METAL AND TRACE ELEMENT CONCENTRATION EVALUATION IN SEDIMENT PROFILES OF THE TIETÊ RIVER, STATE OF SÃO PAULO, BY INAA AND ICP OES TECHNIQUES

Josiane S. SOARES[2], Flavio R. Rocha[1], Déborah I. T. FÁVARO[1]

[1]Laboratório de Análise por Ativação Neutrônica - LAN-CRPq, Instituto de Pesquisas Energéticas e Nucleares (IPEN –CNEN/SP), Av. Professor Lineu Prestes, 2242, 05508-000, São Paulo, SP, Brazil,
defavaro@ipen.br

[2]Laboratório de Análises Químicas - LAQ- CQuiM, Instituto de Pesquisas Tecnológicas do Estado de São Paulo (IPT/SP), Av. Profº Almeida Prado, 532, 05508-901, São Paulo, SP, Brazil
josi.s@usp.br

ABSTRACT

The present study presents concentration results for heavy metals, major and trace elements, in two sediment cores collected along the Tietê River: Salto de Itu to Porto Feliz (Core 4 at point T-5) and Laras to Anhembi (Core 6 at point T18). As, Ba, Br, Co, Cr, Cs, Hf, Rb, Sb, Sc, Ta, Th, U and Zn concentrations by Instrumental Neutron Activation Analysis (INAA) and Al, Ba, Cd, Co, Cr, Cu, Mn, Ni, Pb, Ti, V and Zn concentrations by Inductively Coupled Plasma Optical Emission Spectrometry (ICP OES) were determined. The enrichment factor (EF), to assess the presence of anthropogenic pollution sources, was calculated and showed **FE > 1.5** values for As, Br, Cs, Hf, Rb, Ta, Th, U and Zn, confirming the anthropogenic contribution for these elements, in all fractions from both cores. As, Cd, Cr, Cu, Ni, Pb and Zn concentrations were compared to guideline values (TEL and PEL) from the Canadian Council of Ministers of the Environment (CCME) and adopted by the São Paulo State Environmental Company (CETESB) and concentration values between TEL and PEL were found, for all fractions from both cores, presenting good and or regular sediment quality classification, the worst being Core 6.

Key words: metals, trace elements, sediments, INAA, ICP-OES, Tietê River

1. INTRODUCTION

The Tietê is the most important river in the State of São Paulo due to its hydroelectric potential, which is well explored in almost of its entire 1,100 km length. The Tietê River drains an area composed of six sub-basins (Alto Tietê, Sorocaba / Médio Tietê, Piracicaba-Capivari-Jundiaí -Tietê / Batalha, Tietê / Jacaré and Baixo Tietê). In spite of all its historical contribution, hydroelectric potential and being one of the most economically important rivers in the state of São Paulo, the Tiete River is also one of the world's most polluted rivers, especially in the municipality of the city of São Paulo.

Tietê River is the largest river of the southeast part of Brazil. Its drainage basin is important for food and energy production, with more than ten hydroelectric power plants along the main channel of the river and tributaries. Over the years, with the increased population and consequent development of industry and agriculture, the river waters and sediment quality deteriorated. [1]

In general, environmental degradation of this river is mainly due to industrial activities in the São Paulo Metropolitan Region (SPMR) and surroundings, an intense industrial region, by heavy metals contamination, untreated domestic sewage, agricultural production and also organic compounds in the High Tietê River Basin. In the countryside region (Medium and Low basin) the mainly contamination sources are agro-industrial park for the production of sugar, alcohol, and citric juices. [3]

In recent years, attention has been focused to the problem of the Tietê River pollution related to the presence of heavy metals in the sediments [2-6]. River sediment can accumulate and integrate the temporal variability of heavy metals in river water originating from anthropogenic activities into spatial river sediment [7]

Mortatti et al [1] studied the heavy metal distribution in bottom sediment along the Tietê River Basin since the SPMR till its mouth at Parana River. They concluded that the pollution by heavy metals around SPMR is mainly due to municipal wastes and industrial effluents with reinforced downstream by agricultural activities. They observed that the heavy metal concentration increased is particularly important for Zn in the upper basin and Cu, Co ad Cr at mouth.

 Nascimento & Mozeto [2], analyzed bottom sediment samples from Tietê River basin in order to establish regional reference concentrations of metals and metalloids, since the upper reaches of the river down to its effluent into the Paraná River. The reference concentrations determined by this study showed significant deviations from the assumed global geological reference for some elements and also difference among concentrations of the same element from the different regions of the basin. Four different sets of reference concentrations values were proposed for the different regions of the studied basin.

