

NAA and XRF technique bottom sediment assessment for major and trace elements: Tietê River, São Paulo State, Brazil

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Abstract The concentration and distribution of selected trace and major elements, in river bottom sediments (12 sites) along the Tietê River basin were investigated. Total concentration for major by XRF and trace by INAA elements were determined. Physicochemical parameters pH, DO, Eh and conductivity were measured and discussed. Enrichment factor, geoaccumulation index, TEL and PEL criteria used to assess contamination levels allowed to classify the river as: less polluted (sites 1A, 1B—headwaters), more polluted (sites 2A–3C—after crossing São Paulo county) and moderately polluted (sites 4, 5, 6 and 7—far from São Paulo city).

Keywords Metals · Trace elements · Sediments · Enrichment factor · IGeo · Tietê River

Introduction

The Tiete River drains an area composed of six sub-basins (Alto Tiete, Sorocaba/Médio Tiete, Piracicaba-Capivari-Jundiá, Tiete/Batalha, Tiete/Jacaré and Baixo Tiete). Along its extension (1100 km), its margins bathe 62 municipalities. In spite of all its historical contributions, its hydroelectric and economic importance in the São Paulo

State, the Tiete River is also considered one of the world's most polluted rivers.

The springs of the Tietê River basin are located in Salesópolis City, about 60 km east of São Paulo City. After cutting across the city, the Tietê River flows through the state from east to west and drains into the Paraná River at the São Paulo and Mato Grosso do Sul state border [1]. The main effluent sources that contribute to the environmental degradation in the basin are predominantly untreated domestic sewage, intense industrial activity in the São Paulo Metropolitan Region (SPMR), agricultural production and the agro-industrial park for the production of sugar, alcohol, and citric juices in the lower and mid Tietê region [1].

The upper region of the Tiete River (URTR) includes Salesópolis city up to the Rasgão Storage Dam in Pirapora do Bom Jesus city, an agricultural area [2]. Depleted water oxygen levels, excessive organic matter content and contaminants are evidence of the negative impacts to the river. Regarding inorganic contaminants, metals such as Cu, Fe and Zn are essential for living organisms when present at very low concentrations. However, other metals such as Cd, Hg and Pb are toxic even at relatively low concentrations and may affect living organisms by several routes [3, 4].

In addition, other important sources of metal release into aquatic environments are industrial and domestic discharge of effluents into waterways [5].

Many environmental studies have been developed in the Tiete River basin [1, 2, 5–11]. Nascimento and Mozeto [1] established reference values for metals and metalloids in sediments along the Tietê River basin due to the importance of this river for São Paulo State and its degree of pollution levels.

The present study was performed in water reservoirs of the upper region of the Tietê River in São Paulo State, Brazil: Usina Parque Reservoir, located near Salesópolis

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city; Edgard de Souza Reservoir, at Santana do Parnaíba city; and Pirapora do Bom Jesus Reservoir, at Pirapora do Bom Jesus city. Four other sites were also chosen along the Salto de Itu and Porto Feliz cities, for investigation. The objective was to verify the concentration and distribution of selected metals, trace and major elements, in bottom sediments of this highly polluted river in the southeast region of Brazil. For this purpose, two nuclear analytical techniques were applied and the respective elements were analyzed: instrumental neutron activation analysis (INAA): As, Ba, Br, Ca, Co, Cr, Cs, Hf, Rb, Sb, Sc, Ta, Th, U and Zn; X-ray fluorescence spectrometry (XRF): major elements and loss on ignition. In addition, the concentration of dissolved oxygen (DO), pH, conductivity and oxidation–reduction potential (Eh) in the sediment and water samples from all sampling sites were measured as well. The obtained data were compared to North American shale composite (NASC) reference values [12] and Nascimento and Mozeto reference values [1] for the region. The enrichment factor (EF), geoaccumulation index (IGeo), threshold effect level (TEL) and probable effect level (PEL) oriented values from Environment Canada [13] were applied in order to verify the pollution level for the analyzed elements.

Study area

In order to keep up with the energy needs of rapid urban and industrial development beginning in the 1950s, 11 reservoirs were constructed in the basin to produce

hydroelectric power, ranging from the state capital to the extreme west. The lithology of the spring's region is basically formed by migmatites and granites and the soils are reddish-yellow podzolic type [14]. Figure 1 shows the sediment sampling locations, covering six municipalities, in areas subjected to anthropogenic contamination. In this study twelve bottom sediment samples were collected, in the upper region of the Tiete River (URTR) (sites 01–03) and beginning of the middle region of the Tiete River (MRTR) (sites 04–07).

The URTR flows through a highly populated area, which in turn intensively modifies its natural conditions. In the upper region, the river flows freely with reduced width and depth and high sinuosity. In the county of Mogi das Cruzes the river widens and deepens to an average of 1.5 m during the dry season. When it flows through São Paulo city the river has an artificial bed of 26 km and its width measures 45–56 m with a normal depth of 5.7 m. Downstream of the State capital, there is a short extension of free flowing water with an irregular bed followed by two small dams [15].

