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Major and trace element assessment of Tietê river sediments, São Paulo, Brazil

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Abstract The objective of this study was to quantify major and trace elements present in sediments collected from the one of Brazil's most important rivers, Tietê River. Sediments from 5 different sampling points (P_0–P_4), in 3 campaigns (2008/2009), from the headwaters to Suzano County upstream from São Paulo city were collected. X-ray fluorescence was applied for measuring total concentration of major elements and instrumental neutron activation analysis (INAA) for trace elements. The elements Cd, Hg and Pb were determined by atomic absorption spectrometry after digestion using the US EPA 3,051 procedure. These metal concentrations were compared to the PEL and TEL oriented values from CCME. The sampling sites P_3 and P_4, near industrialized areas, showed the highest concentrations for potentially bioavailable metals, mainly Pb and Hg. The results obtained by INAA were compared to upper continental crust values. A strong enrichment was found for the elements As, Br, Sb, Th, U and Zn. These results evidenced contamination by industrial effluents and sewage even relatively close to the Tietê River headwaters. The worst biological effects (acute toxicity) on benthonic organism *Hyalella azteca* were also observed at P_3 and P_4.

Keywords Metals · Trace elements · Sediments · Enrichment factor · INAA · Tietê river

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Introduction

Tiete is the most important river flowing to the South of Brazil. An area of 5.775 km^2 is covered as the river flows from its origin to Paraná River. The water quality is not good even very close to the spring due to extensive usage. The upper region of the tiete river (URTR) includes the Salesópolis County up to the Rasgão Storage Dam, an agricultural area [1].

Negative impacts to the river are evidenced by depleted water oxygen levels, excessive organic matter content and contaminants. Regarding inorganic contaminants, certain metals are essential for living organisms when present at very low concentrations. On the other hand, other metals at high concentrations may impact living organisms by several routes. Several countries apply Cu to control algae reproduction at water reservoirs. Another important means of metal release into aquatic environments is industrial and domestic discharge of effluents into waterways.

There is a general consensus that sediment plays a fundamental role in the transport dynamics, accumulation and availability of pollutants [2]. In the sediment quality triad, considered one of the best approaches for the study of anthropogenic contaminated aquatic systems, the chemical and biological data (bioassays and benthic community analysis) are combined to show the degradation of each site. Consequently, values for metals, metalloids and other

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toxic substances are a central question in research regarding sediment as an indicator of pollution, since they are vital in the determination of degrees of contamination and consequently in the establishment of quality criteria for sediment and ecological risk assessment [3]. Nascimento and Mozeto [4] established reference values for metals and metalloids in sediments of the Tietê River Basin, located in one of the most developed regions in Brazil and for this reason has been the focus of many environmental studies [5–9]. The choice of metals Ag, Cd, Co, Cr, Cu, Hg, Ni, Pb, Th, Ti, U, V, Zn and the metalloids As and Se was based on toxicological criteria. Furthermore, these elements are the most significantly affected in the global geochemical cycle by anthropogenic activities [4].

Brazilian standard limits for heavy metals in sediments were established by CONAMA 344 Resolution, 2004, the Brazilian Council for Environment [10]. The studied USTR (Upper Side of the Tiete River) is also an important industrial area which concentrates metallurgical, chemical and pharmaceutical activities, releasing thousands of different compounds through their effluents.

The goal of this study was to quantify some metals, major and trace elements, contained at field-collected sediments from USTR by using X-ray fluorescence (XRF) and NAA analytical techniques, collected in 3 sampling campaigns. These results were compared to upper continental crust (UCC) values [11] and regional reference values (RRV) obtained by Nascimento and Mozeto [4] for this region. The enrichment factor in relation to UCC values using Sc as a normalizer element was also calculated. The elements Cd, Hg and Pb were determined by AAS after digestion procedure by US EPA 3051. These results were compared to TEL and PEL oriented values from Environment Canada [12] and CONAMA 344 resolution from the Brazilian Council of Environment [10]. Complementary studies assessed the biological effects (ecotoxicity) of sediments in order to evaluate the potency for biological damages of determined contaminants on that environmental matrix. Amphipods, as benthonic organisms, are dependent on sediments the reason why *Hyalella azteca* was exposed to these sediments samples.

Materials and methods

Sampling and sample preparation

The Tietê river spring basin is located in the municipality of Salesópolis, approximately 60 km east of the city of São Paulo. The river crosses the state from east to west and drains into the Paraná River at the border between the states of São Paulo and Mato Grosso do Sul [4]. The Tietê river basin is composed of Upper, Middle and Low Tietê. In the present study five bottom sediment samples (P_0–P_4) were collected in the upper side of the tiete river (USTR). The site of USTR is represented by the following counties and corresponding sample identifications: Ponte Nova's Reservoir in Salesópolis (P_0), Biritiba-Mirim city (P_1 and P_2), Mogi das Cruzes (P_3) and Suzano (P_4) cities. The samplings were carried out in 2008 March (2nd campaign), 2008 September (3rd campaign) and 2009 February (4th campaign), respectively. In the 1st campaign sediment samples were not collected for chemical analysis. A van Veen sampler was used for sediment sampling. Figure 1 shows the sampling locations [1]. Sediment samples were dried at 45 °C in a ventilated oven until constant weight and then passed through a 2 mm sieve, ground in a mortar, once again passed through a 200 mesh sieve and then homogenized before analysis. The total fraction (<2 mm) was analyzed.