Almeida & Rocha [4], by using the sediments quality triad for the study of anthropogenic contaminated aquatic systems selected some reservoirs along the Tietê River for this purpose. The results allow the classification of the reservoir based on their respective sediment quality and indicate the degradation vectors they are subject to. The spatial distribution of sediment potentially toxic accompanied the trophic gradient of Tietê River, i.e., the downstream reservoirs are less eutrophicated than the upstream ones. Therefore, the quality of the sediments improves with the distance from the SPMR confirming the origin of most pollutant substances. The concentration of Cd, Cu, Pb, Ni and Zn in the sediment samples was quantified.

More recently, Rocha et al. [6] assessed bottom sediment samples from along Tietê River. Three reservoirs including the Usina Parque de Salesópolis, the springs of the river, Edgar de Souza reservoir (Santana de Parnaíba city) and Rasgão reservoir (Pirapora do Bom Jesus county), all inside in the SPMR were evaluated according to the concentration and distribution of some metals and trace elements in bottom sediments. They concluded the poor sediment quality of the studied area, mainly in the last two reservoirs located after the São Paulo city.

The vertical metal concentration profile in river sediment can indicate not only the pollutants in sources but also the pollutants transported or contributed into reservoir through the river [7].

The present study takes part of the research project entitled: "Evaluation of the Extension and Pollution History by Metals and Trace Elements in River Sediments - Case Study, Tietê River, State of Sao Paulo" and had a financial support from FAPESP (Process n[0] 2014/20805-6).

The aim of this study was to evaluate the concentration of metal, major and trace elements in surface and sediment core samples, in several points from its headwaters in Salesopolis until the mouth, Parana River. The present study presents major, trace and metal concentration in a 2 sediment cores collected along the Tietê River, by 2 analytical techniques (INAA and ICP OES). The enrichment factor (EF), geochemical tools to assess the presence of anthropogenic pollution sources, were used. The concentrations for As, Cd, Cr, Cu, Ni, Pb and Zn in the samples were compared to guideline values (TEL and PEL).

2. MATERIAL AND METHODS

2.1. Study area

In this project, 34 bottom sediment samples were collected along the Tietê River. Figure 1 shows the sampling location along the Tietê River. Also six sediment cores were collected at strategic points such as Salesópolis, cores 1 (point T-1); Santana de Paranaiba, core 2 (point T-2); Pirapora do Bom Jesus, core 3 (point T-3); from Salto de Itu to Porto Feliz, core 4 (Point T-5); from Porto Feliz to Tietê, core 5 (Point T-11) and core 6 (Point T-18) from Laras to Anhembi. In the present study the results for Cores 4 and 6, situated in the Medium Tietê River Basin – Region 2 (Figure 1), from Tietê until Laras (Anhembi) municipalities, for heavy metal and trace element concentration are presented.
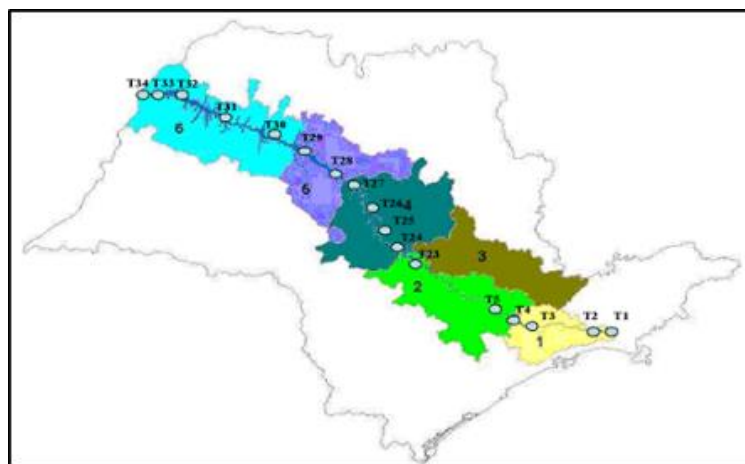

Figure 1: Sampling points location along Tietê River basin

2.2. Sampling and sample preparation

Sediment cores were collected by using a core sampler to which was attached a 100 cm long and 70 mm in diameter PVC pipe. Soon after the collection, the samples were frozen and then sliced every 2 cm in the laboratory.

Core 4 was collected at point T-5, at a 33 cm depth resulting in 13 sediment samples (fractions). Core 6, collected at point T-18, at a 88 cm depth resulting in 40 sediment samples (fractions) but only 20 were analyzed.

At the laboratory, sediment samples were dried at 40°C in a ventilated oven until constant weight. Sediment samples were passed through a 2 mm sieve, ground in a mortar, and passed again through a 125-mesh sieve to be homogenized before analysis. The total fraction ($<$ 2 mm) was analized.

