Journal of Radioanalytical and Nuclear Chemistry (2018) 316:805–818
https://doi.org/10.1007/s10967-018-5821-5

Metal and trace element assessments of bottom sediments from medium Tietê River basin, Sao Paulo State, Brazil: part II

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Received: 17 October 2017

Abstract

Concentration of metals in 15 bottom sediment samples from Tietê River, a significantly polluted river, were assessed. Total and partial trace element concentrations were determined, and As, Cd, Cr, Cu, Ni and Zn were found above local reference values. These metals were also higher than the threshold effect level (TEL) in some sampling points and Zn was higher than probable effect level (PEL) oriented values in almost all sampling points. The most polluted points were identified from Tietê to Barra Bonita Counties. Regarding sediment quality, this river is still polluted and precautions to minimize environmental problems caused by toxic metals to biota and to human health are necessary.

Keywords Metals · Trace elements · Bottom sediments · Tietê River · Enrichment factor · Geoaccumulation index

Introduction

Heavy metal (As, Cd, Cr, Cu, Hg, Mn, Ni, Pb and Zn) contamination in the aquatic environment has attracted global attention due to the abundance, persistence and environmental toxicity of these contaminants. Both natural and anthropogenic activities are responsible for the presence of heavy metals in the environment [1]. Because of their bioaccumulation capacity, special attention has been paid to these contaminants. Some, like Mn, Cu, Cr and Zn, are considered essential for human beings, but may become toxic when present in excess. On the other hand, other metals and semi-metals (As, Cd, Hg, Ni and Pb) may become toxic even when present in very low concentrations [2].

Large amounts of hazardous chemicals, including heavy metals, have been released into rivers worldwide, due to global rapid population growth and intensive domestic activities, as well as expanding industrial and agricultural production [3]. Rivers in urban areas have also been associated with water quality problems, due to the practice of discharging untreated domestic and industrial waste into these water bodies, which, in turn, leads to increased metals levels [3]. In addition, pesticides and herbicides widely used in agriculture in developing countries may contain arsenic (As) and other heavy metals that are easily transferred into rivers via agricultural runoff. Once released into riverine systems, heavy metals from these sources in these water bodies may then easily accumulate in sediments [2]. Therefore, heavy metal assessments in river water and sediments have been applied worldwide to evaluate these anthropogenic and industrial impacts, since heavy metal pollution is a main problem in many developing countries [1–5].

Bottom sediment assessments have been used as useful tools for aquatic ecosystem contamination level determinations, due to the capacity of sediment metal and trace element accumulation, as well as other pollutants (geoaccumulation) [6]. Pollutants in the water body can interact with clay, silt, stick to living organisms, bind to organic material and be deposited in sediment in low current areas [7].

Several polluted rivers exist in Brazil [2, 8, 9], with the Tietê River considered the most polluted, located in the state of São Paulo [10]. This river drains an area composed

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of six sub-basins, with a 1100 km extension and its margins bathe 62 municipalities and is considered one of the most economically important rivers, even with its polluted status.

In general terms, the environmental degradation of the Tietê River is mainly due to industrial activity from the Metropolitan Region of São Paulo (MRSP) and its surroundings, caused by heavy metals and organic toxic compound contamination in the High Tietê River Basin. In the countryside, other contamination sources, such as agricultural production (sugar cane and oranges), ethanol, sugar and citric juice production and untreated domestic sewage are the most noteworthy pollution sources [11, 12].

Water quality, especially that of the Tietê River Basin, and of the water supply reservoirs, has generated many studies related to sediment quality evaluations of these aquatic environments [13–21].

Rocha et al. [21] reported major and trace elements in bottom sediment samples in the reservoirs of the upper Tietê River region by instrumental neutron activation analysis (INAA) and X-ray fluorescence (XRF) analytical techniques. Their results confirmed the anthropogenic influences of São Paulo city and its surroundings, mainly related to untreated domestic sewage, as well as industrial and agricultural effluents, and confirmed the poor sediment quality of the area. This study was a part of a project entitled “Evaluation of the Extension and Pollution History by Metals and Trace Elements in River Sediments—Case Study, Tietê River, State of São Paulo”.

Continuing this project, the present study presents 15 bottom sediment sample assessments for metal and trace elements, from the middle Tietê River Basin. For this purpose, the following analytical techniques and their analyzed elements were applied: INAA: As, Ba, Br, Co, Cr, Cs, Fe, Hf, Na, Rb, Sb, Sc, Ta, Th, U and Zn; XRF: major elements and loss of ignition; ICP OES: Al, Ba, Co, Cr, Cu, Fe, Mn, Ni, Ti, V and Zn. The enrichment factor (EF) and geoaccumulation index (*IGeo*) were applied to assess the presence of anthropogenic pollution sources, using North American Shale Composite (NASC) [22] as a reference value. Cd, Cr, Cu, Ni, Pb and Zn concentrations determined by optical emission spectrometry with inductively coupled plasma (ICP OES) and graphite furnace atomic absorption spectrometry (GF AAS) were compared to TEL and PEL oriented values stipulated by the Canadian Council of Ministers of the Environment (CCME) [23] and adopted by São Paulo Environmental Company (CETESB).

Study area

The Tiete River drains an area comprising six sub-basins (High Tiete, Sorocaba/Middle Tiete, Piracicaba-Capivari-Jundiai, Tiete/Batalha, Tiete/Jacaré and Low Tiete). During the development of the aforementioned project, 34 bottom sediment samples were collected throughout the entire Tietê River extension (1100 km) (Fig. 1). The present study presents reports the results for the Sorocaba/Middle Tiete and Piracicaba-Capivari-Jundiai basins, sampling points from T8 to T22 (Fig. 1). The Sorocaba/Middle Tiete River Basin comprising 34 municipalities, of which 16 are located in the Upper Tietê sub-basin and 18 in the Sorocaba River Basin, with an area of 12,099 km^2 and a population of about 2000.000 inhabitants. The Middle Tietê Basin comprises the stretch of the Tietê River, from the Pirapora Reservoir to the Barra Bonita Dam, with a length of 367 km and a drainage area of 6830 km^2. Sorocaba River is formed by Sorocabuçu and Sorocamirim rivers, with a drainage area of 5269 km^2, with 180 km located in rural area, flowing into the Tietê River from the Laranjal Paulista County. In addition, the Sorocaba Basin receives impacts and a high polluting load from the Alto Tietê Hydrographic Basin, which covers the Metropolitan Region of São Paulo [24]. The Piracicaba-Capivari-Jundiai basin covers a drainage area of 14,178 km and has a surrounding population of about 5000.000 habitants. The main economic activities in the area are agriculture and industrial production, including a petrochemical complex, textile industries, high-technology pole, metal-mechanic industries, veneer production, sugarcane and alcohol industries and, finally, a national ceramic pole. This basin is formed by the Atibaia, Atibainha, Cachoeira, Camanducaia, Capivari, Corumbatai, Jaguari, Jundiaí, and Piracicaba Rivers. The main Tietê River tributaries from the right margin are Jundiai, Capivari and Piracicaba Rivers, and from the left margin, Sorocaba River [25].