The lithology of the spring′s region is basically formed by migmatites, and granites and the soils are of the reddish-yellow podzolic type [13].

X-ray fluorescence analysis (XRF)

X-ray fluorescence spectrometry (XRF) was applied for the determination of major elements in sediments. Samples were prepared according to Mori et al. [14] at the Institute of Geosciences, University of São Paulo and the measurements were done in a X-Ray Philips PW 2400 spectrometer. The precision and accuracy of the analytical methodology were verified by means of JB-1a and JG-1a reference materials (Geological Survey of Japan) [15]. Major elements were determined by wavelength-dispersive XRF using fused glass discs. The precision of these measurements was better than 5 % RSD. Loss on ignition (LOI) was determined by dry samples at 1,000 °C.

Instrumental neutron activation analysis (INAA)

For multielemental analysis, approximately 200 mg of sediment (duplicate samples) and reference materials were weighed and sealed in pre-cleaned double polyethylene bags, for irradiation. Single and multi-element synthetic standards were prepared by pipetting appropriate 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 h, under a thermal neutron flux of 10^{12} cm^{-2} s^{-1} at the IEA-R1 nuclear reactor in IPEN. Two series of counting were made: the first, after 1 week decay and the second, after 15–20 days. Gamma spectrometry was performed using a Canberra gamma × hyperpure Ge detector and associated electronics, with a resolution of 0.88 and 1.90 keV for ^{57}Co (121.97 keV) and ^{60}Co (1332.49 keV),

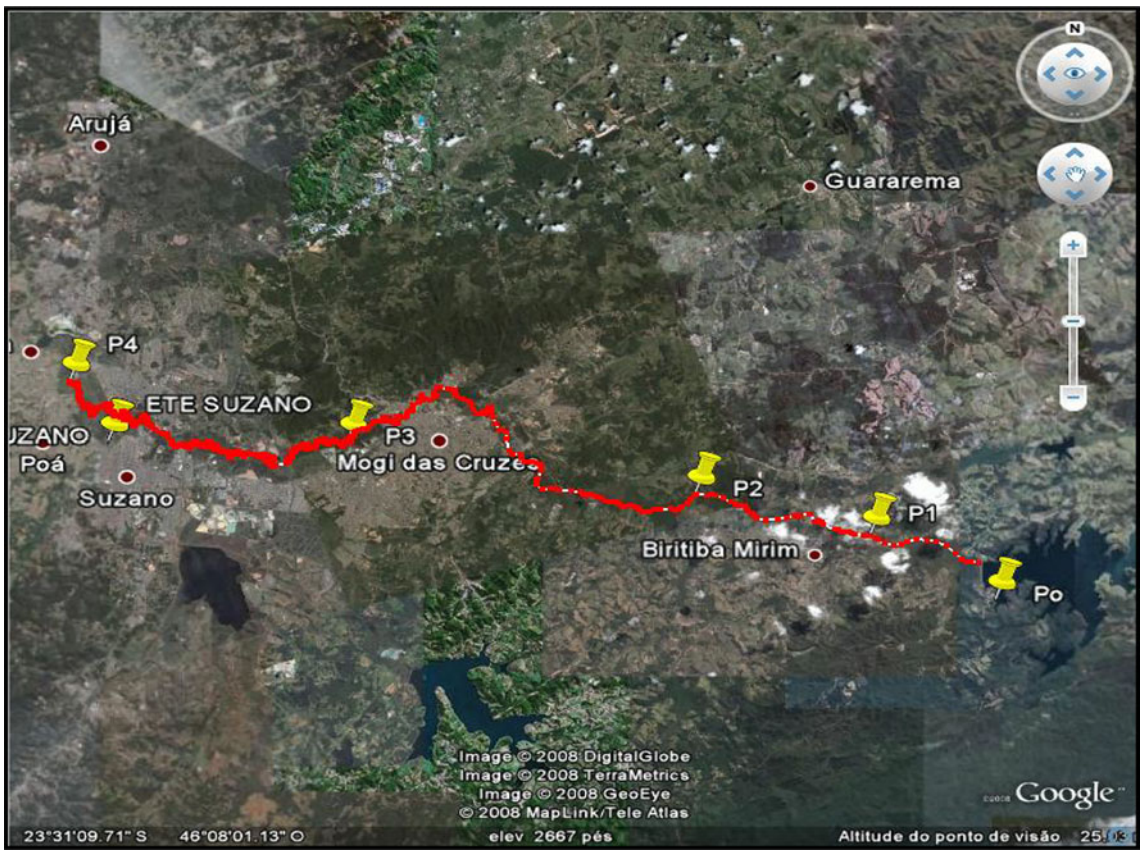

Fig. 1 Sampling sites location at Tietê River

respectively. Details of the analytical methodology are described by Larizzatti et al. [16].

The elements determined 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 uncertainties of the results were calculated by error propagation. Methodology validation was done by analyzing reference materials BEN (Basalt-IWG-GIT) and Soil 7 (IAEA). The relative standard deviations ranged from 1.1 to 8.2 % and relative errors, from 3.3 to 10 % for the elements analyzed by INAA.