2.3 Chemical analysis

2.3.1. Instrumental Neutron Activation Analysis (INAA)

For multielemental determination by INAA about 150 mg of sediment (duplicate samples) and reference materials were accurately weighed and sealed in pre-cleaned double polyethylene bags. Sediment samples and reference materials were irradiated for a daily cycle (6-7 hs), under a thermal neutron flux of 10^{12} n cm^{-2} s^{-1} in the IEA-R1 nuclear reactor at IPEN. Two series of counting were made: the first, after one week decay and the second, after 15-20 days. The measurements of the induced gamma-ray activity were carried out in a gamma-ray spectrometer with a GX20190 hyper pure Ge detector (Canberra) and associated electronics, with a resolution of 0.88 Kev and 1.90 Kev for ^{57}Co and ^{60}Co, respectively. The elements analyzed by using this methodology were As, Ba, Br, Co, Cr, Cs, Fe, Hf, Na, Rb, Sb, Ta, Th, U and Zn. The analysis of the data was made by using in-house gamma ray software, VISPECT program to identify the gamma-ray peaks and by an ESPECTRO program to calculate the concentrations. The uncertainties of the results were calculated by errors propagation. The methodology validation was verified by measuring the reference materials Lake Sediment (IAEA SL1), Soil 5 (IAEA) and BEN (Basalt –IWG-GIT). The results showed good accuracy (relative errors to certified values $<$ 5%) and good precision (relative standard deviations $<$ 10%). Details of the analytical methodology is given at Favaro *et al* [5].

2.3.2. Inductively Coupled Atomic Emission Spectrometry (ICP-OES)

Inductively Coupled Plasma Atomic Emission Spectroscopy is an analytical technique that utilizes argon plasma as an excitation source for atomic emission. The sample is injected in a nebulizer by a pumping system, where it is converted into a fine aerosol which is then transported into the plasma source through the injector tube of the instrument's torch. By absorbing energy from the plasma, the sample's atoms are promoted to an excited state and generate element-specific emission radiation when returning to their ground state. This

emission spectrum is detected as the analytical signal and its intensity, for a specific wavelength, is proportional to the concentration of the analyte in the sample. Quantification of the analyte is possible by comparing the sample's analytical signal to a calibration curve for that element. [8]

The purpose of the present study is the determination of the concentrations of the metals Al, Ba, Cd, Co, Cr, Cu, Fe, Mn, Na, Ni, Pb, Ti, V e Zn in sediment samples from the Tietê River.

All samples and certified reference materials were prepared by microwave assisted acid digestion, in order to achieve solubilization of the metals in study according to the United States Environmental Protection Agency recommendations (USEPA SW-846 3051A, 2007 [9]). This digestion method allows the quantification of the potentially available elements present in the samples. About 0.5 g of sediment and 0.25 g of certified reference material were weighed and digested according to the 3051 method from US EPA in a mixture of 10 mL of HNO_3: HCL (3:1) both concentrated.

After the digestion stage, the samples, MRCs and preparation blanks were filtered to remove undissolved material through medium speed filter paper and collected into 50 mL conical centrifuge tubes. Ultrapure water was added to dilute the solutions to a suitable final volume. For control of the analytical results along with the samples for each batch (38 tubes), a sample of certified reference material (CRM) Sandy Clay Soil (CRM 049 (Sigma)) was analyzed. Sediment samples digested as described above have been quantified for the metals Al, Ba, Cd , Co, Cr, Cu, Fe, Mn, Na, Ni, Pb, Ti, V, and Zn in the ICP OES MPX-Varian equipment at Chemical Analyses Laboratory - LAQ/IPT-SP.

2.4 Validation of methodologies

2.4.1. Validation of INAA methodology

INAA methodology validation, for precision and accuracy verification of the method was carried out through the analysis of certified reference materials: Soil-5 (IAEA), SL1-Lake Sediment (IAEA), BEN (Basalt-IWG-GIT), that have certified values for almost all elements analyzed. The calculation of the standardized difference or "Z" value of an analytical result is given by:

$$Z_i = C_i - C_{refi} / (\sigma^2 + \sigma_{refi}^2)^{1/2}$$

(1)

Where:
C_i: concentration of element i in the analysis of reference material;
$C_{ref,i}$: concentration or certificate value of consensus for the element i;
σ_i: uncertainty of the concentration of the element (i) analysis of reference material;
$\sigma_{ref,i}$: uncertainty of the value of consensus certificate for the element i.

In the case of INAA technique, using the value of "Z" for approval of the results considers that if $|Z| < 3|$ the individual result of the control sample, in this case, the reference material that is being analyzed, must be within the 99% confidence interval of the expected value [10].