Experimental

Sampling and sample preparation

Twelve bottom sediment samples were collected in the Tietê River. Site 01 is located at the Usina Parque de Salesópolis Reservoir (site 1A-entrance of the reservoir, 1B-middle of the reservoir); site 2 is located at the Edgard

Fig. 1 Tiete River extension and sampling site locations



Table 1 Silt, clay and sand contents of the sediment samples

Sites	Sampling location	Clay (%)	Silt (%)	Total sand (%)	Textural classification
1B	Usina Parque de Salesópolis (middle of reservoir)	18.7	5.9	75.4	Very sandy
2A	Santana do Parnaíba reservoir (entrance of the reservoir)	5.7	10.4	83.9	Very sandy
3A	Pirapora do Bom Jesus reservoir (entrance)	22.0	28.0	50.0	Very sandy
4	Salto de Itu County	6.9	7.3	85.8	Very sandy
5	Between Salto de Itu and Porto Feliz Counties	16.5	19.1	64.4	Very sandy
6	Between Salto de Itu and Porto Feliz Counties	14.9	15.4	69.7	Very sandy
7	Porto Feliz County	10.0	10.2	79.8	Very sandy

de Souza Reservoir (Santana de Parnaíba City)(2A-entrance, 2B-middle, 2C-end of the reservoir); site 3 is located at the Pirapora do Bom Jesus Reservoir (3A-entrance, 3B-middle, 3C-end of reservoir); site 4, the Salto de Itu City; site 5, between Salto de Itu and Porto Feliz Cities, site 6, between Salto de Itu and Porto Feliz Cities, 12 km below site 5; site 7, at Porto Feliz City. Sediment samples were collected by using a Van Veen dredge, with a full opening of approximately 60 cm, weighing about 20 kg of stainless material, collecting approximately 1.5 kg of sediment in a depth of 0–5 cm. At the laboratory, the sediment samples were first passed through a 2 mm sieve, then dried at 40 °C in a ventilated oven until constant weight, ground in a mortar, passed through a 0.125 mm sieve and then homogenized before analysis. The total fraction of the sediment was analyzed (<2 mm). Sampling sites are presented in Fig. 1.

Silt, clay and sand contents of the sediment samples

This determination was carried out at the Instituto Agrônomo de Campinas (IAC) according to Camargo et al. [16] and the results are presented in Table 1.

The granulometric classification was accomplished based on the following criteria: silt (particles from 0.004 to 0.063 mm), Clay (<0.004 mm) and sand (>0.063 mm). The granulometric composition of some sediment samples collected along the Tietê River presented a high sand content ($\geq 50\%$). Sediment sample from sites 3A and 04 presented, respectively, the highest (50.0 %) and the lowest (14.2 %) proportions of silt and clay fraction. Samples from sites 1B and 04 presented the lowest proportions of silt (5.9 and 7.3 %, respectively). Samples from sites 2A and 4 presented the lowest clay proportion (5.7 and 6.9 %, respectively) (Table 1).

INAA analytical technique

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, reference materials and synthetic standards were irradiated for 8 h under a thermal neutron flux of $10^{12} \text{ cm}^{-2} \text{ s}^{-1}$ at the IEA-R1 nuclear research reactor in IPEN. Two series of counting were made: the first, after 1 week decay; and the second, after 15–20 days. Larizzatti et al. [17] describe details of the analytical methodology. The elements determined were As, Ba, Br, Co, Cr, Cs, Fe, Hf, Na, Rb, Sb, Sc, Ta, Th, U and Zn. The uncertainties of the results were calculated by error propagation. Methodology validation was performed by analyzing reference materials BEN (Basalt-IWG-GIT) from CNRS (France) and Soil 5 and Lake Sediment (SL1) from 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, proving the precision and accuracy of the analytical technique, respectively.

XRF technique

X-ray fluorescence spectrometry (XRF) was applied for the determination of major elements in sediments. Samples were prepared according to Mori et al. [18] 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-1^a and JG-1^a reference materials (Geological Survey of Japan) [19]. Wavelength-dispersive XRF using fused glass discs was used for major element determinations. The precision of these measurements was better than 5 % RSD (relative standard deviation). Loss on ignition (LOI) was determined by dry samples at 1000 °C.