Atomic absorption spectrometry (GF-AAS and CV-AAS)

In this study samples were digested by following a microwave-assisted method (SW-846-3051) prescribed by US EPA for sediments [17]. About 0.5 g of the sediment sample was weighed in Teflon tubes and 10 mL of conc HNO_3 was added. After dissolution, the solution was filtered and the final volume was made up to 50 mL, in a volumetric flask. The measurements were performed in duplicate, limited to a deviation $\leq$20 % and the concentration values were obtained using an analytical calibration curve. A calibration blank and a reagent blank were also measured and their values had to be less than the detection limit (DL) of the method to assure the quality of reagents and methodological procedures, respectively. The measurements were performed in a Perkin Elmer AANALYST 800 instrument. The precision and accuracy of the method were evaluated by checking the recovery (%) of analyte present in the Certified Reference Material SS-1 and SS-2 (contaminated soils from EnviroMAT^{TM}) used. Our results are within the confidence interval (95 %) of the certified reference materials. The mean concentration for Cd in the SS2 reference material was 2.07 ± 0.08 mg kg^{-1}, (2-consensus value); for Pb, SS2 reference material, 121.3 ± 2.5 mg kg^{-1}, (126-consensus value, 116–136 CI) and SS1, 219.4 ± 1.1 mg kg^{-1}, (233-consensus value, 219–247 CI).

The total Hg determination in sediment samples was carried out by CV-AAS. Details of the methodology are described by Fávaro et al. [18]. Quality control was performed by analyzing the certified reference materials Lake Sediment (BCR 280), Lake Sediment (IAEA, SL-1) and Marine Sediment reference material for trace metals and other constituents (MESS-3, NRCC). The results agreed with certified values presenting relative errors and relative

standard deviations less than 10 %. The mean concentrations found for total Hg were: 0.685 ± 0.030 mg kg^{-1} for BCR 280 (0.670 ± 0.019 mg kg^{-1}); 0.135 ± 0.005 for IAEA-SL1 (0.130 mg kg^{-1}) and 0.082 ± 0.007 mg kg^{-1} for MESS-3 (0.091 ± 0.09 mg kg^{-1}).

Ecotoxicological assays

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

Hyalella azteca were exposed to the sediments according to procedures given by the Brazilian standard method, NBR 15470 [19]. The sample preparation consisted of one part of raw sediment and four parts of natural water. After 10 days of exposure the percentage of lethality obtained was compared to the control. The results are reported as acute effects and calculations included a bioequivalence constant (B = 0.89) for *H. azteca*, recommended by Bertoletti et al. [20], using Toxstat 3.5 version [21]. Reference toxicity test with KCl was conducted in conjunction with sediment tests in order to determine possible changes in the condition of test species (*H. azteca*). In this case the assay lasted only 48 h.

Results and discussion

The results obtained for the major elements determined by XRF in the sediment samples are shown in Table 1 as well as the upper continental crust (UCC) values [11]. SiO_2, Al_2O_3 and Fe_2O_3 are the dominant constituents of the sediments, whose concentrations are similar to those found in the UCC. CaO, Na_2O and MgO are minor constituents, generally totaling <1 %. Only K_2O is present in significant amounts, probably reflecting mica and illite in the sediments.

Table 2 presents the mean and standard deviations (mg kg^{-1}) for the elements analyzed by INAA for the sediment samples collected in the 3 sampling campaigns. Table 2 also shows the UCC values [11] and regional reference values (RRV) from Nascimento and Mozeto [4] determined for bottom sediments of the Upper Tiete River Basin, the region of the samples collection.

It is well known that metals originating from the same source generally group together in silt and clay fractions. Enrichment if it occurs can be observed by using a normalization procedure that offsets the variability in mineralogy and grain size [22–24] by establishing the enrichment factor (EF). EF is defined as a ratio between the element concentration and the conservative element concentration in the sample and in the background reference values, in this case, the UCC values. The elements of natural origin that are structurally combined with one or more mineral phases are considered conservative. The main assumption for the application of a geochemical normalization for conservative elements is the existence of a linear relationship between the normalizer and other metals [22–24]. In this study, Sc was used as a normalizer [25] according to Eq. (1):

$$EF = [C_n/C_{Sc}]_{sample}/[C_n/C_{Sc}]_{(background)} \quad (1)$$

where C_n—element concentration and C_{Sc}—Sc concentration.

According to Zhang and Liu [26], if $0.5 < EF < 1.5$, the elemental concentration is probably entirely due to crustal

Table 1 Concentrations (%) of major elements in sediments by XRF and upper continental values [11]

