and their geographical positions

2.2 Sampling, sample preparation and preservation

The procedures for sediments collection and storage followed NBR15469 [5]. During sediments transportation the samples were kept chilled in styrofoam boxes with ice. At the laboratory, samples were separated for biological tests (kept near 7º C) while some parts of sediments were frozen until processing and chemical quantification. Subsequently, the samples treatment were performed for the extraction of aqueous phase from sediment, toxicity measurements were applied on porewater, whole sediment and its elutriate. All the adopted procedure was represented as a flowchart, represented in Figure 2.

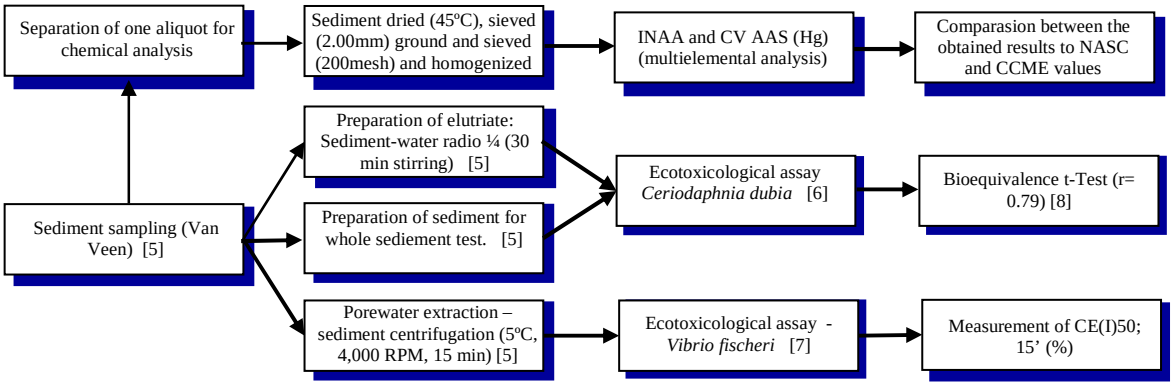

Figure 2 – Procedures adopted since the sampling until the processing of samples

2.3 Ecotoxicological assays

Ceriodaphnia dubia were used as living organisms which were investigated for whole sediment assessment and elutriate. V*ibrio fischeri* was applied for porewater evaluation.

The cladoceran *C. dubia* grown at the Laboratory of Environmental and Biological Testing of Center of Radiation Technology, CTR/IPEN. During the tests, pH, dissolved oxygen and non-ionized ammonia parameters were determined.

To achieve the whole sediment test using *Ceriodaphnia dubia*, 5 mL of whole sediment samples were introduced in beakers of 40 mL and added 20 mL of water (the same water that used in the cultures). To prevent the re-suspension of sediments, the water in the beaker was carefully transfered. After 24 hours, a newborn organism was added to each of the replicates, totaling 10 for each sampling site.

The elutriate was obtained by mixing 1 part of sediment with 4 parts of dilution water, under stirring for 30 minutes. This mixture was subjected to sedimentation during two hours and the supernatant was used in toxicity tests. When the total suspended material was decanted, the sample was centrifuged (4,000 rpm for 5 minutes). For the toxicity test only the supernatant was used. Fifteen mL of supernatant and one organism (newborn) in each replicate were added, totaling 10.

The time of exposure for whole sediment and elutriate assays was 7 days. The water renewing was performed each two days.

The tests were validated when the average number of *C. dubia* newborns from the control was more than 15. The sensitivity of the organisms test were evaluated monthly with potassium chloride at original concentration of 1000 ppm.

The marine bacterium *V. fischeri* was acquired from Unwelt©, in frozen condition. This test consisted by exposing the bacteria to the sample for 15 minutes. The luminescence values obtained were compared before and after the exposition time and the loses of luminescence

intensity were related to the sample concentration. The M500 Toxicity Analyzer (Microbics ®) was applied and the concentrations selected for porewater assays were 81.9%, 40.95%, 20.47%, 10.23% and control. The organism sensitivity to phenol was used for validation the experiments.