The lithology of the region (middle Tietê region) is predominantly composed by diabasics and arenites, and the soils are reddish-yellow and dark red latosoil type [26].

Experimental

Sampling and sample preparation

Fifteen bottom sediment samples were collected at the Tietê River, from Points T8 to T22. The sampling point locations, geographical positions and collection dates are presented in Table 1.

Sediment samples were collected with a Van Veen dredge at 20 cm in depth. At the laboratory, the sediment samples were first sieved through a 2 mm sieve and then dried at 40 °C in a ventilated oven until constant weight. Subsequently, samples were quarted, ground with a mortar and pestle, passed sieved through a 0.125 mm sieve and then analyzed. Sampling stations are displayed in Fig. 1.

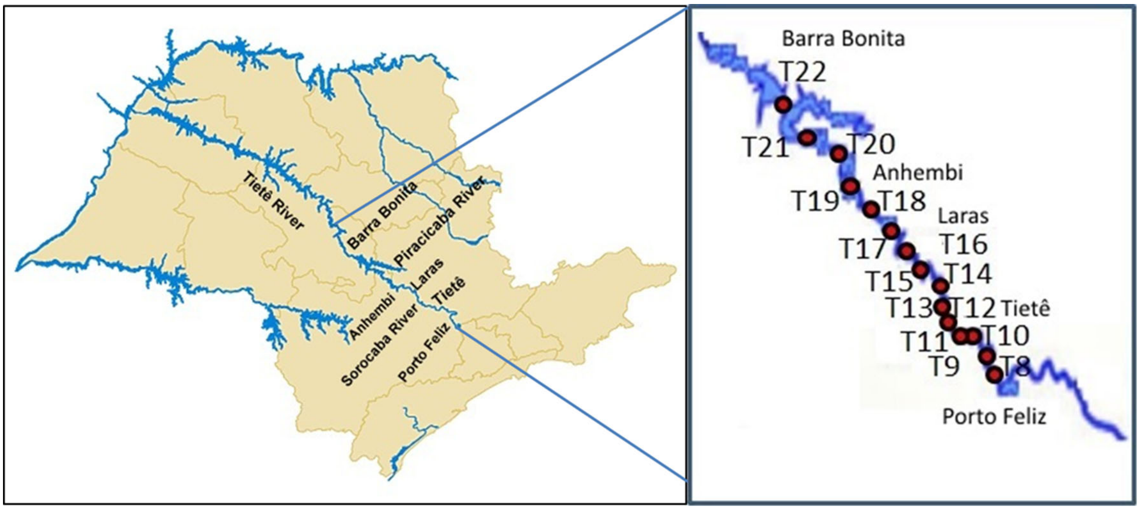


Fig. 1 Sampling point locations

Table 1 Sampling points along the Tietê River, sampling date and geographical coordinates

Sampling points	Area	Sampling date	Geographical coordinates
T8	From Porto Feliz to Tietê city	01/12/2012	23°13′47″S 47°34′27″
T9	From Porto Feliz to Tietê city	01/12/2012	23°11′33″S 47°34′54″
T10	Tietê city	01/12/2012	23°08′31″S 47°36′11″
T11	Tietê city	01/12/2012	23°07′89″S 47°40′178″
T12	From Tietê to Laras city	02/16/2014	23°04′31″S 47°44′25″
T13	From Tietê to Laras city	02/16/2014	23°01′37″S 47°47′34″
T14	From Tietê to Laras city	02/16/2014	22°58′59″S 47°51′30″
T15	From Tietê to Laras city	02/16/2014	22°58′59″S 47°51′30″
T16	From Laras to Anhembi city	08/23/2014	22°54′01″S 47°56′28″O
T17	From Laras to Anhembi city	08/23/2014	22°53′34″S 47°59′28″O
T18	From Laras to Anhembi city	08/23/2014	22°49′55″S 48°03′00″O
T19	From Laras to Anhembi city	08/23/2014	22°47′54″S 48°06′46″O
T20	From Anhembi to Barra Bonita city	06/08/2016	22°42′847″S 48°09′893″O
T21	From Anhembi to Barra Bonita city	06/08/2016	22°40′449″S 48°14′787″O
T22	From Anhembi to Barra Bonita city	06/08/2016	22°36′853″S 48°20′626″O

Sediment granulometric analysis and organic matter content

Both parameters were carried out at the Campinas Agronomic Institute (Instituto Agronômico de Campinas—IAC). The granulometry analysis (pipetting methodology) and organic matter content determinations were carried out according to Camargo et al. [27]. The results are presented in Table 2.

Physical–chemical parameters

Conductivity, temperature, oxidation–reduction potential (ORP), pH and dissolved oxygen (DO) measurements were performed in situ for water and sediment samples during the sampling campaigns. All the equipment used for the measurements were provided by Digimed Ind. e Comércio, as well as the certified reference material for equipment calibration.

INAA analytical technique

Approximately 200 mg of sediment (in duplicate) and reference materials were weighed 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 Whatman No. 41 filter paper sheets. Sediment samples, reference materials and synthetic standards were irradiated for a daily cycle (about 7 h), under a thermal neutron flux of 1–5 × 10^{12} cm^{-2} s^{-1} at the IEA-R1 nuclear research reactor at IPEN. Two counting series were

Table 2 Granulometric classification and organic matter (OM) content for the sediment samples and physico-chemical parameters

Sampling points	pH	Conductivity (µS cm^{-1})	Tempe rature (°C)	ORP (mV)	DO (mg L^{-1})	OM (g dm^{-3})	Clay (%)	Silt (%)	Total sand (%)	Textural classification
T8	7.33	514	26	375	1.16	18	12.2	10.8	77.0	Mostly sandy
T9	7.31	517	26.2	435	1.27	n.d.	11.0	14.3	74.7	Mostly sandy
T10	7.33	502	26.4	502	1.61	n.d.	5.9	5.0	89.1	Sandy
T11	7.30	494	26.4	486	2.02	n.d.	17.3	17.9	64.8	Lightly sandy
T12	7.05	582	26.8	68	0.4	25	20.4	26.7	52.9	Mostly clay sandy
T13	7.0	574	26	88	0.6	37	34.5	49.1	16.4	Mostly clay silty
T14	7.03	573	27	87.4	0.7	26	13.7	16.0	70.3	Mostly sandy
T15	7.16	570	28	170	0.9	24	18.0	21.5	60.5	Mostly sandy
T16	7.16	570	28		2.12	27	19.0	25.2	55.8	Mostly sandy
T17	7.45	563	21.4		1.3	37	27.9	45.2	26.9	Mostly clay
T18	7.24	542	22.4		2.67	40	41.3	52.8	5.9	Clay silt
T19	7.3	579	23.5		4.75	17	15.4	15.7	68.9	Mostly sandy
T20	7.67	543	20.4	245	7.67	36	36.4	49.4	14.2	Mostly clay silty
T21	7.69	365	22	224	7.69	2	0.4	4.5	95.1	Sandy
T22	8.5	236	22	237	8.5	13	24.8	7.5	67.7	Mostly clay sandy