Statistical treatment

Before statistical analysis, data were standardized (Z score). STATISTICA 10 (STATSOFT) statistical

Table 2 Physicochemical parameters measured in the water column during the sampling collection (sites 1–7)

Sampling sites	GPS position	Depth of water column (m)	pH	Conductivity ($\mu\text{S}/\text{cm}$)	Temperature ($^{\circ}\text{C}$)	Eh (mV)	DO (ppm)
T1A	23°24'19"S 45°49'40"O	2.0	6.5	33.3	18.3	230.0	8.52
T1B	23°33'77"S 45°49'85"O	4.0	6.37	34.2	22.4	261.0	8.68
T2A	23°27'19"S 49°54'32"	4.5	7.03	686	20.8	−397.0	1.18
T2B	23°27'90"S 46°54'05"	5.5	7.0	690	22.7	−330.0	1.74
T2C	23°27'60"S 46°54'35"	8.0	7.0	691	22.3	−328.0	1.12
T3A	23°23'02"S 46°57'61"	8.0	7.2	640	19.2	−279.0	0.43
T3B	23°23'46"S 46°58'49"	5.0	7.16	628	20	−282.5	n.d. ^a
T3C	23°23'26"S 46°59'32"	4.5	7.26	619	20.9	−280.8	n.d. ^a
T4	23°12'18"S 47°18'37"	3.0	7.42	450	25.2	145.3	6.76
T5	23°10'18"S 47°22'37"	1.0	5.48	441	25.8	123.0	3.74
T6	23°11'18"S 47°25'37"	2.0	7.17	432	26.8	58.9	1.9
T7	23°10'9"S 47°29'23"	2.0	7.19	430	26.8	108.0	1.1
Minimum			5.48	33.3	18.3	−397.0	0
Maximum			7.26	691	26.8	261.0	8.68

^a Not detectable

program was used. The principal component analysis (PCA) was applied in order to detect interrelationships among sites and chemical parameters. The cluster analysis, frequently applied to environmental evaluations, was used to group samples according to their similarities.

Results and discussion

Physicochemical parameters

The physicochemical parameters measured in situ in the water column showed the differences among the environments especially in terms of dissolved oxygen (DO) and Eh (Table 2). Low conductivity values for the T1A and T1B sites (Usina Parque de Salesópolis, beginning of the Tiete River) were found. The DO is close to the ideal value for natural waters, as shown by the results in Table 2. Oxidation–reduction potential (Eh) values indicate an oxidant status for untreated water.

In sites T2 and T3, at the Santana do Parnaíba and Pirapora do Bom Jesus dams, respectively, the conductivity reaches its maximum value, up to now, reaching 700 μS and Eh reaching lower values −400 mV, indicating high-polluted water levels. In general, conductivity levels above 100 μS are indicative of impacted environments [20]. In these sampling sites, the DO is practically zero and the pH values increased probably due to the organic matter excess accumulated in these reservoirs, due to the great amount of untreated sewage discharge. These sites show a strong reductor environment. These sites are the most polluted ones because they are located immediately after the river crossing the São Paulo County. These parameters are inversely proportional to that of the beginning of the Tiete River.

Silva et al. [6] in the Tietê River study described that Pirapora Reservoir receives water from the Pinheiros River, increasing the pollution load and resulting in the poor quality of the Pirapora Reservoir indicated by the dark color of the water, formation of foam along the dam and

the intense smell of gases (probably CH_4 and H_2S). These authors also found a complete absence of DO and Eh values of -583 mV in this reservoir similar to those found in the present study. They concluded that the absence of DO could be explained by the microbial activity that metabolizes the high levels of organic matter from domestic and industrial wastes [6].

Sites 1–3 are located at High Tietê (URTR), approximately 750 m above sea level, where the highest concentration of pollutant agents in the river can be found (sites 2 and 3). From these sites, the river presents a fall of more than 200 m flowing to the countryside of São Paulo State. This fact promotes a partial oxygenation of the river waters that can be observed in the physicochemical parameter results for site 4, located immediately after a waterfall known as Salto de Itú. In sites located from 4 to 7, the oxygen level varied from 6.86 ppm (point 4) to 1.1 ppm (point 7), where the water oxygenation is promoted by a series of rapids. Thus, aquatic life (fish) is restricted to this region of the river. The increase of Eh and decrease of pH values were also observed at these sites.

Concentration of major and trace elements and contamination assessment by TEL and PEL oriented values

Table 3 shows the results obtained for the INAA and XRF analytical techniques for all sediment samples analyzed, NASC values [12], regional reference values (RRV) for bottom sediments of the URTR [1] (Upper Region Tiete River—from Salesópolis until Pirapora do Bom Jesus), the region that comprehends sampling sites from 01 to 03 in this study, and TEL and PEL oriented values [13].