2.4.2 Analytical method validation for ICP OES

Validation of this analytical method, with regard to accuracy and precision, was performed by analyzing the certified reference material *Sandy Clay1 – CRM049 (Trace Metal)*, which has certified concentration values for all the elements by using USEPA 3051A digestion procedure. [9]

2.5 Enrichment Factor calculation

To verify if an anthropogenic influence is occurring or not in a given site, assessment tools, such as the enrichment factor (EF) [11,12] are used. In the present study, Sc as a normalizer element was used. The values of enrichment Factor (EF) can be obtained using equation 2:

$$FE = (C_x/C_{ref})_{amostra}/(C_x/C_{ref})_{"Background"} \qquad (2)$$

Where:
$(C_x/C_{ref})_{amostra}$: relationship between the element in the sediment sample and the normalizer element in the sample;
$(C_x/C_{ref})_{"Background"}$: relationship between the element analysed and normalizer element in the reference material or background value;

In the present study, the EF was calculated using NASC (North American Shale Composite) values as reference values. If $0.5<FE<1.5$, indicates that the concentration of the element is probably related to natural origin or weathering; values $EF>1.5$ indicate anthropogenic contributions. [11,12]

2.6 Sediment Quality Guide Values (VGQS)

Guide sediment quality values are tools that synthesize information of the relationship between the concentrations of chemicals in sediments and any adverse biological effect resulting from exposure of these in the aquatic environment. They were proposed by the Canadian Council of Ministers of the environment, CCME (Canadian Council of Ministers of the Environment) with the intent to protect aquatic life. Oriented values were established based on the total concentration of As, metals and organic compounds in sediments in order to evaluate possible adverse effects on aquatic biota. These data are compiled in a database of biological effects to sediment, BEDS (Biological Effects Database for Sediments) in order to calculate two values: TEL (Threshold Effect Level) and PEL (Probable Effect Level). Thus, three ranges of concentrations are consistently defined: below TEL, or the concentration range in which are adverse biological effects are rarely expected (less than 25% of occurrence); between TEL and PEL intervals, in which occasionally occur adverse biological effects; and above PEL values, indicating frequent occurrence of adverse biological effects (more than 50% of occurrence).[13]

Table 1: Guide values of sediment quality for aquatic life protection (mg kg^{-1}) (fresh water) [14]

ELEMENT	VERY GOOD	GOOD	REGULAR	BAD	POOR
As (mg kg^{-1})	< 5.9	≥ 5.9-11.5	>11.5-<17.0	17.0-25.5	>25.5
Cd (mg kg^{-1})	< 0.6	≥ 0.6-2.1	>2.1-<3.5	3.5-5.3	>5.3
Cr (mg kg^{-1})	< 37.3	≥ 37.3-63.7	>63.7-<90.0	90.0-135.0	>135.0
Cu (mg kg^{-1})	< 35.7	≥ 35.7-166.4	>166.4-<197.0	197.0-295.5	>295.5
Ni (mg kg^{-1})	< 18	≥ 18-27	>27-< 36	36-54	>54
Pb (mg kg^{-1})	< 35.0	≥ 35.0-63.2	> 63.2-<91.3	91.3-137.0	>137.0
Zn (mg kg^{-1})	< 123	≥ 213-219	>219-<315	315-473	>473

3. RESULTS AND DISCUSSION

3.1. Results for sediment analysis by INAA

3.1.1 Validation of the methodology of INAA: calculation of *Z-score* (Z_i)

For precision and accuracy of the method of INAA verification, *Z-Score* (Z_i) was used.Z values were calculated only for the elements with certified concentration values. Information values have been excluded in this scan.