n.d. not determined due to operational problems, *ORP* oxidation–reduction potential, *DO* dissolved oxygen, *OM* organic material

carried out: the first, after 1 week of decay and the second, after 20 days. The following elements were determined: As, Ba, Br, Co, Cr, Cs, Hf, Na, Rb, Sb, Sc, Ta, Th, U and Zn. 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), respectively. Details of the analytical methodology are described in Larizzatti et al. [28]. The expanded uncertainties were calculated by using coverage factor ($k = 2$) and the combined uncertainties from contributions from counting statistical (major contribution), certified reference material uncertainties and samples and reference material masses. Methodology validation was performed by analyzing the reference materials BEN (Basalt-IWG-GIT), Soil-5 (IAEA) and Lake Sediment (IAEA-SL-1). The relative standard deviations ranged from 2.5 to 9.2% and relative errors from 5.3 to 10.8% for the elements analyzed by INAA, confirming adequate precision and accuracy of the analytical technique, respectively. This methodology validation was previously conducted in other studies, also proving the precision and accuracy of the INAA technique [20, 21].

XRF analytical technique

For major element determination in sediments, the X-ray fluorescence spectrometry (XRF) analytical technique was used. Samples were prepared according to Mori et al. [29] at the Institute of Geosciences, University of São Paulo, and the measurements were carried out in a X-Ray Philips PW 2400 spectrometer. The precision and accuracy of the analytical methodology were verified by means of JB-1^{a} reference material analysis (Geological Survey of Japan) [30]. The precision of these measurements was better than 5% relative standard deviation (RSD). Major elements were determined by wavelength-dispersive XRF using fused glass discs. Loss on ignition (LOI) was determined in dry samples at 1000 °C. The major elements determined were SiO_2, TiO_2, Al_2O_3, Fe_2O_3, MnO, MgO, CaO, Na_2O, K_2O and P_2O_5.

ICP OES and GF AAS analytical techniques

For these analytical techniques, the sediment samples were first submitted to digestion according to 3051 EPA procedure [31], in order to obtain the accessible/bioavailable fraction of the element content. This method provides a rapid multielement acid leaching digestion prior to analysis. For the digestion procedure validation, the certified reference material Sandy Clay Soil (CRM 049) (Sigma), that lists concentration values for several elements after applying the 3051 US EPA digestion procedure, was used. Three independent replicate analyses of this material were performed. For the sample analyses, in each digestion batch, about 0.5 g of each sediment sample (in triplicate) and, for quality control of the results, one 0.25 g replicate of the certified reference material Sandy Clay Soil (CRM 049) (Sigma), were weighed directly in Teflon vessels belonging to a MARS-6 microwave oven (CEM Corporation). In the following step, 10 mL of a HNO_3: HCl (3:1) mixture were added to the Teflon tubes, which were left for about an hour at room temperature before being submitted to the MARS 6 microwave digestion program (38 Teflon tubes in each batch). After cooling, the Teflon tubes were opened, the samples filtered and transferred to Falcon tubes and the volumes were completed to 50 mL with Milli-Q water. The sample measurements were performed on an ICP-Vista MPX (VARIAN) at the Chemical Analysis Laboratory (CQuiM) belonging to the Instituto de Pesquisas Tecnológicas (IPT).

For Cd and Pb determinations, an AANALYST 800 from Perkin Elmer Graphite Furnace Atomic Absorption Spectrometry (GF AAS) was used in the same samples, reference materials and blanks prepared for ICP OES measurements, located at LAN IPEN—CNEN/SP.

The expanded uncertainties for both analytical techniques were calculated by using a coverage factor ($k = 2$) and the combined uncertainties, considering the uncertainty contributions of the concentration values, calibration curve, analytical blank, volume, dilution factor and weighing.

Results and discussion

Granulometric composition, organic matter content and physico-chemical parameters

Table 2 presents the results for the granulometric and organic matter content and the physico-chemical parameters measured in situ during the sampling campaign.

The granulometric composition of most sediment samples collected along the Tietê River presented high sand content. Sediment samples from points T13, T17, T18 and T20 presented the highest proportion of silt and clay fractions (> 70.0%) and points T10 and T21, the lowest (10.9 and 4.9%, respectively) with the lowest amounts of silt (5.0 and 4.5%, respectively) and clay (5.9 and 0.4%, respectively). The finer the sediment, the greater its ability to retain chemicals including metals, due to its high surface area, providing the capacity to interact with various molecules and ions.

In relation to physico-chemical parameters of points T8 to T11, from Porto Feliz until Tietê City, river rapids maintain dissolved oxygen (DO) levels at 1–2 mg L^{-1} with high ORP levels.

High dissolved oxygen consumption, conductivity increases and, consequently, ORP level decreases from Tietê City occur, probably due to the amount of untreated domestic sewage and industrial effluents in the area.

Points T12 to T15, from Tietê City to Laras County, presented low DO and ORP levels, indicating a lower reduction potential of the river in this region. From T13, the Tietê River receives Sorocaba River waters, promoting a slight alteration in physico-chemical characteristics, by dilution of Tietê River polluted waters. From points T18 to T22, water quality recovery, with pH ranging from 7.16 to 8.5, ORP from 170 (T15) to 236 mV (T22), DO from 2.12 to 8.5 mg L^{-1} and conductivity, from 570 to 236 µS cm^{-1}.

Total major and trace element assessments

Total concentrations of the elements determined in the sediment samples were obtained by means of the INAA and XRF analytical techniques.

Tables 3 and 4 display the results of the XRF (%) and INAA (total mass fraction) analytical techniques, respectively, for all analyzed sediment samples, alongside NASC values [22] and TEL and PEL oriented values from CCME [23] and reference values for bottom sediments from Tietê River (RVBST) [16].

Major elements and their contents (Table 3) are quite representative of the differences in the geological formations of surroundings areas, that contribute to these elements in sediments. The results obtained for these elements and their elemental ratios indicate different deposition and geochemical environments. Points T13, T17, T18 and T20 presented the lowest SiO_2 concentrations and the highest Al_2O_3, Fe_2O_3, MgO, CaO and K_2O concentrations.

The high (SiO_2/Al_2O_3) ratio values results from the increase of the quartz proportion, which is the main sediment constituent and was confirmed by the textural classification of the samples T8, T10, T11 and T21, which presented 77.0, 89.1, 69.0 and 95.1% sand in their compositions, respectively. The high (Fe_2O_3/SiO_2) and (MnO/SiO_2) ratio values for points T13, T17, T18 and T20 also indicate the contribution of Fe and Mn oxyhydroxides to the total metal content observed in these points, as observed in Table 4.