Major elements and their contents are quite representative of the differences in the geological formations in the surrounding areas that contribute these elements to the sediments. The results obtained for these elements and their elemental ratios indicate three different deposition and geochemical environments. The first one composed by the Salesópolis samples with the highest concentrations of SiO_2 and K_2O and the lowest concentrations of Fe_2O_3 and CaO ; the second composed by the samples from Santana do Parnaíba and Pirapora do Bom Jesus presenting the highest concentrations of Al_2O_3 , TiO_2 , Fe_2O_3 , MnO , MgO , CaO , Na_2O and P_2O_5 and the third one composed by the samples from Itú to Porto Feliz presenting high concentrations of SiO_2 and generally intermediate concentrations of the other elements. Silva et al. [6] also found a high content of Al in the São Paulo Metropolitan Region (SPMR) (Pirapora and Rasgão reservoirs) where granites, phyllites, schists, quartzites, and meta-lime-stones are the predominant geological formations. Thus weathering processes could explain the observed differences since only

the granulometric variation (Table 1) is not enough to justify the variation in the observed concentrations. The high $\text{SiO}_2/\text{Al}_2\text{O}_3$ value results from the increase of the quartz proportion which is the main constituent of the sediment [21]. Nevertheless, the anoxic and reducing condition observed in the sampling sites 2 and 3 (presenting higher $\text{Fe}_2\text{O}_3/\text{SiO}_2$ and MnO/SiO_2 ratios) also contribute to the Fe and Mn oxi-hydroxides formation, which in turn, can also concentrate other minor and trace elements.

Comparing the major element contents with NASC reference values higher contents were found for: SiO_2 : sites 1A, 1B, 4, 5, 6 and 7; TiO_2 : from 2A to 3C; Al_2O_3 : 2B, 2C, 3A and 3C and Fe_2O_3 : 2B and 3C. The other major elements analyzed presented lower concentration than NASC reference values.

The results for the semi-metal As and metals Cr and Zn were compared to the oriented values TEL and PEL. These oriented values were established by the Canadian Sediment quality guidelines [13] and adopted by CETESB (Environmental Company of São Paulo State) for sediment quality monitoring programs. 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.

As can be seen in Table 3 for As (TEL—5.9 and PEL—17.0 mg kg^{-1}), samples from sites 2A, 2B, 3A and 3C, surpassed TEL values and none of the sampling sites exceeded the PEL value. For Cr (TEL—37.3 and PEL—90.0 mg kg^{-1}), samples from sites 06 and 07 exceeded the TEL value and sites from 2A to 3C, surpassed the PEL value. For Zn (TEL—123 and PEL—315 mg kg^{-1}), samples from sites 6 and 7, exceeded TEL value and samples from points 2A to 05, the PEL value.

The results for Cr and Zn in sediment samples from sites 2A–3C showed a high contamination level for these elements and can be classified as poor quality for As (>5.9 mg kg^{-1}) according to the TEL and PEL oriented values and adopted by CETESB.

The RRV corresponds to the total concentration (average \pm SD), for about 20 sampling points in the URTR. Our results for the same region (in mg kg^{-1}) were: As (5.2 ± 3.3), Co (12.8 ± 8.1), Cr (117 ± 65), Th (20.3 ± 1.6), U (4.9 ± 0.6) and Zn (514 ± 347). The results for As, Co and U were much lower, Cr and Zn much higher and Th, in the same order of magnitude of those obtained by Nascimento and Mozeto [1].

Favaro et al. [5], in a previous study performed in the URTR region before São Paulo city in bottom sediments, found similar values for most analyzed elements, including high values for Hf, U and Th.

The present study also detected the decreasing distribution $\text{Zn} > \text{Cr}$ concentrations observed by Mortatti et al.

Table 3 Concentration (mean, mg kg⁻¹) for elements determined by INAA, major elements (%) by XRF and NASC values [12] and RRV [1] values for the Upper Tieté region (URTR), TEL and PEL oriented values