As can be seen in Figure 2, all elements analyzed in the 3 certified reference materials, presented Z values within the range of -2 to 2, indicating good precision and accuracy of the INAA method.
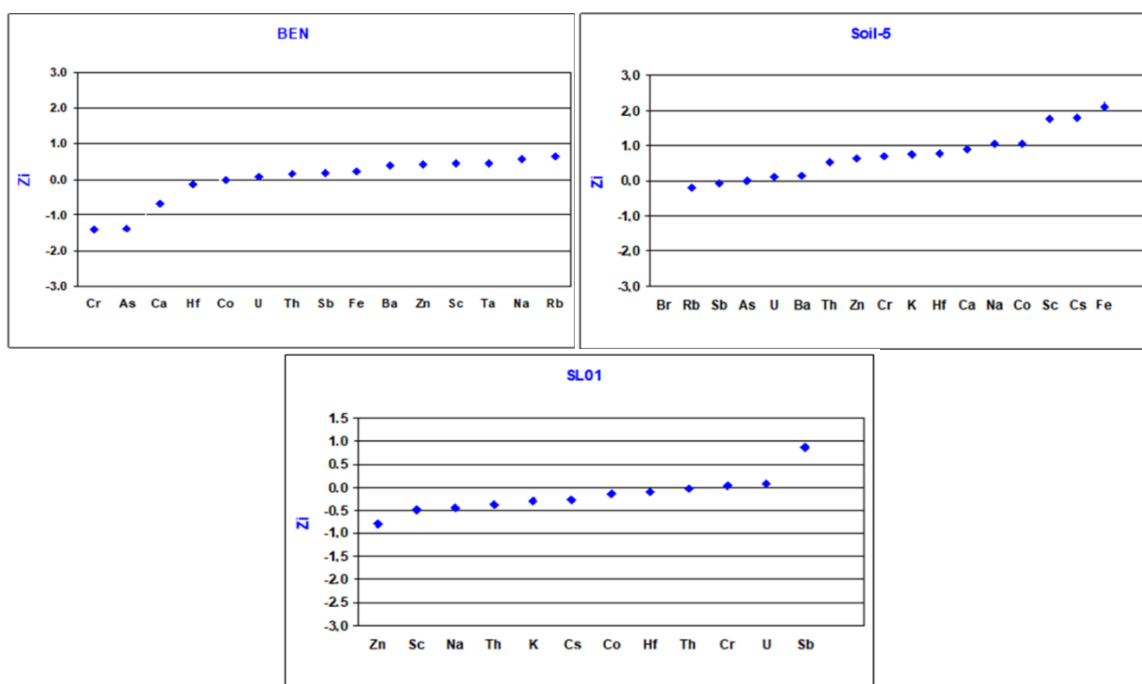

Figura 2: Z-score results for the reference materials BEN, SL1 and SL5

3.1.2 Results by INAA

Tables 2 and 3 present the results obtained in Core-4 and Core-6 analyzes respectively using INAA.

Table 2: Results (mg kg^{-1}) for the sediment samples from Core 4 (point T-5), by INAA

Depth (cm)	Ident.	As	Ba	Br	Co	Cr	Cs	Fe %	Hf	Na	Rb	Sb	Sc	Ta	Th	U	Zn
0	C4-1	3.7	529	4.2	13	119	4.3	3.6	11.4	1879	92	1.5	10.8	1.8	15.3	4.1	474
3	C4-2	2.3	382	1.8	8.0	59	2.8	2.0	12.7	1848	74	0.8	6.8	1.2	14.4	3.1	240
6	C4-3	4.0	504	2.6	10.0	79	4.1	2.5	14.6	2368	111	1.3	8.4	2.3	14.8	4.0	319
9	C4-4	4.9	600	2.6	10.1	95	4.3	3.3	12.0	2225	98	1.4	9.8	1.6	15.2	4.2	355
12	C4-5	4.4	642	2.4	10.7	105	5.0	3.4	11.7	2092	104	1.6	10.5	1.7	16.1	4.1	396
15	C4-6	4.1	581	2.0	8.8	83	5.4	2.5	13.3	3132	124	1.3	8.5	2.7	15.8	4.9	314
18	C4-7	4.1	488	1.5	8.1	60.8	5.0	2.3	12.7	3006	124	1.0	7.2	2.2	13.1	4.1	217
21	C4-8	4.7	457	1.5	9.3	71.9	6.9	2.8	11.4	3590	154	1.5	8.1	2.1	14.7	4.3	192
23	C4-9	4.5	468	1.3	9.3	71.4	6.3	2.9	11.0	3101	147	1.1	9	2.1	15.0	4.6	178
26	C4-10	3.8	430	1.7	10.1	77.8	6.3	3.0	11.4	2919	146	1.3	9.1	1.9	14.9	4.3	211
29	C4-11	3.6	433	1.5	7.8	50.3	4.7	2.4	12.8	3038	125	1.0	6.3	3.0	10.0	6.1	109
31	C4-12	5.0	519	1.7	10.7	76.6	9.1	3.2	11.8	3797	210	1.6	9.9	3.2	19.4	9.5	133
33	C4-13	6.3	517	2.5	12.5	101.5	8.1	3.6	11.4	1950	183	1.9	11	4.2	20.8	9.5	175
	Average	4	504	2	10	81	5.6	2.9	12.0	2688	130	1.3	9	2.3	15.0	5.1	255
	NASC	2	636	1	28	125	5.2	4.0	6.0	7500	125	2.1	15	1.1	12.0	2.7	85

Table 3: Results (mg kg^{-1}) for the sediment samples from Core 6 (point T-5), by INAA