As, Cr and Zn values listed in Table 4 were compared to TEL and PEL oriented values from CCME [23] and adopted by CETESB [32] for sediment quality criteria classification. The values that surpassed TEL values are marked with * and for PEL, ** in the aforementioned table. For As, only points T13, T18 and T20 surpassed the TEL value (5.90 mg kg^{-1}). For Cr, many points surpassed TEL values, including T18 and T20, while T13 exceeded PEL value (90 mg kg^{-1}). For Zn, the situation was much worse with almost all points surpassing TEL (123 mg kg^{-1}) and points T11, T12, T13, T16, T17, T18 and T20 over the PEL value (315 mg kg^{-1}). Points T13, T18 and T20 were more critical regarding the concentration assessment for the semi metal As and metals Cr and Zn. These points are also

Table 3 XRF results (%) for the sediment samples from points T8 to T22

	T8	T9	T10	T11	T12	T13	T14	T15
SiO_2	82.4	79.9	87.0	74.2	74.7	54.6	79.5	76.8
TiO_2	0.5	0.6	0.5	0.7	0.7	0.9	0.8	0.7
Al_2O_3	7.1	8.4	5.4	10.9	10.4	19.8	8.6	9.6
Fe_2O_3	2.4	2.8	1.8	3.6	3.6	6.7	3.1	3.6
MnO	0.1	0.1	0.04	0.1	0.1	0.1	0.1	0.1
MgO	0.1	0.2	0.1	0.2	0.2	0.5	0.2	0.2
CaO	0.3	0.3	0.2	0.3	0.3	0.5	0.2	0.3
Na_2O	0.02	0.1	0.1	0.1	0.1	0.1	0.03	0.1
K_2O	1.4	1.6	1.5	1.6	1.5	1.7	1.3	1.5
P_2O_5	0.4	0.5	0.3	0.6	0.6	1.1	0.2	0.7
LOI	4.2	4.4	2.3	6.7	6.4	12.7	5.7	6.0
TOTAL	98.7	98.8	99.1	99.0	98.6	98.7	99.7	99.6
(SiO_2/Al_2O_3)	11.7	9.6	16.1	6.8	7.2	2.8	9.2	8.0
(Fe_2O_3/SiO_2)	0.03	0.04	0.02	0.05	0.05	0.12	0.04	0.05
$MnO/SiO_2) \times 10^4$	6.3	7.8	4.5	8.4	9.9	20.7	6.5	11.2

	T16	T17	T18	T19	T20	T21	T22	NASC
SiO_2	75.9	61.9	52.3	81.8	58.6	96.1	77.2	64.8
TiO_2	0.7	0.8	1.0	0.6	0.9	0.1	0.6	0.78
Al_2O_3	9.5	15.5	20.6	7.3	17.7	1.5	8.3	16.9
Fe_2O_3	3.5	5.6	7.2	2.6	6.0	0.3	3.6	6.33
MnO	0.1	0.1	0.1	0.05	0.1	0.004	0.1	0.06
MgO	0.2	0.4	0.6	0.3	0.7	0.1	0.3	2.85
CaO	0.3	0.5	0.5	0.2	0.5	0.04	0.2	3.56
Na_2O	0.1	0.1	0.02	0.2	0.2	< 0.02	< 0.02	1.15
K_2O	1.5	1.6	1.6	1.3	1.6	0.6	0.4	3.99
P_2O_5	0.7	1.2	1.0	0.3	0.8	0.02	0.4	0.11
LOI	6.1	11.0	13.7	4.0	12.0	0.9	7.5	
TOTAL	98.5	98.6	98.6	98.5	99.0	99.6	98.5	
(SiO_2/Al_2O_3)	8.0	4.0	2.5	11.2	3.3	64.1	9.3	
(Fe_2O_3/SiO_2)	0.05	0.09	0.14	0.03	0.10	0.003	0.05	
$MnO/SiO_2) \times 10^4$	11.1	19.4	20.6	5.7	15.4	0.4	17.9	

LOI loss on ignition

affected by the higher proportions of silt and clay, organic matter and Fe/Mn oxyhidroxides, which may also contribute to the observed values related to the total concentrations of these elements.

Mortatti et al. reported values varying from 223 to 439 mg kg^{-1} for Zn and 135–149 mg kg^{-1} for Cr in the region of points T18 to T20 [19]. Silva et al. reported values up to 230 mg kg^{-1} for Zn and 168 mg kg^{-1} for Cr for the same region [13]. These values indicate that the pollution sources have been maintained in the last decade.

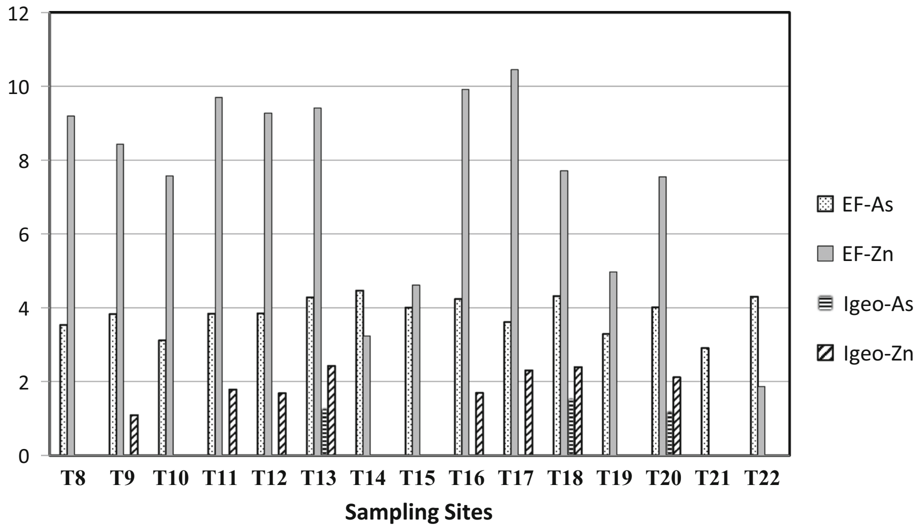
Compared with the values reported by Nascimento and Mozeto [16] for sediment baseline values for the Tietê River, it seems that the metals Cr and Zn present higher values in the same points where TEL and PEL values were surpassed, confirming their anthropogenic origin. Cardoso-Silva et al. found similar background values for Cr and Zn, of 40 and 82 mg kg^{-1}, respectively [33]. On the other hand, the As baseline value established by those authors is much higher them the values for this elements found in all the analyzed points in this study, and even higher than the PEL value. Silva et al. reported background values for As ranging from 6.3 to 12 mg kg^{-1}, for the Baixada Santista, on the coast of the state of São Paulo, depending on the grain size sediment fraction [34]. These results indicate that As may be enriched in São Paulo soil, in values over the global average and TEL and PEL values.