Points	1A	1B	2A	2B	2C	3A	3B	3C	4	5	6	7	NASC	RRV	TEL	PEL
As	0.2	0.5	6.3	9.4	5.7	7.6	4.8	7.0	1.5	1.7	2.4	2.5	2	23 ± 17	5.9	17.0
Ba	556	468	683	726	555	659	648	679	580	384	458	445	636			
Br	3.5	6.8	3.2	6.5	3.2	3.6	2.2	4.0	1.2	2.0	2.1	1.4	0.69			
Co	3.1	4.6	29.3	13.3	10.2	14.3	11.2	16.6	6.7	7.3	7.5	6.1	28	19 ± 3		
Cr	21	30	145	215	130	158	99	142	46	68	56	47	125	36 ± 7	37.3	90.0
Cs	2.4	3.5	3.5	5.0	3.4	4.7	3.6	4.8	2.4	2.0	3.0	2.2	5.2			
Hf	24.5	18.0	19.6	10.1	14.2	13.3	24.0	10.0	12.4	9.5	16.2	13.6	6.3			
Rb	91	96	79	86	82	86	88	102	80	49	69	71	125			
Sb	0.05	0.29	2.41	3.03	1.86	2.57	1.56	2.49	0.57	0.77	0.82	0.59	2.09			
Sc	3.1	4.9	11.2	13.6	10.6	13.4	10.6	13.8	4.5	5.0	5.7	5.1	15			
Ta	1.5	1.5	1.8	1.8	1.6	2.4	1.8	1.9	1.5	1.0	1.4	1.2	1.12			
Th	23.1	20.1	20.6	19.4	18.0	22.0	19.9	19.7	13.8	9.4	25.6	11.9	12	24 ± 8		
U	5.2	4.9	4.5	4.3	3.9	5.6	5.8	5.1	3.1	2.5	3.4	2.6	2.7	12 ± 5		
Zn	29	38	668	1017	551	706	377	727	218	361	244	209	85	82 ± 14	123	315
SiO ₂	83.3	82.1	61.6	45.4	60.0	55.9	67.4	50.0	83.5	81.1	80.0	83.3	64.8			
TiO ₂	0.49	0.34	0.97	1.04	0.93	0.97	0.95	1.04	0.65	0.47	0.69	0.56	0.78			
Al ₂ O ₃	7.66	8.34	16.3	22.6	17.3	19.7	15.1	22.6	7.01	7.59	8.75	7.44	16.9			
Fe ₂ O ₃	1.08	1.21	5.91	6.61	5.39	6.19	4.50	6.55	2.05	2.44	2.81	2.23	6.33			
MnO	0.026	0.020	0.051	0.055	0.046	0.050	0.049	0.053	0.039	0.038	0.059	0.043	0.06			
MgO	0.22	0.15	0.69	0.84	0.67	0.64	0.70	0.79	0.23	0.22	0.27	0.23	2.85			
CaO	0.11	0.10	0.78	1.14	0.97	0.72	0.79	0.88	0.28	0.28	0.27	0.23	3.56			
Na ₂ O	0.28	0.23	0.40	0.41	0.40	0.33	0.44	0.36	0.32	0.19	0.25	0.28	1.15			
K ₂ O	2.84	2.21	1.71	1.83	1.93	1.85	1.99	1.94	1.94	1.12	1.59	1.57	3.99			
P ₂ O ₅	0.05	0.06	0.50	0.88	0.53	0.64	0.32	0.60	0.23	0.40	0.36	0.29	0.11			
Loi	3.75	5.54	10.9	18.4	11.9	12.9	7.6	14.5	3.87	6.36	5.04	3.66				
SiO ₂ /	10.9	9.8	3.8	2.0	3.5	2.8	4.5	2.2	11.9	10.7	9.1	11.2				
Al ₂ O ₃																
Fe ₂ O ₃ /SiO ₂	0.01	0.02	0.10	0.15	0.09	0.11	0.07	0.13	0.03	0.03	0.04	0.03				
MnO/	3.1	2.4	8.3	12.1	7.7	8.9	7.3	10.6	4.7	4.7	7.4	5.2				
SiO ₂ × 10 ⁻⁴)																

Loi loss on ignition

[8] in the upper basin; however, results showed that Zn concentrations decreased from the middle basin (which was not observed by these authors). Mortatti et al. [9] also detected an influence of anthropogenic sources at superficial sediments from the headwaters of upper Tietê River basin. Results obtained in the present study corroborates with Almeida et al. [11] that concluded: the quality of the sediments improves with the distance from the metropolitan area of São Paulo confirming the origin of most pollutant substances.

Contamination assessment by EF and IGeo indexes

The EF [22, 23], an index used as a tool to evaluate the extent of metal and trace element pollution in a given environment was calculated by using the equation below:

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

where $[M]/[RE]_{sed}$ = ratio between concentration of the element of interest and reference element in the sample. $[M]/[RE]_{ref}$ = ratio between concentration of the element of interest and reference element in the reference value.

In the present study, Sc was chosen as a reference element for normalization purposes and NASC as reference values for sediments [12]. 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 [24].

Table 4 shows the results obtained for the EF calculated using NASC values as reference values for the elements determined by INAA.

Table 4 EF values calculated for sediment samples using NASC as reference values

Elements	1A	1B	2A	2B	2C	3A	3B	3C	4	5	6	7
As	0.5	0.8	4.2	5.2	4.0	4.3	3.4	3.8	2.5	2.5	3.2	3.7
Ba	4.3	2.2	1.4	1.3	1.2	1.2	1.4	1.2	3.0	1.8	1.9	2.1
Br	24.8	29.9	6.2	10.3	6.6	5.8	4.5	6.3	5.7	8.7	8.1	6.0
Co	0.5	0.5	1.4	0.5	0.5	0.6	0.6	0.6	0.8	0.8	0.7	0.6
Cr	0.8	0.7	1.6	1.9	1.5	1.4	1.1	1.2	1.2	1.7	1.2	1.1
Cs	2.3	2.0	0.9	1.1	0.9	1.0	1.0	1.0	1.6	1.1	1.5	1.3
Hf	19.1	8.7	4.2	1.8	3.2	2.4	5.4	1.7	6.5	4.6	6.8	6.4
Rb	3.6	2.4	0.8	0.8	0.9	0.8	1.0	0.9	2.1	1.2	1.4	1.7
Sb	0.1	0.4	1.5	1.6	1.3	1.4	1.1	1.3	0.9	1.1	1.0	0.8
Ta	6.7	4.2	2.2	1.8	2.0	2.4	2.2	1.8	4.3	2.8	3.3	3.2
Th	9.4	5.1	2.3	1.8	2.1	2.1	2.3	1.8	3.8	2.4	5.6	2.9
U	9.5	5.6	2.3	1.7	2.1	2.3	3.0	2.0	3.8	2.8	3.3	2.8
Zn	1.7	1.4	10.5	13.2	9.1	9.3	6.3	9.3	8.5	12.9	7.6	7.3