2.4 Sediment preparation for chemical analysis

Sediment samples were dried at 45^{o}C in a ventilated oven until constant weight. Sediment samples were passed through a 2 mm sieve, ground in a mortar, and passed again through a 200 mesh sieve to be homogenized before analysis. The total fraction (< 2 mm) was sent to Neutron Activation Analysis Laboratory from CRPq (IPEN /CNEN-SP) for chemical analysis. The multielemental determination was done.

2.5. Instrumental Neutron Activation Analysis

For multielemental determination about 200 mg of sediment (duplicate samples) and 150 mg of reference materials were accurately weighed and sealed in pre-cleaned double polyethylene bags, for irradiation. Sediment samples and reference materials were irradiated for 16 hours, under a thermal neutron flux of 1012 n cm-2 s-1 in the IEA-R1 nuclear 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 analyzed 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 methodology validation was verified by measuring the reference materials Buffalo River Sediment (NIST SRM 2704), Soil 7 (IAEA) and BEN (Basalt –IWG-GIT). Details of the analytical methodology is given at Favaro *et al* [12]

2.6 Total Hg determination

About 500 mg of sediment samples were digested with a mixture of concentrated HNO_3, H_2SO_4 and hydrogen peroxide 30 % in TEFLON® vials. The vials were closed and left overnight at room temperature. At the following day, the vials were put into an aluminum block at 90 0C and left there for 3 hours and allowed to cool at room temperature and the final volume was completed to 50 mL with Milli-Q water. Total mercury determinations were performed using CV AAS, using a FIMS from Perkin Elmer. The analytical procedure used (wet digestion) was suggested by Horvat [11] with some modifications. Methodology validation for total Hg determination was carried out with reference material analyses Marine Sediment (IAEA 433), Estuarine Sediment (NIST SRM 1646a) and Buffalo River Sediment (NIST SRM 8704).

2.7 Statistical Analysis

The results of toxicity tests using *Ceriodaphnia dubia* were treated using the Bioequivalence t-Test [9] and the bioequivalence constant (B=0,79) estimated by Bertoletti et al [8].

Statistical tests were performed with the TOXSTAT program, Version 3.5 [10]. After statistical analysis, the samples were classified as "toxic" or "not toxic".
The results obtained with samples of porewater for *V. fischeri* were expressed by EC (I)50, representing the concentration that reduced 50% of the luminescence produced by the bacteria during an exposure of 15 minutes at 15º C. From raw data was generated a linear regression curve with values of gamma (ratio of initial light and light lost) and concentrations of serial dilution, using the specific statistical program from Microbics®

3. RESULTS AND DISCUSSION

The average of newborns obtained for whole sediments and porewater assays, as well as control, was organized at Figure 2. On the other hand the data for toxicity was presented at Table 1, while the related contaminants were presented at Table 3.