	2nd Sampling campaign					3rd Sampling campaign					UCC
	P_0	P_1	P_2	P_3	P_4	P_0	P_1	P_2	P_3	P_4	
SiO_2	66.39	61.87	90.21	40.74	51.24	61.39	71.42	69.97	69.11	48.02	61.5
Al_2O_3	16.93	17.12	4.38	26.35	22.56	19.35	14.50	14.25	14.61	25.81	15.1
MnO	0.022	0.073	0.021	0.040	0.053	0.024	0.023	0.060	0.021	0.042	0.10
MgO	0.14	0.27	0.14	0.49	0.48	0.13	0.20	0.34	0.30	0.40	3.7
CaO	0.10	0.17	0.08	0.82	0.63	0.06	0.11	0.31	0.40	0.32	5.5
Na_2O	0.08	0.36	0.24	0.26	0.34	0.07	0.31	0.56	0.28	0.32	3.2
K_2O	0.31	3.00	2.01	1.44	1.66	0.28	2.69	4.22	1.86	1.95	2.4
TiO_2	1.015	0.696	0.356	1.121	1.362	1.220	0.634	0.881	0.713	1.481	0.68
P_20_5	0.067	0.252	0.055	0.954	0.563	0.069	0.105	0.177	0.314	0.412	0.18
FE_20_3	4.55	4.74	0.63	6.68	6.75	5.04	2.41	2.75	3.35	7.05	6.28
LOI	10.24	11.42	1.00	21.82	14.44	12.03	6.78	5.93	9.48	14.06	
TOTAL	99.84	99.97	99.12	100.72	100.08	99.66	99.18	99.45	100.44	99.87	

Table 2 Concentrations (mean ± SD, mg kg^{-1}) for some elements in sediments by INAA, and UCC and RRV values

	2nd Campaign					3rd Campaign				
	P_{0-2}	P_{1-2}	P_{2-2}	P_{3-2}	P_{4-2}	P_{0-3}	P_{1-3}	P_{2-3}	P_{3-3}	P_{4-3}
As	n.d	2.3 ± 0.1	n.d.	13.2 ± 0.4	19.7 ± 0.7	10.0 ± 0.2	2.8 ± 0.1	3.6 ± 0.2	8.1 ± 0.3	34.2 ± 0.9
Ba	124 ± 9	492 ± 37	286 ± 19	451 ± 50	469 ± 43	178 ± 28	470 ± 55	653 ± 44	447 ± 32	560 ± 90
Br	n.d.	15.3 ± 0.7	1.4 ± 0.2	14.8 ± 0.4	17.9 ± 0.5	9.1 ± 0.1	3.6 ± 0.1	4.2 ± 0.1	4.9 ± 0.1	7.0 ± 0.2
Ce	35.4 ± 0.9	96 ± 3	222 ± 10	153 ± 5	115 ± 3	56 ± 2	100 ± 2	171 ± 5	81 ± 2	122 ± 3
Co	1.97 ± 0.03	3.95 ± 0.06	0.82 ± 0.02	7.2 ± 0.1	13.2 ± 0.4	2.66 ± 0.05	3.97 ± 0.07	5.0 ± 0.1	9.0 ± 0.2	10.4 ± 0.2
Cr	31.2 ± 0.4	19.9 ± 0.8	14.2 ± 0.6	95 ± 4	122 ± 4	39 ± 2	21.4 ± 0.8	31 ± 1	142 ± 2	110 ± 6
Cs	1.12 ± 0.04	5.0 ± 0.2	2.6 ± 0.2	7.6 ± 0.3	4.2 ± 0.2	1.2 ± 0.1	3.9 ± 0.1	4.5 ± 0.2	4.3 ± 0.2	5.1 ± 0.3
Eu	0.42 ± 0.01	0.93 ± 0.04	0.63 ± 0.04	1.33 ± 0.03	0.96 ± 0.03	0.63 ± 0.02	0.80 ± 0.02	1.15 ± 0.02	0.81 ± 0.03	1.12 ± 0.04
Fe(%)	2.77 ± 0.01	3.04 ± 0.02	0.41 ± 0.01	4.80 ± 0.03	4.43 ± 0.02	3.85 ± 0.02	1.76 ± 0.01	2.15 ± 0.01	2.64 ± 0.01	4.83 ± 0.03
Hf	19.8 ± 0.3	19.3 ± 0.4	25.8 ± 0.5	11.6 ± 0.3	21.1 ± 0.4	34.0 ± 0.6	20.8 ± 0.4	54.6 ± 1.3	13.8 ± 0.2	24.6 ± 0.5
La	21.7 ± 0.6	47.2 ± 0.2	100.4 ± 0.5	64.2 ± 0.3	34.7 ± 0.8	30.6 ± 0.1	40.5 ± 0.2	85.4 ± 0.5	43.3 ± 0.3	43.2 ± 0.2
Lu	0.22 ± 0.02	0.38 ± 0.02	0.43 ± 0.03	0.46 ± 0.04	0.72 ± 0.05	0.36 ± 0.02	0.44 ± 0.02	0.79 ± 0.03	0.42 ± 0.02	0.85 ± 0.11
Mn	174 ± 4	691 ± 6	182 ± 4	304 ± 25	395 ± 15	210 ± 3	195 ± 1	649 ± 23	163 ± 5	372 ± 11
Nd	6.8 ± 1.4	26 ± 3	86 ± 8	19 ± 3	23 ± 3	8 ± 2	29 ± 2	68 ± 5	34 ± 3	34 ± 3
Rb	13.1 ± 0.7	130 ± 5	80 ± 4	60 ± 4	50 ± 3	17 ± 1	120 ± 6	145 ± 7	79 ± 4	67 ± 6
Sb	n.d.	0.23 ± 0.03	n.d.	1.0 ± 0.1	4.8 ± 0.3	0.46 ± 0.05	0.29 ± 0.02	0,25 ± 0.02	1.18 ± 0.05	3.8 ± 0.5
Sc	5.04 ± 0.07	5.2 ± 0.1	1.42 ± 0.03	13.9 ± 0.2	17.3 ± 0.2	7.60 ± 0.03	5.31 ± 0.02	6.1 ± 0.1	8.5 ± 0.1	20.6 ± 0.2
Sm	3.13 ± 0.05	7.5 ± 0.1	14.6 ± 0.2	20.2 ± 0.3	5.6 ± 0.1	4.2 ± 0.1	7.2 ± 0.1	12.9 ± 0.3	5.8 ± 0.1	7.0 ± 0.1
Ta	2.0 ± 0.1	2.1 ± 0.2	2.3 ± 0.3	3.9 ± 0.2	2.1 ± 0.1	3.2 ± 0.3	2.5 ± 0.2	2.9 ± 0.2	2.1 ± 0.1	2.5 ± 0.2
Tb	0.35 ± 0.04	0.8 ± 0.1	1.2 ± 0.1	2.0 ± 0.2	1.4 ± 0.3	0.5 ± 0.1	0.7 ± 0.1	1.4 ± 0.2	0.7 ± 0.1	1.8 ± 0.3
Ti (%)	0.67 ± 0.03	0.47 ± 0.01	0.26 ± 0.02	0.69 ± 0.06	0.92 ± 0.1	0.87 ± 0.08	0.45 ± 0.04	0.763 ± 0.003	0.45 ± 0.02	0.85 ± 0.02
Th	20.2 ± 0.7	23.1 ± 0.6	56.7 ± 1.6	27.7 ± 0.5	19.6 ± 0.7	30.3 ± 0.8	23.9 ± 0.8	44 ± 2	18.4 ± 0.7	27 ± 1
U	2.8 ± 0.5	6.5 ± 0.3	7.3 ± 0.3	7.4 ± 0.3	6.3 ± 0.4	6.8 ± 0.3	6.8 ± 0.3	9.5 ± 0.6	5.1 ± 0.2	9.0 ± 0.5
V	53 ± 7	42 ± 1	10.1 ± 0.2	119 ± 10	111 ± 1	85 ± 3	50 ± 6	40 ± 1	70 ± 5	135 ± 2
Yb	1.8 ± 0.1	2.4 ± 0.1	2.9 ± 0.1	3.4 ± 0.1	5.2 ± 0.2	2.3 ± 0.1	3.0 ± 0.1	4.9 ± 0.2	2.7 ± 0.1	7.3 ± 0.4
Zn	33 ± 1	55 ± 2	16.2 ± 0.9	459 ± 17	929 ± 36	36.5 ± 1.3	39 ± 1	50 ± 3	285 ± 15	386 ± 15