Table 4 Total mass fraction (mean ± expanded uncertainty, mg kg^{-1}) for some elements by INAA, NASC values [22], TEL and PEL oriented values [23] (values* > TEL; values** > PEL) and Reference Value for Bottom Sediment from Tietê River (RVBST) [16]

Sampling points	As	Ba	Br	Co	Cr	Cs	Hf
T08	2.2 ± 0.1	379 ± 17	1.3 ± 0.2	7.2 ± 0.1	49 ± 2	2.1 ± 0.2	10.7 ± 0.2
T09	2.9 ± 0.2	412 ± 18	1.4 ± 0.2	8.5 ± 0.1	56 ± 2	2.9 ± 0.2	12.1 ± 0.3
T10	1.6 ± 0.1	346 ± 12	0.8 ± 0.1	5.4 ± 0.1	35 ± 1	2.1 ± 0.1	11.7 ± 0.4
T11	4.1 ± 0.2	480 ± 25	3.0 ± 0.3	8.5 ± 0.1	90 ± 3*	3.5 ± 0.2	11.5 ± 0.3
T12	4.0 ± 0.2	469 ± 27	2.3 ± 0.3	12.5 ± 0.2	79 ± 5*	3.3 ± 0.2	14.3 ± 0.4
T13	*7.3 ± 0.4*	582 ± 35	5.0 ± 0.3	17.8 ± 0.3	146 ± 5**	5.1 ± 0.3	9.0 ± 0.3
T14	4.0 ± 0.2	365 ± 15	1.9 ± 0.2	7.6 ± 0.2	46 ± 2*	3.0 ± 0.2	21.6 ± 0.5
T15	3.8 ± 0.2	403 ± 17	1.9 ± 0.2	7.6 ± 0.2	57 ± 2*	3.0 ± 0.2	20.2 ± 0.5
T16	4.1 ± 0.5	450 ± 21	2.2 ± 0.2	12.7 ± 0.2	77 ± 2*	2.8 ± 0.1	18.1 ± 0.4
T17	5.1 ± 0.2	512 ± 25	3.6 ± 0.2	18.0 ± 0.2	17 ± 3	3.8 ± 0.2	13.0 ± 0.3
T18	8.8 ± 0.4*	646 ± 53	6.5 ± 0.5	22.6 ± 0.3	42 ± 4*	5.9 ± 0.2	9.7 ± 0.3
T19	2.4 ± 0.1	404 ± 29	1.2 ± 0.1	6.9 ± 0.1	42 ± 1*	2.3 ± 0.1	10.7 ± 0.3
T20	6.9 ± 0.1*	498 ± 78	4.1 ± 0.5	16.6 ± 0.6	101 ± 6**	5.5 ± 0.1	12.1 ± 0.4
T21	0.31 ± 0.02	155 ± 15	0.4 ± 0.1	0.9 ± 0.1	7.2 ± 0.6	0.5 ± 0.1	13.6 ± 1.3
T22	3.9 ± 0.4	139 ± 30	6.9 ± 0.5	8.5 ± 0.3	31 ± 2	2.9 ± 0.5	8.6 ± 0.4
Mean	**4.2**	**427**	**3.0**	**10.9**	**72**	**3.3**	**13.1**
Std	**2.1**	**144**	**2.3**	**5.9**	**41**	**1.4**	**4.0**
Max	**8.8**	**646**	**8.8**	**22.6**	**146**	**5.9**	**21.6**
Min	**1.6**	**130**	**0.4**	**0.8**	**5**	**0.5**	**8.0**
NASC	**2.0**	**636**	**0.69**	**28**	**125**	**5.2**	**6.3**
RVBST	**24 + 11**			**24 + 9**	**44 + 14**		
TEL*	**5.90**				**37.3**		
PEL**	**17.0**				**90**		

Sampling points	Na	Rb	Sb	Sc	Ta	Th	U	Zn
T08	1719 ± 33	65 ± 3	0.56 ± 0.04	4.8 ± 0.1	1.04 ± 0.07	11.7 ± 0.3	2.9 ± 0.2	248 ± 10*
T09	2056 ± 42	75 ± 3	0.79 ± 0.07	5.7 ± 0.1	1.32 ± 0.06	10.7 ± 0.3	3.1 ± 0.2	272 ± 9*
T10	1789 ± 37	59 ± 2	0.47 ± 0.04	3.8 ± 0.1	1.12 ± 0.04	8.6 ± 0.2	2.2 ± 0.1	161 ± 5*
T11	1712 ± 37	86 ± 4	1.1 ± 0.1	8 ± 0.2	1.23 ± 0.06	12.5 ± 0.3	3.3 ± 0.3	439 ± 15**
T12	2014 ± 41	67 ± 3	0.9 ± 0.1	7.8 ± 0.2	1.5 ± 0.1	16.6 ± 0.5	4.0 ± 0.3	410 ± 14**
T13	1655 ± 34	82 ± 4	1.6 ± 0.1	12.8 ± 0.3	1.8 ± 0.2	17.3 ± 0.5	5.3 ± 0.3	685 ± 24**
T14	1690 ± 34	56 ± 2	0.9 ± 0.1	6.6 ± 0.2	1.18 ± 0.04	14.7 ± 0.3	3.8 ± 0.2	122 ± 4
T15	2058 ± 42	66 ± 2	0.8 ± 0.1	7.2 ± 0.2	1.25 ± 0.04	14.0 ± 0.3	3.9 ± 0.2	187 ± 6*
T16	1885 ± 32	62 ± 2	0.9 ± 0.1	7.3 ± 0.1	1.22 ± 0.07	12.4 ± 0.3	3.1 ± 0.2	412 ± 11**
T17	1700 ± 29	78 ± 3	1.2 ± 0.1	10.6 ± 0.2	1.27 ± 0.08	15.5 ± 0.3	4.3 ± 0.3	629 ± 16**
T18	1439 ± 23	97 ± 4	1.8 ± 0.1	15.3 ± 0.3	1.8 ± 0.1	19.4 ± 0.4	4.7 ± 0.3	669 ± 17**
T19	1736 ± 29	51 ± 2	0.44 ± 0.03	5.5 ± 0.1	1.0 ± 0.1	9.1 ± 0.2	2.7 ± 0.2	154 ± 4*
T20	1644 ± 32	76 ± 5	0.90 ± 0.10	12.2 ± 0.4	1.80 ± 0.20	15.8 ± 0.7	4.5 ± 0.3	518 ± 16**
T21	308 ± 7	17 ± 1	0.12 ± 0.02	0.8 ± 0.1	0.2 ± 0.1	2.9 ± 0.3	1.1 ± 0.2	6 ± 1
T22	297 ± 9	28 ± 3	0.96 ± 0.08	6.6 ± 0.2	0.8 ± 0.2	10.3 ± 0.9	2.2 ± 0.2	66 ± 4
Mean	**1590**	**65**	**0.88**	**7.7**	**1.2**	**12.8**	**3.4**	**334**
Std	**541**	**22**	**0.43**	**3.8**	**0.4**	**4.3**	**1.1**	**225**
Max	**2058**	**97**	**1.76**	**15.3**	**1.8**	**19.4**	**5.3**	**685**
Min	**318**	**18**	**0.10**	**0.8**	**0.2**	**2.8**	**1.1**	**6**
NASC	**7500**	**125**	**2.09**	**15**	**1.1**	**12**	**2.7**	**85**
RVBST						**11 + 3**	**3.8 + 1.2**	**104 + 10**
TEL*								**123**
PEL**								**315**

Fig. 2 EF > 2.0 and *IGeo* > 1.0, for the elements analyzed by INAA



Contamination assessment applying the EF and IGeo indices

For the other elements determined by INAA without an oriented value for comparison, the EF and *IGeo* indexes were calculated by using NASC as reference values and Sc as a normalizer element for EF calculations. Sc was used due to its low occurrence variability, asit is a conservative element, and has been applied in other studies [20, 21, 35]. These tools are generally used for contamination index evaluations regarding metal and trace elements in soil and sediments [36–38]. Details of these calculations have been described previously in Rocha et al. [21].