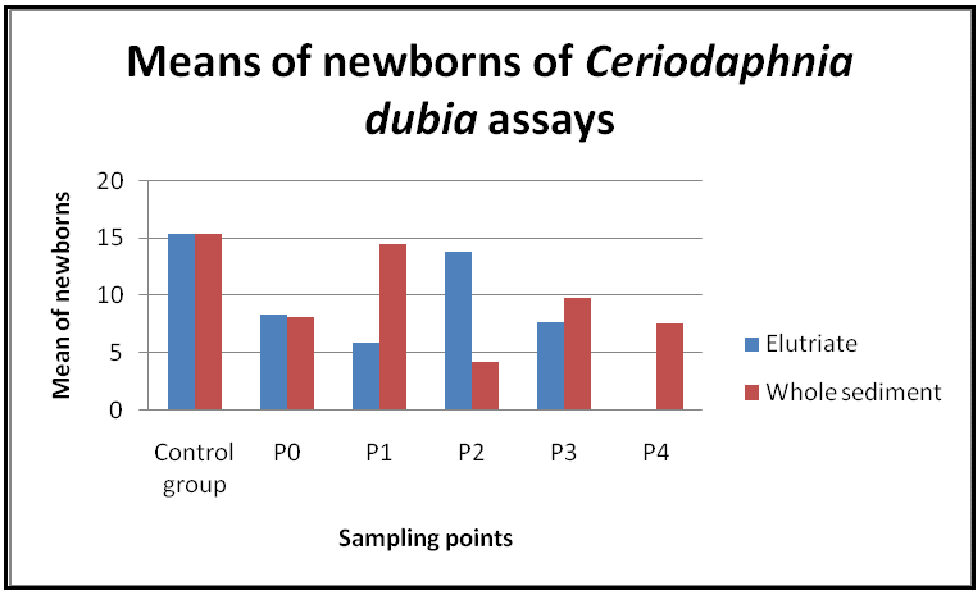

Figure 2 – Average of *Ceriodaphnia dubia*'s newborn obtained during the porewater and whole sediment assays.

The results obtained after the Bioequivalence t-Test statistical treatment of the results from biological assays are presented in the Table 2.

We can evidence that P0 (Ponte Nova Reservoir) is affected by pollution and was one of the sites which resulted in positive toxicity for all the measurements. P1 results, allow us to conclude, that the elutriate and porewater were worst than the whole sediment while in P2 the whole sediment, was critical for *Ceriodaphnia dubia*, resulting in the less reproduction number. The toxicity on P3 and P4 were similar, although P4 evidenced acute toxicity.

Table 2 – Results of ecotoxicological assays after statistical treatment

	P0	P1	P2	P3	P4
Whole Sediment (*C. dubia*)	**CT**	**NT**	**CT**	**NT**	**CT**
Elutriate (*C. dubia*)	**CT**	**CT**	**NT**	**CT**	**AT**
Porewater CE (I) 50 (*V.fischeri*)	**81.90% (γ= 0.7081)**	**22.6% (16.05 – 31.84)**	**81.90% (γ= 0.3696)**	**16.25% (7.74 – 34.08)**	**24.46% (21.61 – 29.99)**

AT – Acute toxicity; CT – Chronic toxicity e NT – No toxicity.

Table 3 presents the mean and standard deviation values (mg kg^{-1}) for the elements analyzed by INAA and total Hg content (µg kg^{-1}) by CV AAS, for the sediment samples. Also shown is the NASC (North American Shale Composite) [13] and TEL (Threshold Effect Level) and PEL (Probable Effect Level) oriented values from the Canadian Council of Minister of the Environment (CCME) [14]. These are the limits established by Canadian legislation and adopted by São Paulo Environmental agency (CETESB). TEL 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 3 – Results obtained for the elements analyzed by INAA (mg kg^{-1}) and CV AAS (µg kg^{-1}): mean (duplicate), standard deviation (std), NASC, TEL and PEL values