	4th Campaign					RRV	UCC
	P_{0-4}	P_{1-4}	P_{2-4}	P_{3-4}	P_{4-4}		
As	7.0 ± 0.1	2.7 ± 0.1	1.2 ± 0.1	12.9 ± 0.4	19.5 ± 0.3	23 ± 17	2
Ba	180 ± 12	450 ± 28	661 ± 36	623 ± 77	485 ± 44		668
Br	5.5 ± 0.1	6.1 ± 0.1	1.8 ± 0.1	10.9 ± 0.2	8.2 ± 0.1		1.6
Ce	52 ± 2	115 ± 4	245 ± 6	163 ± 5	114 ± 3		65.7
Co	2.27 ± 0.05	4.00 ± 0.09	4.46 ± 0.07	12.5 ± 0.3	7.4 ± 0.15	19 ± 3	11.6

Table 2 continued

	4th Campaign					RRV	UCC
	P_{0-4}	P_{1-4}	P_{2-4}	P_{3-4}	P_{4-4}		
Cr	34 ± 2	26 ± 1	33 ± 2	109 ± 7	101 ± 4	36 ± 7	35
Cs	1.9 ± 0.1	4.4 ± 0.2	5.0 ± 0.2	7.0 ± 0.4	4.5 ± 0.2		5.8
Eu	0.81 ± 0.02	1.10 ± 0.04	1.65 ± 0.04	1.64 ± 0.06	1.16 ± 0.04		0.95
Fe(%)	3.37 ± 0.02	2.82 ± 0.02	1.61 ± 0.01	4.39 ± 0.03	4.95 ± 0.02		3.09
Hf	28.3 ± 1.1	40 ± 2	73 ± 4	13.9 ± 0.7	22.1 ± 0.8		5.8
La	31.4 ± 0.1	54.3 ± 0.2	122.4 ± 0.8	85.9 ± 0.7	41.8 ± 0.2		32.3
Lu	0.33 ± 0.01	0.65 ± 0.01	1.23 ± 0.07	0.82 ± 0.07	0.90 ± 0.05		0.27
Mn	177 ± 4	352 ± 21	349 ± 8	381 ± 26	334 ± 20		527
Nd	23 ± 4	42 ± 4	99 ± 9	74 ± 9	44 ± 8		25.9
Rb	11 ± 1	103 ± 4	151 ± 7	95 ± 9	56 ± 2		110
Sb	0.43 ± 0.03	0.20 ± 0.02	0.22 ± 0.03	1.6 ± 0.1	2.2 ± 0.1		0.31
Sc	10.1 ± 0.2	10.1 ± 0.2	6.3 ± 0.1	14.2 ± 0.3	18.4 ± 0.2		7
Sm	4.1 ± 0.1	8.7 ± 0.2	16.7 ± 0.2	10.9 ± 0.2	6.3 ± 0.2		4.7
Ta	2.6 ± 0.2	2.4 ± 0.1	2.9 ± 0.3	4.4 ± 0.5	3.0 ± 0.30		1.5
Tb	0.8 ± 0.1	1.7 ± 0.1	2.5 ± 0.2	1.5 ± 0.2	0.9 ± 0.1		0.5
Ti (%)	0.62 ± 0.04	0.50 ± 0.06	0.51 ± 0.01	0.65 ± 0.02	0.72 ± 0.07	0.63 ± 0.12	0.312
Th	24.9 ± 0.8	29 ± 1	57 ± 2	28 ± 1	24.4 ± 0.7	24 ± 8	10.3
U	5.4 ± 0.3	8.7 ± 0.7	12.1 ± 0.5	8.6 ± 0.6	7.2 ± 0.3	12 ± 5	2.5
V	82 ± 8	46 ± 4	36 ± 2	94 ± 8	99.4 ± 0.2	59 ± 20	53
Yb	2.7 ± 0.1	4.5 ± 0.4	7.4 ± 0.3	5.4 ± 0.5	7.1 ± 0.5		1.5
Zn	35 ± 1	46 ± 2	49 ± 2	367 ± 18	297 ± 12	82 ± 14	52