Figure 2 displays EF > 2.0 values for As and Zn, that presented enrichment in all sampling points. Zn presented the higher EF values for points T13, T17, T18 and T20. Cr did not present a high EF value, because its NASC value is high (125 mg kg^{-1}), even higher than PEL value (90 mg kg^{-1}). By definition. EF > 1.5 values indicate anthropogenic contributions, and the higher EF value, the more severe the anthropogenic contribution [35]. In addition, Br (from 4.8 to 10.9), Hf (from 2.2 to 4.1), Ta (from 2.1 to 4.1), Th (from 2.1 to 4.4) and U (from 2.0 to 7.6) presented EF > 2.0 at most sites. The concentration values detected in the present study for these elements (Br, Hf, Ta, Th and U) were very similar to values observed in studies performed on sediments from others points of the Tietê River from its headwaters until Suzano County [20] and from it headwaters till Pirapora do Bom Jesus County (High Tiete Sub Basin) [21]. For U and Th, the values were quite similar to those reported by Nascimento and Mozeto for background Tietê River sediment values [16]. Therefore, these high concentrations observed for Br, Hf, Ta, Th and U were considered to be related to the lithology of the region and not due to the presence of contamination.

Figure 2 also displays the *IGeo* values obtained for the INAA results. According to the *IGeo* classification [36], As presented 1 < *IGeo* < 2, considered moderately polluted; Zn, 2 < *IGeo* < 3, moderate to polluted; Br presented 2 < *IGeo* < 3 and Hf 1 < *IGeo* < 2 only in certain sampling points, which were not classified, according to the above discussion for EF values. For the other analyzed elements, *IGeo < 0* were calculated, classified as non-contaminated. Similar results were observed comparing the EF and *IGeo* indices results, and once again, points T13, T17, T18 and T20 exhibited the highest values (Fig. 2).

Partial metal concentration assessments

The accessible/bioavailable fraction of the elements from sediments obtained by means of the 3051 EPA digestion procedure were measured by the ICP OES and GF AAS techniques.

Table 5 displays the results for the Sandy Clay certified reference material analyses by ICP OES. Recoveries ranging from 80 to 97% were obtained for most analyzed metals, proving the accuracy of the analytical data, except for Al and Zn.

Table 6 displays the results for Al, Ba, Co, Cr, Cu, Fe, Mn, Ni, Ti, V and Zn obtained by ICP OES and Cd and Pb by GF AAS, as well as the TEL and PEL oriented values for Cd, Cr, Cu, Ni, Pb and Zn. Most of the analyzed points presented concentrations values for these metals lower than the TEL or between TEL and PEL oriented values, with good or regular sediment quality classifications. However, Zn presented values that surpassed PEL values (315 mg kg^{-1}), for many points, namely T11, T12, T13, T16, T17, T18 and T20, with bad or poor sediment quality classifications (T13, T17, T18 and T20). Comparing the values obtained for the partial extraction in the present

Table 5 Results for the Sandy Clay reference material analysis by ICP OES (mean ± expanded uncertainty ($k = 2$), $n = 3$)

CRM 049–sandy clay 1				
Elements	Unity	Certified values	Obtained values	Recovery (%)
Al	%	1.01 ± 0.15	1.25 ± 0.62	124.1
Fe		0.6600 ± 0.0256	0.59 ± 0.24	88.7
Ba	mg kg^{-1}	549 ± 11	518 ± 102	94.3
Cd		87.9 ± 1.8	84 ± 4	96.1
Co		218 ± 5	212 ± 28	97.1
Cr		135 ± 2	126 ± 18	93.4
Cu		134 ± 3	130 ± 26	96.9
Mn		1110 ± 36	897 ± 10	80.8
Ni		288 ± 6	280 ± 36	96.0
Pb		340 ± 7	319 ± 10	93.9
Ti		66.7 ± 6.1	56.5 ± 11.6	84.6
V		148 ± 2	141 ± 32	95.5
Zn		433 ± 8	484 ± 16	111.8

n number of determinations)

study with those presented by Nascimento and Mozeto [16], for Tietê River sediment background values (Table 6), Cd and Zn presented higher values at all sampling points, except for T21 and T22. Cr and Cu exhibited higher values at points T11, T12, T13, T17, T18 and T20; Ni, at points T13, T17, T18 and T20 and Pb, at points T13 and T18. In general, the higher values for all metals were found at sampling points T13, T17, T18 and T20.

According to the granulometric classification (Table 2) these sampling points also contain 83.6, 73,1, 94.1 and 85.8%, respectively, of silt + clay in their composition, classified as mostly having a clay sandy or clay silt texture. As stated previously, 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.

Water physico-chemical characteristics, organic matter content and sediment granulometric distribution also aid in explaining the obtained results for the partial dissolution concentrations. Anoxic conditions with low ORP decrease the degradation of organic matter, favoring metal adsorption in the sediment by incorporation of sulfide compounds [39, 40]. Low dissolved oxygen values and anoxic conditions have been previously reported in Tietê River water by Abe et al. [41].

Except for point T21, that was comprised almost entirely of sand (95.1%), points T8 to T10, characterized by high ORP values and high amounts of sandy material, presented low metal concentrations in the extracted fraction by the 3051 EPA procedure. From point T12, an increase in the concentrations of all elements in the extracted fraction, as well as low DO and ORP levels and increasing amounts of OM, were observed, indicated a low reduction potential of the river in this region.

In general, heavy metal sources in the environment are mainly associated to: **Cd**: welding, electroplating, pesticides, fertilizer, batteries; **Cr**: mining, electroplating, textile and tannery industries; **Cu**: electroplating, pesticides and tanning; **Pb**: paint, pesticides, batteries, automobile emission, mining and burning of coal; **Ni**: electroplating, zinc base casting, battery and industries; **Zn**: refineries, brass manufacture, metal plating, immersion of painted idols [4]. As described previously in the study area section, all these contributions can be found at Tietê River, due to the larger number of tributaries that contribute with high pollutant amounts. In addition to these contributions, for Cu, Pb and Zn, roadside soil particles are also a source that can be eroded or mobilized by wind, deposited throughout the landscape and washed into nearby water bodies, leading to adverse aquatic and terrestrial impacts. Currently, automobiles are considered one of the major sources of Cu and Zn to the environment [42]. Urban runoff also can be considered as a major cause of pollution that can seriously affect the water quality and ecology of receiving waters [43].