Depth (cm)	Ident.	As	Ba	Br	Co	Cr	Cs	Fe %	Hf	Na	Rb	Sb	Sc	Ta	Th	U	Zn
0-10	C6-1	11.5	678	5.9	26	173	6.2	5.5	8.2	1458	108	2.1	8.4	1.8	20.9	5.3	913
13-15	C6-2	8.5	609	6.2	22	136	5.6	5.0	10.4	1465	112	1.7	7.5	1.5	18.2	4.4	634
17-19	C6-3	24.1	557	18.1	21	120	5.2	5.0	9.8	1476	100	1.6	7.7	1.7	18.0	5.2	498
21-23	C6-4	9.6	535	5.2	22	128	5.5	5.4	7.7	1306	114	1.6	8.1	1.6	18.9	5.2	513
25-27	C6-5	8.2	713	5.1	22	120	5.7	5.2	7.6	1174	104	1.6	8.2	1.6	18.3	4.5	436
29-31	C6-6	8.1	465	5.9	12	78	n.d.	3.3	23.9	1597	68	1.0	10.9	1.6	16.8	3.9	222
33-35	C6-7	11.6	550	8.4	17	117	n.d.	4.2	13.4	1862	89	1.7	9.8	1.5	16.0	3.1	436
37-39	C6-8	7.7	514	n.d.	13	97	n.d.	3.7	14.0	1929	83	1.2	10.1	1.5	14.7	2.8	354
41-43	C6-9	13.4	655	9.4	16	123	n.d.	4.8	10.3	1549	97	2.1	9.4	1.8	18.8	n.d	378
45-47	C6-10	7.5	634	n.d.	12	90	n.d.	3.4	13.1	2117	83	1.3	8.6	1.5	13.8	2.9	269
49-51	C6-11	8.3	781	6.1	14	151	6.2	4.9	13.3	1731	99	1.7	9.9	1.8	21.4	4.4	n.d
53-55	C6-12	6.7	669	5.0	12	130	5.4	4.0	11.9	2047	97	1.7	7.7	1.3	18.0	3.9	500
57-59	C6-13	7.9	525	3.5	11	103	4.7	4.0	10.5	1927	88	1.3	8.1	1.6	17.5	4.3	323
61-63	C6-14	7.4	460	2.9	10	93	4.4	3.5	17.1	1728	91	1.1	9.3	1.4	17.6	4.1	270
65-67	C6-15	9.1	457	3.5	12	101	4.9	4.2	10.9	1579	86	1.3	9.8	1.3	18.5	4.3	290
69-71	C6-16	2.3	379	1.6	5	43	2.6	1.7	17.3	1996	75	0.5	11	0.8	10.1	2.5	114
73-75	C6-17	5.9	594	3.1	10	97	3.8	3.3	10.3	2231	97	1.3	8.6	1.6	13.1	3.6	341
77-79	C6-18	8.6	555	5.4	13	165	5.1	4.6	102	1767	113	2.2	9.5	1.5	17.7	4.3	642
81-83	C6-19	8.8	664	5.4	14	150	5.7	5.0	11.0	1691	122	1.8	9.7	1.6	20.6	5.4	449
85-88	C6-20	9.9	577	6.9	15	142	6.2	5.4	9.8	1472	125	1.5	16.6	1.8	21.8	4.7	390
	Average	9.2	504	2.0	10	117	5.1	2.9	12.0	2688	96	1.5	9.4	1.5	17.3	4.1	421
	NASC	2	636	1.0	28	125	5.2	4.0	6.0	7500	125	2.1	15	1.1	12.0	2.7	85

n.d.- not determined

The results in Table 2, for most elements, do not present a great concentration variation with depth. The exceptions were for Cr, Hf, Ta, Th, U and especially Zn, with values higher than the values of NASC reference throughout the profile.

In the segment of the to Anhembi Counties (T18-Core 6) (Table 3), high concentrations of Hf, Ta, Th, U and especially Zn were found, throughout the profile, compared to NASC reference values.

In this region agricultural, sand mining, metal structure and chemical industry activities, possibly contribute to the increase of the concentration of the elements analyzed. [15]

Another relevant factor that may be significantly contributing to the increase in pollution of the Tietê River sediments is the fact that four other rivers drain into the Tietê River in this region, namely the Peixe, das Conchas, Moquém and Jibóia Rivers [15].

3.1.3 Enrichment Factor Results (FE)

Enrichment factors (EF) were calculated based on the concentration results found by INAA, having NASC values as reference and Sc as the normalizer element.

Figures 3 and 4 present the EF values only for the elements that presented EF> 1.5 values indicative of pollution of anthropogenic origin at the sampling sites. The other elements presented 0.5 <EF <1.5 values, indicative of concentrations probably related to the natural origin or weathering consequences.