EF > 1.5—highlighted values are italicised

Fig. 2 EF for As, Br, Cr, Sb and Zn in all sampling sites

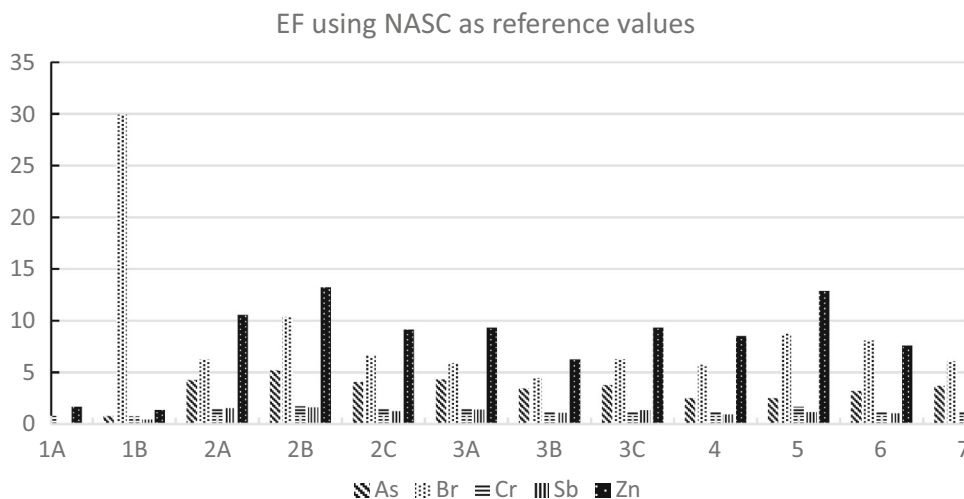


Table 5 Factor loadings for each element/parameter and significant PC

	PC1	PC2
As	0.985858	-0.077914
Ba	0.847814	0.369245
Br	0.310173	0.516264
Co	0.737463	-0.083879
Cr	0.961953	-0.127105
Cs	0.873402	0.314823
Hf	-0.248137	0.659410
Rb	0.363698	0.836995
Sb	0.985367	-0.097390
Sc	0.985390	0.020111
Ta	0.767722	0.471134
Th	0.299514	0.679428
U	0.448086	0.813653
Zn	0.941190	-0.225611
SiO ₂	-0.976468	-0.044908
TiO ₂	0.966001	-0.028452
Al ₂ O ₃	0.973161	0.101303
Fe ₂ O ₃	0.988866	-0.100726
MnO	0.725709	-0.422581
MgO	0.977168	0.051089
CaO	0.957739	-0.070204
Na ₂ O	0.801736	0.200333
K ₂ O	-0.110584	0.926876
P ₂ O ₅	0.886675	-0.355611
LOI	0.928895	-0.012596
pH	0.478764	0.178114
Cond	0.836762	-0.462303
Eh	-0.954986	0.073874
DO	-0.739627	0.432176

According to the results, an EF > 1.5 was found for As in the sampling sites 2A to 07; and for the elements Br, Hf, Ta, Th, U and Zn in most of the sampling sites. Sites 2A to 3C presented the higher EF values for As, Cr and Zn and sites 1A and 1B for Br, Hf, Rb, Ta, Th and U. All other analyzed elements showed 0.5 < EF < 1.5, indicating that these elemental concentrations are probably due to crustal or natural weathering origins.

Figure 2 shows the EF values for the elements As, Br, Cr, Sb and Zn in all sampling sites.

Points 1A and 1B located in the springs of Tiete river is mainly an agricultural region and the high values of EF found can be related to soil fertilizers. According to Favaro et al. [5], the Upper Side of the Tietê River, that comprehends sites 2 and 3, is an important industrial area, which concentrates metallurgical, textile, chemical and pharmaceutical activities, releasing thousands of different compounds through their effluents. This can explain the higher

EF values for As, Cr, Sb and Zn at sites 2A–3C. Sites from points 4 to 7 are dominated by urban, industrial (paper, cellulose, food, textile, leather, steel, oil, sugar and alcohol) and agricultural areas (mostly coffee and sugar cane crops) [25].

Favaro et al. [5] in a previous study also found EF > 1.5 for the elements Hf, Th and U for the same region and attributed to the presence of an ore mining operation (VCN mining).