	Point 0	Point 1	Point 2	Point 3	Point 4	NASC [13]	TEL [14]	PEL [14]
As	n.d.	2.3 ± 0.1	n.d.	13.2 ± 0.4	19.7 ± 0.7		5.9	17.0
Ba	124 ± 9	492 ± 37	286 ± 19	451 ± 50	469 ± 43	636		
Br	n.d.	15.3 ± 0.7	1.4 ± 0.2	14.8 ± 0.4	17.9 ± 0.5			
Ce	35.4 ± 0.9	96 ± 3	222 ± 10	153 ± 5	115 ± 3	73		
Co	2.0 ± 0.1	4.0 ± 0.1	0.8 ± 0.1	7.2 ± 0.1	13.2 ± 0.4	26		
Cr	31.2 ± 0.4	19.9 ± 0.8	14.2 ± 0.6	95 ± 4	122 ± 4	125	37.3	90
Cs	1.1 ± 0.1	5.0 ± 0.2	2.6 ± 0.2	7.6 ± 0.3	4.2 ± 0.2	5.2		
Eu	0.42 ± 0.01	0.93 ± 0.04	0.63 ± 0.04	1.33 ± 0.03	0.96 ± 0.03	1.24		
Fe (%)	2.77 ± 0.01	3.04 ± 0.02	0.411 ± 0.004	4.80 ± 0.03	4.43 ± 0.02			
Hg (µg kg^{-1})	61 ± 10	76 ± 8	< 10	449 ± 49	583 ± 33		170	486
La	21.7 ± 0.6	47.2 ± 0.2	100.4 ± 0.5	64.2 ± 0.3	34.7 ± 0.8	32		
Lu	0.22 ± 0.02	0.38 ± 0.02	0.43 ± 0.03	0.46 ± 0.04	0.72 ±0.05	0.48		
Na	n.d.	2516 ± 22	1649 ± 17	1744 ± 18	2189 ± 28			
Nd	7 ± 1	26 ± 3	86 ± 8	19 ± 3	23 ± 3	33		
Rb	13.1 ± 0.7	130 ± 5	80 ± 4	60 ± 4	50 ± 3	125		
Sb	n.d.	0.23 ± 0.03	n.d.	1.00 ± 0.06	4.8 ± 0.3			
Sc	5.0 ± 0.1	5.2 ± 0.1	1.40 ± 0.08	13.9 ± 0.2	17.3 ± 0.2	15		
Sm	3.1 ± 0.1	7.5 ± 0.1	14.6 ± 0.2	20.2 ± 0.3	5.6 ± 0.1	5.7		
Ta	2.0 ± 0.1	2.1 ± 0.2	2.3 ± 0.3	3.9 ± 0.2	2.1 ± 0.1			
Tb	0.35 ± 0.04	0.78 ± 0.07	1.2 ± 0.1	2.0 ± 0.4	1.4 ± 0.3	0.85		
Th	20.2 ± 0.7	23.1 ± 0.6	57 ± 2	27.7 ± 0.5	19.6 ± 0.7	12		
U	2.8 ± 0.5	6.5 ± 0.3	7.3 ± 0.3	7.4 ± 0.3	6.3 ± 0.4	2.7		
Yb	1.8 ± 0.1	2.4 ± 0.1	2.9 ± 0.1	3.4 ± 0.1	5.2 ± 0.2	3.1		
Zn	33 ± 1	55 ± 2	16.2 ± 0.9	459 ± 17	929 ± 36		123	315

n.d. – not determined

When the concentration values for As and metals Cr, Hg and Zn in the sediment samples were compared to TEL oriented values from Canadian legislation and adopted by CETESB, it was concluded that points 3 and 4 exceeded the TEL values for As (5.9 mg kg^{-1}), Cr (37.3 mg kg^{-1}), Hg (170 µg kg^{-1}) and Zn (123 mg kg^{-1}). Regarding PEL values, point 4 presented the highest concentration values surpassing the limits for all elements (As, Cr, Hg and Zn). Points 0, 1 and 2 presented concentration values much lower than TEL values for these elements (Table 3).

Comparing NASC values with the concentration values obtained in the present study it was possible to verify enrichment for rare earth elements (Ce, La, Lu, Eu, Nd, Sm, Tb and Yb), U and Th mainly at points 3 and 4, which were much polluted regarding metals, trace and rare earth elements. Near these points are Mogi das Cruzes and Suzano industrialized cities with lots of environmental negative interferences and discharge of effluents as well.

The widespread use of chemical compounds and mixtures continuously modify the ecosystem by accumulating at sediments McCauley [15]. In our case the results obtained at Ponte Nova Reservoir indicate the regional impacts even at a relatively protected area. Total chromium reinforced the toxicity results. Looking to Table 3 data it is easy to affirm that from site 1 to 4 the impact enhanced considerably and especially for chromium, mercury and zinc the numbers are alarming. The biological assays results confirmed the bias.

Heavy metals and organics were related to toxicity at Santander Bay, Spain, Coz et al [16]. *Vibrio fischeri* and *Daphnia similis* evidenced effects at Columbia river and four dams below the Hanford site, United States, Delistraty & Yokel [17]; Besser *et al* [18] studied the toxicity of sediments downstream of lead–zinc mining areas in southeast Missouri, using chronic sediment toxicity tests with amphipod *Hyalella azteca*, and pore-water toxicity tests with the daphnid *Ceriodaphnia dubia*. This study showed a significative correlation between the toxicity and the higher concentration of metals (Ni, Zn, Cd and Pb).