n.d. Not determined

Table 3 Concentrations for Cd and Pb by GF-AAS and Hg by CV-AAS in sediment samples (μg kg^{-1}), PEL and TEL values, CONAMA and regional reference values (RRV)

Samples	Hg (μg kg^{-1})	Cd (μg kg^{-1})	Pb (μg kg^{-1})
2nd Sampling campaign			
P_{0-2}	61 ± 10	44 ± 1	11,090 ± 265
P_{1-2}	76 ± 8	81 ± 2	16,660 ± 158
P_{2-2}	<10	45 ± 2	6,360 ± 481
P_{3-2}	449 ± 19	679 ± 38	60,490 ± 550
P_{4-2}	583 ± 33	1464 ± 24	90,920 ± 620
3rd Sampling campaign			
P_{0-3}	132 ± 3	39.8 ± 0.5	12,990 ± 244
P_{1-3}	73 ± 1	136 ± 6	19,120 ± 220
P_{2-3}	90 ± 1	62 ± 7	16,140 ± 357
P_{3-3}	274 ± 4	243 ± 2	38,730 ± 1534
P_{4-3}	438 ± 3	833 ± 17	47,060 ± 890
4th Sampling campaign			
P_{0-4}	149 ± 2	57 ± 2	11,050 ± 394
P_{1-4}	98 ± 1	52 ± 9	20,900 ± 108
P_{2-4}	62.7 ± 0.5	47 ± 1	10,410 ± 215
P_{3-4}	405 ± 3	466 ± 16	55,840 ± 598
P_{4-4}	456 ± 2	483 ± 8	47,520 ± 427
TEL (mg kg^{-1})	0.17	0.6	35.0
PEL (mg kg^{-1})	0.486	3.5	91.3
CONAMA(level 1)	0.17	0.60	35.0
CONAMA(level 2)	0.486	3.5	91
RRV (mg kg^{-1})	0.14 ± 0.05	0.22 ± 0.08	61 ± 7

or natural weathering origin; values above 1.5 indicate anthropogenic contribution. The higher the EF value the more severe is the anthropogenic contribution.

Using the above calculations we obtained EF values higher than 1.5 for As, Br, Hf, Mn, Rb, Ta, Th, Ti, U, Zn and REE:at P_0, for Br (2.4–5.3), Hf (3.4–5.4), Th (1.7–2.7), Ti (2.6–3.0), and Yb (1.7); at P_1 for As (1.6–1.8), Br (2.6–12.9), Hf (4.5–4.8), Ta (1.9–2.2), Th (2.0–3.1), U (2.4–3.6) and RRE; at P_2 for Br (3.0–4.3), Hf (10.8–21.9), Rb (1.5–3.6), Ta (2.2–7.5), Th (5.0–27.2), Ti (1.8–4.1), U (4.4–14.4) and REE; at P_3 and P_4, for As (3.2–5.8), Br (2.0–4.7), Sb (2.6–6.2), U (1.5–1.7) and Zn (2.2–7.2). Therefore anthropogenic contributions can be observed throughout the Tietê River from P_0 (springs) to P_4 (Suzano county). The highest EF was found for Hf (1.0–21.9), Th (0.8 to 27.2), U (1.0–14.4) and REE at P_2.

P_0 is located at Ponte Nova's Reservoir, Salesópolis County, near the springs of the Tietê River. P_1 and P_2 are at Biritiba Mirim city near an ore mining operation (VCN mining) and probably the reason for the higher concentrations of REE, Hf, Ta, Ti, Th and U in these sediment samples, mainly at P_2. P_3 and P_4 showed high contamination of As, Br, Sb and Zn, probably due to industrial effluents and sewage discharges. These two points have heavy industrial activities being P_3 located at Mogi das Cruzes County (near Leon Feffer Park) and P_4 in Suzano County. P_4 is located in the first access to the Tietê River after a sewage treatment plant (ETE-Suzano).