Geoaccumulation index [22, 23] was also calculated for the sediment concentration results obtained by INAA, adopting the same reference values used for the EF calculations (NASC values). The equation below was used for IGeo calculation:

$$IGeo = \log_2 \left(\frac{C_{am}}{1.5C_{ref}} \right)$$

where C_{am} = concentration of the element of interest in the sample, C_{ref} = reference concentration of the element of interest.

The classification of the contamination levels from IGeo values is: <0, basal level; from 0 to 1, not polluted; from 1 to 2, moderately polluted; from 2 to 3, moderately to polluted; from 3 to 4, polluted to lightly polluted; from 4 to 5, very polluted and >5, highly polluted.

Evaluating the results and its relation with the level of sediment contamination described above (based on IGeo values), it can be inferred that site 1A is moderately polluted by Br (1.75) and Hf (1.38). Site 1B is moderately polluted by Br (2.71) and sites from 2A to 3C are moderately polluted by As (1.1–1.6) and Br (1.6–1.9) and moderately to polluted for Zn (2.1–3.0). Site 5 is moderately polluted by Zn (1.5). Similar IGeo value for Zn (0 < IGeo < 4) was found for Mortati et al. [8] for bottom sediments from URTR, mainly after crossing the SPMR. On the other hand a higher value was found for Cr (0 < IGeo < 2) using the continental crust as reference values and Sc as the normalizer element.

High values for contamination index as EF and IGeo mainly for elements such as As, Cr and Zn have been associated to anthropogenic influences [26–28].

Multivariate statistical analysis

Before statistical analysis, data were standardized (Z score). The PCA was performed using the results obtained by INAA and XRF analytical techniques and physicochemical parameters. In this study, PCA indicated that 20 variables and 12 sediment samples were resumed by two significant PC (principal components) which presented variance above or close to 10 % or eigenvalues above or close to 1. These principal components together explained 81.28 % of the total variance in the original data

Fig. 3 Principal component analysis (PC1 × PC2)

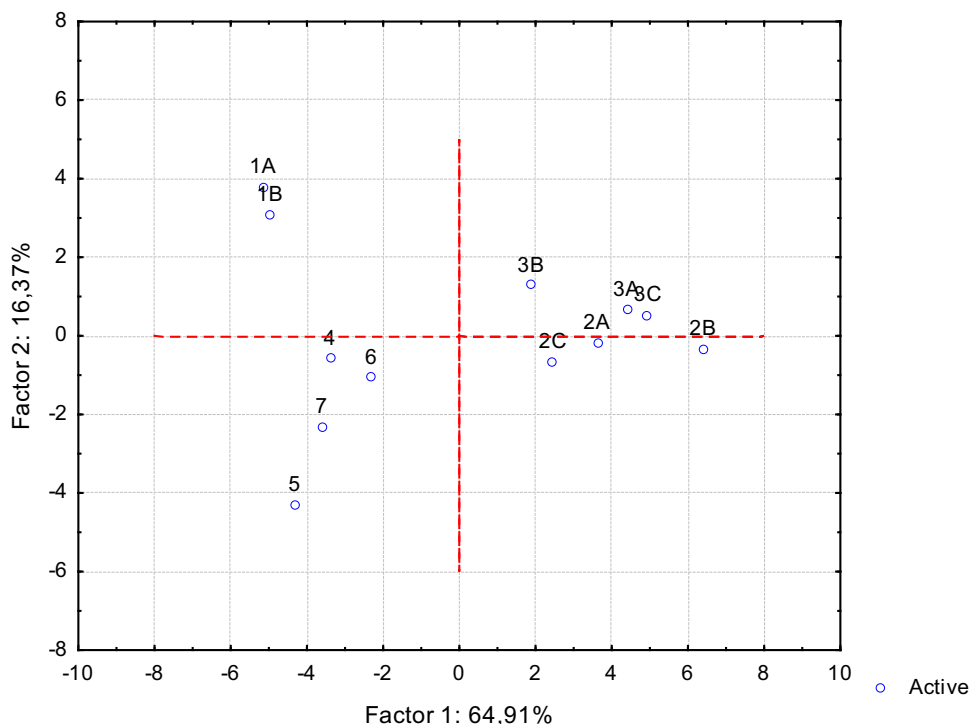
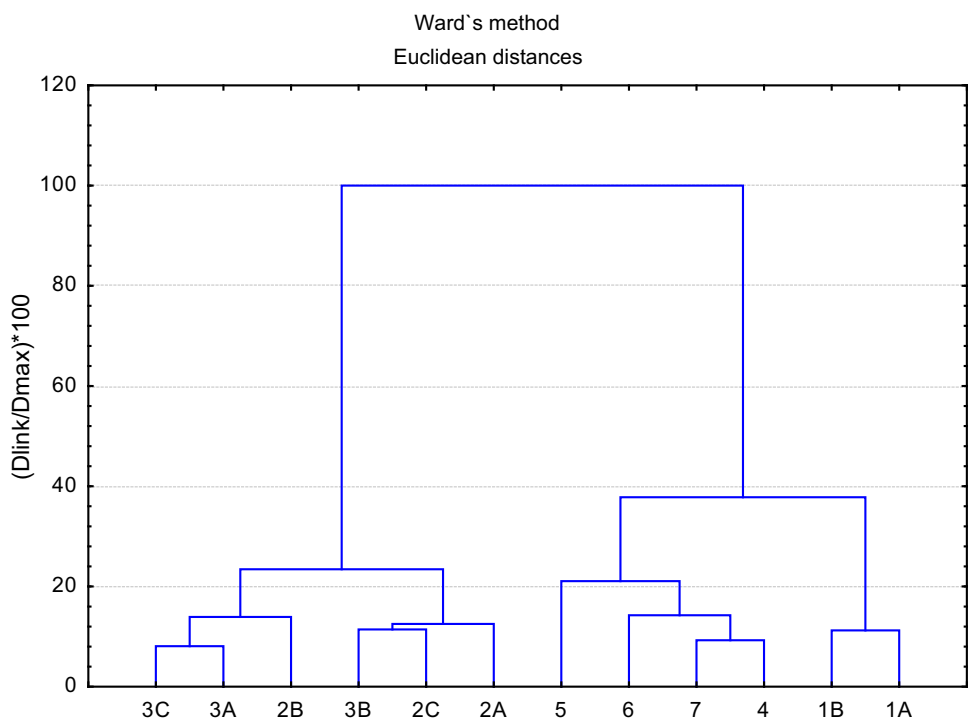