In general, As, Br, Th, U, and Zn presented EF> 1.5 in the two points studied: T5 (Core 4) and T18 (Core 6). The elements Cs, Rb, Hf and Ta presented EF> 1.5 only in some fractions of the cores.
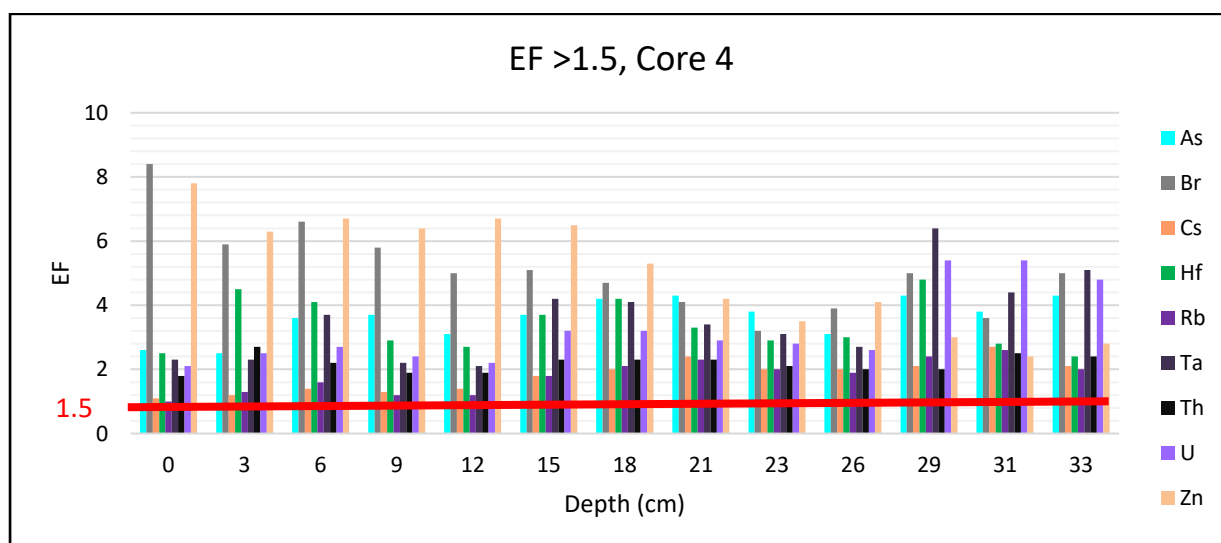

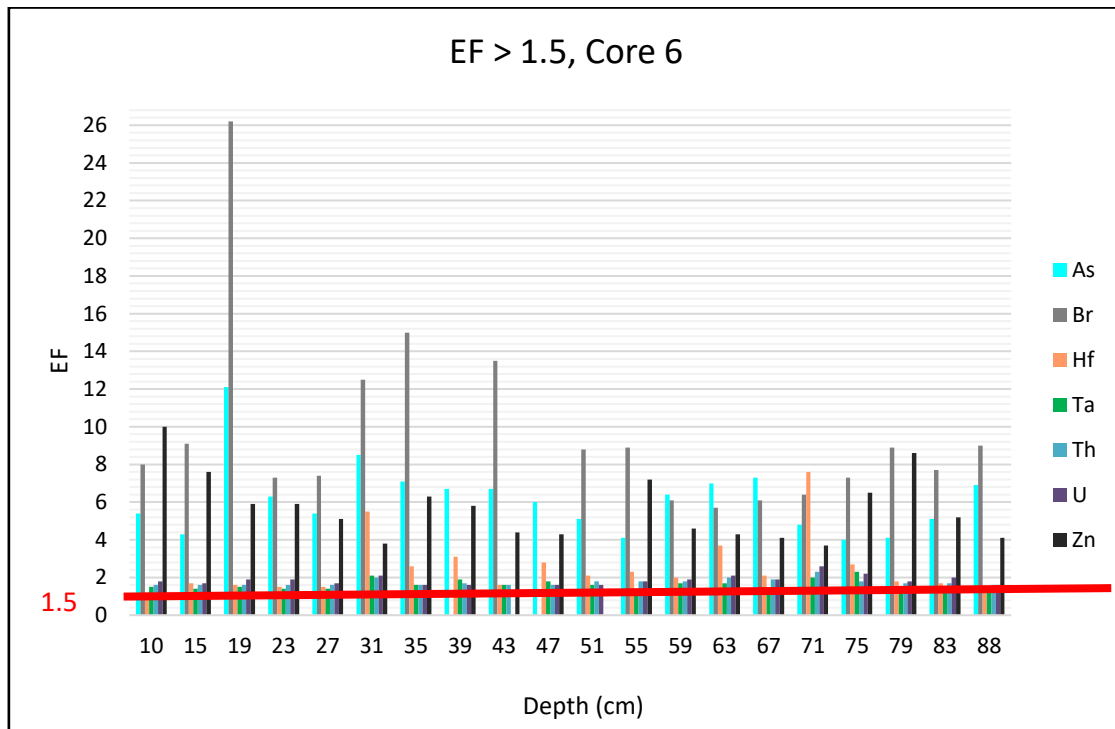**Figure 3: EF values calculated with NASC reference values, Core 4**