The concentration of As, Co, Cr, Ti, Th, U, V and Zn were compared to Regional Reference Values (RRV) for sediments from USTR (Upper Side Tiete River—from Salesópolis until Pirapora do Bom Jesus) determined by Nascimento and Mozeto [4] for bottom sediments from this region. These sediment samples were collected in small streams and rivers as close as possible to their upper

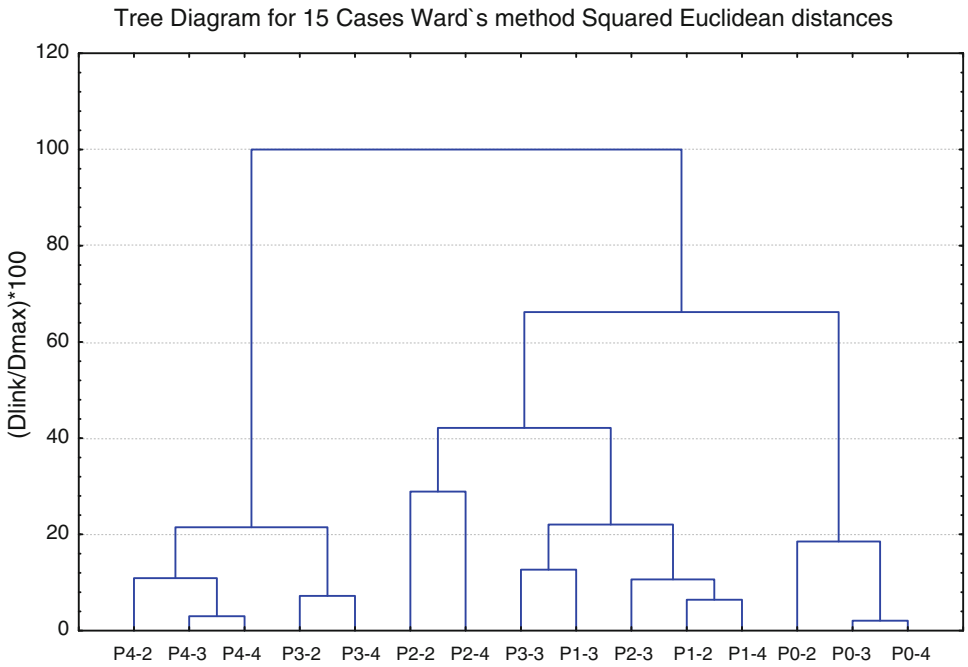

Fig. 2 Dendrogram comparing the similarity of the sediment samples at the sampling points (cases) in the three sampling campaigns

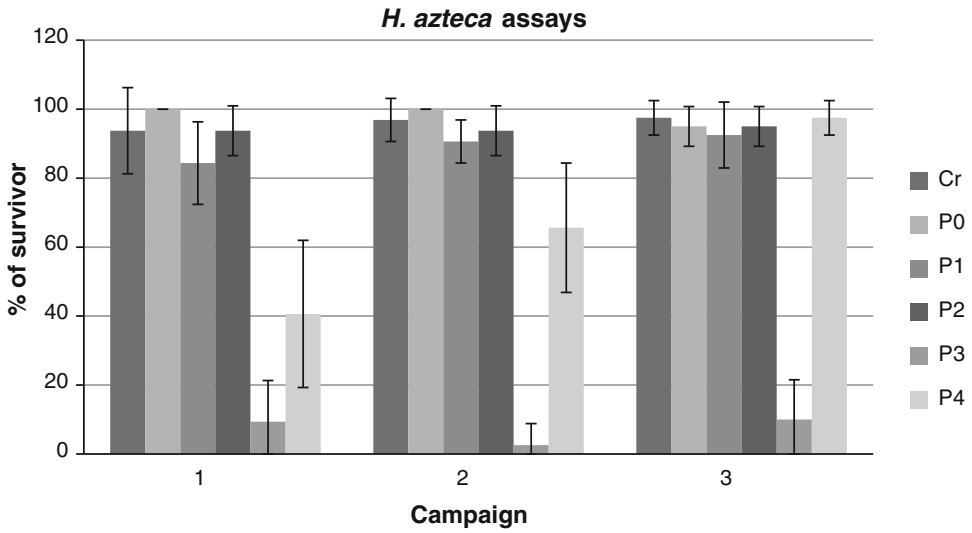

Fig. 3 Survival percentage of *H. azteca* during exposition to whole sediment

reaches, as well as in rivers and reservoirs in locations minimally affected by human contamination. In the present study, the elements Cr, Ti, V and Zn had concentrations higher than RRV at P_3 and P_4 in all sampling campaigns. Th showed higher RRV values in many points but mainly at P_2 and P_3. The reference value for As (23 ± 17 mg kg^{-1}) is much higher than the results obtained in the present study (1.2–19.5 mg kg^{-1}), except for P_4 in the 3rd campaign (34.2 mg kg^{-1}).