The segment of the river from points T12 to T15, Tietê to Laras Counties, receives all discharge residue contributions from the textile industries located in the Tietê City region, mainly for metals Cd, Cr, Cu and Ni. These discharges include dyes, pigments and untreated sewage effluents, and low DO and ORP levels were detected in those sampling points, indicating a low reduction potential of the river in this region. At point T13, Tietê River also receives Sorocaba River waters, which may explain the high level of contamination at this point. Points T17 and 18

Table 6 ICP OES and GF AAS (Cd and Pb) results (mean ± expanded uncertainties) for the sediment samples from sampling points T8 to T22

Elementos	T8	T9	T10	T11	T12	T13	T14	T15
Al (%)	0.47 ± 0.04	0.51 ± 0.06	0.30 ± 0.11	0.72 ± 0.02	0.73 ± 0.02	1.58 ± 0.15	0.54 ± 0.01	0.58 ± 0.06
Fe (%)	1.07 ± 0.03	1.34 ± 0.15	0.68 ± 0.13	1.61 ± 0.27	1.80 ± 0.09	3.27 ± 0.13	1.45 ± 0.04	1.57 ± 0.06
Ba	75 ± 7	77 ± 7	43 ± 9	122 ± 11	115 ± 4	222 ± 15	73 ± 7	83 ± 3
Cd (μg kg^{-1})	423 ± 3	449 ± 6	237 ± 18	877 ± 10	577 ± 16	1261 ± 38	322 ± 10	457 ± 7
Co	5.3 ± 0.7	6.4 ± 0.6	4.2 ± 1.5	5.6 ± 0.4	9.7 ± 0.8	14.5 ± 1.2	5.6 ± 1.1	5.6 ± 1.1
Cr	34 ± 1	39 ± 2	19 ± 4	60 ± 4	57.1 ± 0.8	113 ± 4	29.8 ± 0.8	35.3 ± 0.7
Cu	47 ± 2	56.9 ± 0.7	26 ± 4	85 ± 4	76 ± 2	146 ± 4	32.4 ± 1.4	40.5 ± 0.6
Mn	278 ± 5	381 ± 15	199 ± 17	385 ± 19	482 ± 17	758 ± 21	313 ± 6	461 ± 7
Ni	20.1 ± 1.4	25.4 ± 1.9	14 ± 2	24.7 ± 0.8	28.3 ± 1.9	44 ± 4	13.2 ± 0.4	13.8 ± 1.6
Pb	12.9 ± 0.2	15.7 ± 0.4	7.85 ± 0.04	19.3 ± 0.8	17.15 ± 0.09	34.1 ± 0.7	13.4 ± 0.1	15.1 ± 0.1
Ti	46 ± 30	94 ± 5	39 ± 20	71 ± 6	97 ± 13	143 ± 5	71 ± 4	80 ± 4
V	15.0 ± 2.5	17.5 ± 2.8	10 ± 4	25 ± 1	25 ± 2	48 ± 4	27 ± 1	23 ± 1
Zn	302 ± 37	313 ± 36	208 ± 19	442 ± 27	436 ± 15	715 ± 20	190 ± 5	250 ± 16

Elementos	T16	T17	T18	T19	T20	T21	T22	TEL (mg kg^{-1})	PEL (mg kg^{-1})
Al (%)	0.54 ± 0.18	1.02 ± 0.05	1.20 ± 0.01	0.34 ± 0.06	1.39 ± 0.05	0.07 ± 0.01	0.67 ± 0.13		
Fe (%)	1.81 ± 0.36	2.67 ± 0.19	3.00 ± 0.30	1.10 ± 0.06	2.87 ± 0.17	0.087 ± 0.006	1.735 ± 0.005		
Ba	124 ± 8	170 ± 16	203 ± 32	51 ± 6	186 ± 3	6.1 ± 0.8	96 ± 1		
Cd (μg kg^{-1})	600 ± 11	967 ± 2	1130 ± 11	283 ± 7	952 ± 16	8.8 ± 0.6	84 ± 2	0.6	3.5
Co	10.4 ± 0.9	15.1 ± 1.3	15 ± 3	4.6 ± 0.2	14.9 ± 0.9	n.d.	6 ± 2		
Cr	57 ± 3	85 ± 4	89 ± 17	25 ± 5	77 ± 4	3 ± 1	19 ± 2	37.3	90
Cu	71 ± 1	121 ± 1	123 ± 25	32 ± 6	114 ± 3	2.0 ± 0.8	17 ± 2	35.7	197
Mn	616 ± 11	806 ± 10	672 ± 145	283 ± 17	570 ± 13	16 ± 2	926 ± 22		
Ni	33 ± 3	45 ± 3	43 ± 10	12 ± 1	41 ± 2	n.d.	20 ± 3	18	35.9
Pb	16.5 ± 0.7	26.4 ± 0.8	32.3 ± 1.2	10.7 ± 0.9	26.4 ± 0.6	1.4 ± 0.1	9.8 ± 0.4	35	91.3
Ti	75 ± 51	109 ± 7	104 ± 8	45 ± 10	116 ± 7	6.2 ± 2.5	54 ± 3		
V	21 ± 8	35 ± 3	47 ± 1	15.5 ± 0.6	46 ± 4	7 ± 1	38 ± 3		
Zn	458 ± 16	652 ± 21	612 ± 142	201 ± 17	463 ± 14	5.8 ± 1.8	48.0 ± 0.9	123	315

seem to be the most polluted sampling points, from Laras to Anhembi Counties, although no explanation was found for this. However, a tight band in the river at Point 17 may allow for the accumulation of finer material, higher than 70% silt and clay, which may be the source while it should be noted that the DO content is still low at these points (T17, T18), the former at about 1.3 mg L^{-1}.

In the first part of the present project, Rocha et al. [21] discussed the concentrations and distribution of selected trace and major elements in bottom sediments along the Tietê River, from its headwaters (clean area), crossing the Metropolitan Region of São Paulo (MRSP) (a very polluted area) until point T7, far from the city of São Paulo. Data from this study confirmed the poor sediment quality of the studied area, especially at the MRSP region. The results also confirmed the anthropogenic influences of the city of São Paulo, mainly related to untreated domestic sewage and industrial and agricultural effluents.

This study was a continuation of the aforementioned project, analyzing T8 until T22 sampling points along the Tietê River, from 34 sampling points predicted in the main project. Comparing our results with a previous study [21], the great regeneration capacity of this important river related to metals and trace elements in its sediments was confirmed. The concentration levels detected in all studies were quite below points T2 and T3 from MRSP, classified as very polluted. Points T13, T17, T18 and T20 presented high concentrations values for the elements determined by the EPA digestion method and quantified by ICP OES, as well as for physico-chemical characteristics, OM and granulometric distribution, probably due to the contribution of domestic untreated sewage and industrial effluents from the cities surrounding the river and many tributaries that discharge polluted waters.

These results indicate that the extension of the Tietê River herein analyzed, although less polluted than MRSP, is still a concern regarding sediment quality, and precautions should be taken to minimize environmental problems caused by metals toxic to both the biota and human health.

However, the last analyzed point, T22, presented concentration levels for elements analyzed by INAA and toxic metals determined by ICP OES and GF AAS at the same level as T8, or even lower, in the present study. Furthermore, the concentration levels presented for T22 were at the same level as T-1 bottom sediments located at Tietê River headwaters [20, 21].