Fig. 4 Cluster analysis using all chemical data from sampling sites



set. The PC1, that was comprised of As, Ba, Co, Cr, Cs, Sb, Sc, Ta, Zn; major elements, except K₂O, conductivity, Eh and DO was predominant and accounted for about 64.91 % of total variance. The PC2 (which explained 16.37 % of variance) was comprised of Hf, Rb, Th, U, and K₂O (Table 5).

The PC₁ versus PC₂ plot scores are presented in Fig. 3. The elements that most contributed to PC₁ were those that also presented higher concentrations and lower values for DO and Eh parameters, in sites from 2A to 3C compared to sites 1A, 1B and 4–7. Also the negative loadings for SiO₂, Eh and DO indicate that the redox conditions exert strong

influence on the trace elements distribution in the Tiete River sediments. In PC₂, the identification of sites 1A and 1B was mainly due to the high concentrations of Hf, Rb and K₂O and lower values for pH and conductivity parameters. Sites 4–7 were identified, in general, due to concentration values for most elements and physicochemical parameters in between PC₁ and PC₂.

Cluster analysis was applied in order to confirm the results obtained by PCA. Ward's method and Euclidean distances were used for all chemical data. The same results were found evidencing the existence of three defined groups according to the elemental content and redox conditions as showed in Fig. 4. Group 1 (1A and 1B) was formed by the samples located at Salesópolis, near the headwaters of the Tietê River and showed the lowest concentrations for most of the elements analyzed mainly semi-metal As and metals Cr, Sb and Zn and higher values for the physicochemical parameters DO and Eh, although possibly affected by agricultural activities as discussed in the EF results.

Group 2 formed by samples from sites 2A to 3C, located after crossing the SPMR, showed higher concentration values for most elements analyzed mainly for As, Cr, Sb and Zn, highest conductivity and lowest Eh and DO values, indicating that in this region the Tietê River can be considered very polluted. These evidences are mainly due to intense urbanization and industrialization processes that contribute with large amounts of organic and inorganic pollutants above the assimilation capacity of the river.

Group 3, formed by sites 4–7, presented concentration values for most elements lower than group 2 and higher than group 1. The physicochemical parameters DO and Eh presented higher values and lower conductivity levels than group 2, indicating an improvement of water quality.

Conclusion

The concentration of DO, pH, conductivity and oxidation–reduction potential (Eh) in the sediment and water samples measured in all sampling sites indicated a water quality degradation along the sampling points. Sites 2 and 3 showed a strong reductor environment with high organic matter content, lack of oxygen and high conductivity due to the entrance of pollutants by means of effluents and untreated sewage in the river.

The results for element concentrations and statistical analysis evidenced the existence of three different environments possibly affected by different pollution sources. Near the headwaters of Tiete River, the main contribution must be the agricultural activities although in this point the water still shows its best physicochemical values. From sampling sites 2A–3C, strong influence of urban and

industrial sewage can be observed as found by the EF, IGeo, DO and Eh values. This also can be confirmed by the results for Cr and Zn from sites 2A to 3C that revealed high contamination levels for these elements and can be classified as poor quality for As according to the TEL and PEL oriented values. These results may confirm the anthropogenic influences of São Paulo city mainly related to untreated domestic sewage, industrial and agricultural effluents.

From the data of this study, it was possible to confirm the poor sediment quality of the studied area. These are preliminary results to which more sampling sites along the Tietê River and more chemical analysis will be added. These results may also be used to orient future and more comprehensive studies in this important river.

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