The results obtained for metals Cd, Hg and Pb (Table 3) were compared to the TEL and PEL values from Canadian Council of Minister of the Environment [12] which have been adopted by the Environmental Control Agency of Sao Paulo State (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. CONAMA 344 resolution [10] for heavy metals in sediments uses these two limits: level 1 (similar to TEL values) and level 2 (similar to PEL values). The concentration values for Hg exceeded the TEL values (0.17 mg kg^{-1}) at P_3 and P_4 in all sampling campaigns and PEL at P_4 in the 2nd campaign. Cd exceeded the TEL value (0.6 mg kg^{-1}) at P_3 and P_4 from the 1st campaign and P_4 in the 2nd one. All the other concentration values were lower than TEL limit. Again P_3 and P_4 presented concentration values for Pb higher than TEL (35 mg kg^{-1}) in all sampling campaigns. The concentration values found in points P_0, P_1 and P_2 were lower than TEL.

When the values obtained in the present study were compared to Regional Reference Values (RRV) from Nascimento and Mozeto [4], the same behavior was observed for P_3 and P_4 for Cd and Hg. Only the result for P_{4-2} (Point 4—2nd campaign) (90.9 mg kg^{-1}) was higher than the RRV for Pb (61 ± 7 mg kg^{-1}).

When Cluster Analysis was applied to the chemical data obtained for all elements analyzed three different groups were formed (Fig. 2):

- Group 1: P_3 and P_4 from all sampling campaigns formed a separate group, except for P_{3-3} that joined the group of samples from P_1 and P_2;
- Group 2: formed by P_2 and P_1 (all sampling campaigns) and P_{3-3};
- Group 3: formed by P_0 (all sampling campaigns)

P_{3-3} presented lower concentration values for many elements but mainly for As, Cd, Hg, Mn, Pb and V in comparison with P_{3-2} and P_{3-4} (P_3, 2nd and 4th campaign, respectively). This can possibly explain why this sample's behavior is in Group 2.

In order to investigate the association among the elements in sediments, R-mode factor analysis was performed using the Varimax method. Four factors were extracted considering factor loadings higher than |0.6| and the results can be interpreted as follows:

Factor 1 (F1, which corresponds to 28.2 % of the total variance) is formed mainly by the elements Ce (0.976), Eu (0.650), La (0.945), Lu (0.630), Nd (0.880), Sm (0.863), Tb (0.795), Th (0.784) and U (0.724). These elements are both positively correlated to each other as well as negatively correlated with Br (−0.364), Fe (−0.305), Ti (−0.324) and V (−0.232);

Factor 2 (F2, which corresponds to 31.0 % of the total variance) is formed by metals Cd (0.900), Cr (0.882), Fe (0.845), Hg (0.989), Pb (0.955), Sc (0.894), Ti (0.600), V (0.899) and Zn (0.914) with a very high correlation;

Factor 3 (F3, which corresponds to 14.8 % of the total variance) includes Ba (0.710), Mn (0.622), and Rb (0.648) and is negatively correlated with As (−0.885) and Br (−0.550);

Factor 4, which corresponds to 7.3 % of the total variance) includes Hf (0.584) and Ti (0.588) positively correlated to each other and also negatively correlated to Co (−0.566).

Altogether, the four factors explain 81.3 % of the total variance. It is interesting to note the strong correlation between metals in F2.

Ecotoxicological assays

The toxicity results are presented in Fig. 3. Survival of *H. azteca* was lower when the organisms were exposed to sediments sampled at P_3 and P_4, mainly in the second and third campaigns.

Toxicity results are in accordance with chemical determinations since P_3 and P_4 data for heavy metals are much higher when compared to the other sites. The tests measured interactive toxic effects of complex contaminant mixtures in sediment. P_3 and P_4 sampling sites are relatively close to the industrial area of Suzano County and Sao Paulo Metropolitan Region.

Conclusions

The precision and accuracy of the analytical techniques used in this study for trace and major element determinations were good. P_0, located near the springs of the Tietê River, in general, had the lowest concentration values for all elements determined in the sediment samples analyzed. P_1 and P_2 showed contamination by the elements of REE, Hf, Ta, Ti, Th and U probably due to the influence of an ore mining operation (VCN mining) located near these two points. P_3 and P_4 showed high contamination levels for As, Br, Cd, Hg, Pb, Sb and Zn, probably due to industrial effluents and sewage discharges. These two points are near industrial activities with P_3 located in Mogi das Cruzes County and P_4 in Suzano County. P_4 is located after a sewage treatment plant (ETE-Suzano).

Toxicity results are in accordance with chemical determinations at P_3 and P_4. The *H. azteca* survival rate was lower when the organisms were exposed to sediments sampled at P_3 and P_4, mainly in the second and third campaigns. The results for heavy metals at these points were much higher compared to the other sites (P_0, P_1 and P_2). The tests measured interactive toxic effects of complex contaminant mixtures in sediments. P_3 and P_4 exceeded TEL values for Cd, Hg and Pb in sediments. P_4 presented values between TEL and PEL and the ecotoxicological assays with *H. azteca* proved the occurrence of adverse effects on the biological community. The results presented in this study showed that the assessment of trace and major elements together with ecotoxicological assays with *H. azteca* organism allowed a more complete contamination evaluation of the Tietê River, an important river for the region. This study showed that human activity can provoke serious adverse effects on ecosystems.

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