Brazilian results from Rocha and Almeida reported for different reservoirs concluded that: Rasgão and Billings had the worst sediment quality, followed by Barra Bonita and Bariri where the toxicity and the levels of Cu, Cd, Ni, Pb and Zn were considered high. For the Promissão Reservoir no evidence of impacts was found [19]. Bramorsky evaluated the toxicity of sediments from Tietê and Piracicaba rivers on the Barra Bonita/SP reservoir‘s input, using chemical analysis and ecotoxicological tests with *Daphnia similis* and *Chironomus Xanthus*. The result of this study showed that the Tietê River is the most impacted, mainly due to high concentrations of Mn, Cd, Ni and Pb, where the initial compartments of the dam Barra Bonita, showed rates of bioavailability are often close to 100% [20]. The results obtained in toxicity tests, also showed that the Tietê River before the damming, as the most toxic. Rodgher et al evaluated the water and sediment at Cascade Reservoirs, from Tietê River. Toxicity tests using *Daphnia similis*, *Ceriodaphnia dubia* and *Danio rerio*. In addition to chemical analysis they showed significant correlation between cadmium, copper and zinc in the sediment and chronic toxicity results. In our case the luminescent bacteria *V. fischeri* was the most sensitive organism [21].

5. CONCLUSION

When the results obtained for INAA were compared to NASC values enrichment for rare earth elements (Ce, La, Lu, Eu, Nd, Sm, Tb and Yb), U and Th mainly at points 3 and 4 was observed.

The concentration values obtained for As and metals Cr, Hg and Zn in the sediment samples were compared to the oriented values (TEL and PEL). For sampling sites zero, one and two, none of these elements exceeded the TEL values (As – 5.9, Cr - 37.3, Hg- 0.17 and Zn- 123 mg kg-1) indicating good sediment quality. For site 3, all these elements exceeded the TEL values and PEL values for Cr and Zn. Site 4, all these elements exceeded the TEL, as well as, PEL values (As-17, Cr-90, Hg-0.486 and Zn- 315 mg kg-1) showing serious contamination for these toxic metals. These last two points are located near Mogi das Cruzes and Suzano counties, suffering high impact from industrial activities of the region.

Regarding toxicity, whole sediments and elutriate fractions were evaluated using chronic assays for *Ceriodaphnia dubia*, while the porewater was carried out for *Vibrio fischeri* toxicity assays. Whole sediments and elutriate evidenced negative biological effects, even at Salesópolis county, the control site (less impacted area). The worst effects were obtained at Mogi das Cruzes and Suzano counties (sampling stations 3 and 4). The elutriate fractions collected at the same stations showed chronic toxicity at P3 (Mogi das Cruzes) and acute toxicity at P4 (Suzano) for *C. dubia*. When porewater was assessed, the worst effects were obtained at sites P1, P3 and P4. The results of metal concentrations may justify the biological responses obtained.

ACKNOWLEDGEMENTS

The authors would like to thank Comissão Nacional de Energia Nuclear (CNEN) by the financial support and Fundação de Estudos e Pesquisas Aquáticas (FUNDESPA) by the sampling support.

REFERENCES

1. Companhia de Saneamento Básico do Estado de São Paulo - SABESP. Estação de Tratamento de Esgotos de Suzano, ETE SUZANO (Folheto descritivo), s/ data.
2. Serviço Municipal de Água e Esgotos (SEMAE) “Histórico das redes de esgoto de Mogi das Cruzes”. http.www.semae.pmmc.com.br/sitenovo/.../sistema%20de%20Esgoto.pdf; (2009)
3. R. Baudo, M. Beltrami, D. Rossi, “In situ tests to assess the potential of aquatic sediments”. *Aquatic Ecosystem Health and Management*, **2**, pp.361–365 (1999).
4. C.G. Ingersoll. “Sediment tests”. In: Fundamentals of aquatic toxicology: effects, environmental fate, and risk assessment, G.M. RAND (ed), Taylor & Francis, Washington. (1995).
5. Associação Brasileira de Normas Técnicas – ABNT, “Ecotoxicologia aquática– Preservação e Preparo de Amostras”. ABNT NBR15469. (2007).