Ba, Co, Cr and Zn were determined in the sediment samples by two analytical techniques, INAA (Table 4) and ICP OES (Table 6). The results for Co and Cr obtained by ICP OES were about 30% lower than those detected by INAA, as expected, since the INAA technique detects the total concentration for each analyzed element. Ba results by ICP OES were about 70% lower than INAA results, which may indicate that this element is incorporated in the mineral fraction of the sediment and, consequently, more difficult to be leached during the digestion procedure. On the other hand, Zn results obtained by ICP OES were, in average, 10% higher than the INAA results. This may be related to the comparatively high recovery observed for this element in the applied ICP OES digestion procedure and should be better investigated. In addition, the presence of Zn in sediments is more related to surface sorption, so this element is consequently more leachable when applying the digestion procedure used herein. Mortatti et all [19], evaluating heavy metal distribution in the geochemical phases of Tietê River sediments, observed higher Zn percentages in the labile phase, indicating a greater mobility of this metal and thus, sediment contamination.

Table 7 compares the heavy metal concentrations detected in the Tietê River sediments in the present study, in previous studies, in other rivers in Brazil and in other countries. The levels of the semi metal As and metals Co, Cr and Zn detected in the present study were much lower than those observed in previous studies performed at the High Tiete River Basin, the most polluted stretch of the Tietê River [20, 21]. Comparing the present data with two other rivers in Brazil [2, 8], levels of same magnitude for Cr, Cu, Pb and Zn were observed at the Paraiba do Sul, but much higher than concentrations at Pardo River.

Regarding heavy metals in sediments in other polluted rivers from developing countries, levels in Gan River were higher for Cd, Co, Cr and Pb, while Karnaphuli River presented higher levels of As, Cd and Pb; Korotoa River presented higher levels for Cd, Cr, Cu, Ni and Pb while Ganga River presented higher levels of Cd and Cr than the concentrations determined in the present study.

These results indicate that the extension of Tietê River analyzed herein, although less polluted than the High Sub Basin Tietê River (Table 7), is still of concern regarding sediment quality, and precautions should be taken to minimize environmental problems caused by metals toxic to both the biota and to human health.

Conclusions

DO, pH, conductivity and oxidation–reduction potential (Eh) in the sediment and water samples measured at all sampling sites indicate water degradation along the sampling sites, mainly from T12 to T15 and T17 points. From points T18 to T22, a water quality recovery was observed.

EF was calculated from the INAA results, and EF > 1.5 was observed for As and Zn, indicating probable anthropogenic contributions. Higher EF values were found for points T13, T17, T18 and T20.

According to the *IGeo* classification for the INAA results, As presented $1 < IGeo < 2$, considered moderately polluted; Zn, $2 < IGeo < 3$, considered moderate to polluted (points T13, T17, T18 and T20). For the other analyzed elements $IGeo < 0$ were calculated, classified as non-contaminated.

The results for Cr, Cu, Ni and Zn obtained by ICP OES and Cd and Pb by GF AAS were compared to TEL and PEL oriented values, and most of the analyzed points presented concentrations lower than TEL or between TEL and PEL oriented values, exhibiting good or regular sediment quality classifications. However, Zn presented values that surpassed PEL values (315 mg kg^{-1}), for T11, T12, T13, T16, T17, T18 and T20, with bad or poor sediment quality classification (T13, T17, T18 and T20). In general, for all metals, higher values were found at sampling points T13, T17, T18 and T20. These results confirmed the As and Zn results obtained by INAA, for the same points.

From T12 to T15 the Tietê River receives contributions from textile industry residues from Tietê City, including dyes, pigments and untreated sewage effluent discharges directly into the river waters, while at T13, the Tietê River receives Sorocaba River waters. All these contributions aid in explaining the high level of contamination observed at this point.

Point T17 seems to be the most polluted from Laras to Anhembi Counties, but no explanation was found for this result.

The Tietê River tributaries play an important role in the pollution observed in this river, since they transport considerable amounts of pollutants, as well as heavy metals, into the river. All tributaries join the Tietê River and drain their pollutant input load, adding to the already polluted Tietê River.

According to the granulometric composition, T13, T17, T18 and T20 sampling points show high content of silt + clay, classified mostly as clay sandy or clay silt,

Table 7 Comparative levels of heavy metals in sediments (mg kg^{-1}, dry weight) from Tietê River and other rivers in Brazil and worldwide

Site	As	Cd	Co	Cr	Cu	Ni	Pb	V	Zn	References
Tiete River Brazil (medium sub-basin)	4.2 (1.6–8.8)	0.58 (0.01–1.26)	8.8 (4.2–15.1)	49 (3–113)	66 (2–146)	27 (12–45)	17 (1–34)	27 (7–48)	353 (6–715)	This study
Tiete River Brazil (high sub-basin-Suzano County)	19.7	–	13.2	122	–	–	–	111	929	[20]
Tiete River Brazil (high sub-basin)	4.1 (0.2–9.4)	–	10.9 (3.1–29.3)	96 (21–215)	–	–	–	–	429 (29–1017)	[21]
Pardo River Brazil	0.60	0.03	–	23.6	14.4	5.4	6.9	61.3	29.4	[2]
Paraiba do Sul River Brazil	–	–	–	11–79	1–58	–	7–99	–	44–423	[8]
Gan River China	–	2.3	15.8	59.9	48.0	25.4	60.5	78.5	139	[5]
Karnaphuli River Bangladesh	81.1 (37.2–160.3)	2.0 (0.63–3.6)	–	20.3 (11.6–35.5)	–	–	43.7 (222–73.4)	–	–	[1]
Korotoa River Bangladesh	–	1.2 (0.26–2.8)	–	109 (55–183)	76 (35–118)	95 (37–163)	58 (36–83)	–	–	[3]
Ganga River (Kanpur site) India	–	2.5–6.0	–	5.0–250.0	7.0–17.0	5.0–13.0	2.5	–	23–70	[4]

(−) result is not available

respectively. Therefore, the sediment granulometric composition of these sampling points may also favor metal accumulation.

The results reported herein allow for the conclusion that the impacts of pollution sources are limited in the river regarding the metal and trace element contents present in the river sediments. Points T13, T17, T18 and T20 presented high concentrations, probably due to the contribution of domestic untreated sewage and industrial effluents from the cities surrounding the river, as well as the polluted water discharges by many tributaries. However, the elements analyzed by INAA and toxic metals by ICP OES and GF AAS at the last analyzed point, T22, presented concentrations for at the same level as T8 or even lower. In addition, the concentrations at T22 were at the same level as T1 bottom sediments from the Tiete River headwaters, considered a clean area with no contamination due to anthropogenic activities.

Acknowledgements The authors wish to thank Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP) for financial support (Process no. 2014/20805-6) and Conselho Nacional de Pesquisas (CNPq) for the research fellowship. The authors also thank two anonymous reviewers for their constructive comments, which have improved the quality of our manuscript.

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