6. Associação Brasileira de Normas Técnicas – ABNT, “Ecotoxicologia aquática – Toxicidade crônica – Método de ensaio com *Ceriodaphnia spp* (Crustacea, cladocera)”. ABNT NBR 13373. (2005).
7. Associação Brasileira de Normas Técnicas - ABNT, Ecotoxicologia aquática – Determinação do efeito inibitório de amostras de água sobre a emissão de luz de *Vibrio fischeri* (Ensaio de bactéria luminescente) Parte 2: Método utilizando bactérias desidratadas. ABNT NBR 15411-2. (2006)
8. E. Bertoletti, S. V. Buratini, V. A. Prospéri, R. P. A. Araújo, L. I. Werner. “Selection of Relevant Effect Levels for Using Bioequivalence Hypothesis Testing”. *Journal of the Brazilian Society of Ecotoxicology*. **2(2)**. pp.139-145. (2007).
9. W. P. Erickson & L. L. McDonald, “Tests for bioequivalence of control media in studies of toxicity”. *Environmental Toxicology and Chemistry.*,**14**. pp.1247–1256. (1995).
10. D. Gulley, “Toxstat 3.5”, West Inc. University of Wyoming. Cheyenne, Wyoming. (1996).
11. Horvat.”Mercury Analysis and Speciation in Environmental Samples” in Global and Regional Mercury Cycles: Sources, Fluxes and Mass Balances, pp.1-31, W. Baeyens et al (eds), (1996).
12. D. I. T. Fávaro, S.R. Damatto, E.G. Moreira, B.P. Mazzilli, F. Campagnolli. Chemical Characterization and Recent Sedimentation Rates in Sediment Cores from Rio Grande reservoir, São Paulo, Brazil. *Journal of Radioanalytical and Nuclear Chemistry*, **273(2)**, pp.451-463. (2007).
13. S.R. Taylor & S. M. Mc Lennan. The continental crust: its composition and evolution. Blackwell Scientific, Palo Alto, Ca., pp.25-27. (1985).
14. Canadian Council of Ministers of the Environment – CCME, “Canadian Environmental Quality Guidelines - Summary Tables” http://www.ec.gc.ca/ceqg-rcqe/English/ceqg/sediment/default.cfm. June, (2007).
15. D. J. McCauley, G. M. DeGraeve, T. K. Linton, “Sediment quality guidelines and assessment: overview and research needs”. *Environmental Science & Policy***. 3,** pp. 113–144. (2000).
16. A. Coz, O. Rodríguez-Obeso, R. Alonso-Santurde, M. Álvarez-Guerra, A. Andrés, J. R. Viguri, D Mantzavinos, N. Kalogerakis, “Toxicity bioassays in core sediments from the Bay of Santander, northern Spain”. *Environmental Research*., **106,** pp.304–312. (2008)
17. D. Delistraty & J. Yokel, “Chemical and ecotoxicological characterization of Columbia River sediments below the Hanford site (USA)”. *Ecotoxicology and Environmental Safety*, **66**, pp.16-28 (2007).
18. J. M. Besser, W.G. Brumbaugh, A. L. Allert, B.C. Poulton, C. J. Schmitt, C. G. Ingersoll, “Ecological impacts of lead mining on Ozark streams: Toxicity of sediment and porewater”. *Ecotoxicological and Environmental Safety*, **72**, pp.515–526 (2009)
19. C. A. Almeida & O. Rocha, “Estudo Comparativo da Qualidade dos Sedimentos dos Reservatórios do Rio Tietê (SP)”. *Journal of the Brazilian Society of Ecotoxicology*,**1(2),** pp.141-145. (2006).
20. J. Bramorski, “Avaliação da qualidade de sedimentos dos rios Tietê e Piracicaba nos seus compartimentos de entrada no reservatório de Barra Bonita, SP”. Dissertação de Mestrado. Universidade de São Paulo, Escola de Engenharia de São Carlos, São Carlos. 126p + anexos. (2004).
21. S. Rodgher, , E. L. G. Espíndola, O. Rocha, R. Fracácio, R. H. G. Pereira, M. H. S. Rodrigues, “Limnological and Ecotoxicological studies in the cascade of reservoirs in the Tietê river (São Paulo, Brazil)”. *Brazilian Journal of Biology*, **65(4),** pp.697–710 (2005).