Figure 4: EF values calculated with NASC reference values, Core 6

3.1.4 Comparison with TEL and PEL guideline values

From the data in Figure 5 (Core 4), it can see that for As, concentration values along the entire profile did not exceed TEL value (5.9 mg kg^{-1}), except for the base (30-33 cm). For Cr, all values exceeded TEL value (37.6 mg kg^{-1}) and some fractions within the profile, exceeded PEL value (90 mg kg^{-1}) (C4-1, C4-4, C4-5 and C4-13 fractions). For Zn, in general, all values exceeded TEL value (123 mg kg^{-1}) and the surface fraction (from C4-1 to C-4-6), the PEL value (315 mg kg^{-1}). The classification of this sediment core according to VGQS was of good quality and regular to Cr and Zn, in general. The more superficial fractions were classified as poor quality for Zn.

From the data presented in Figure 6 (Core 6), it can be seen for As, concentration values between TEL and PEL, throughout the profile, with regular classification of sediment for this element. For the Cr, the concentration values exceeded the PEL value, practically in all the fractions throughout the profile, with bad sediment classification for this metal. For Zn, all fractions also exceeded the PEL value. In this case, it was observed in general, a tendency of decrease in content from the top to the base of the profile. For Zn, the sediment can be classified as poor quality.
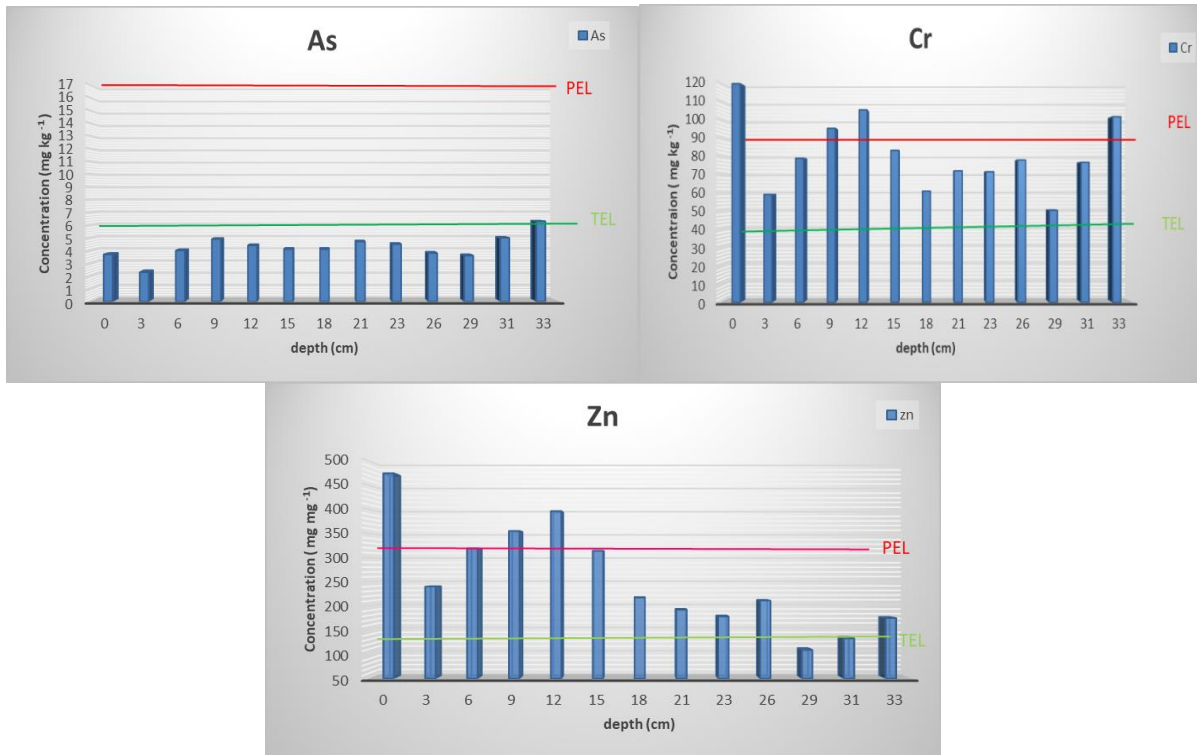
Figure 5: Concentration values for As, Cr and Zn (mg/kg^{-1}) in comparison with the values of TEL and PEL, Core 4
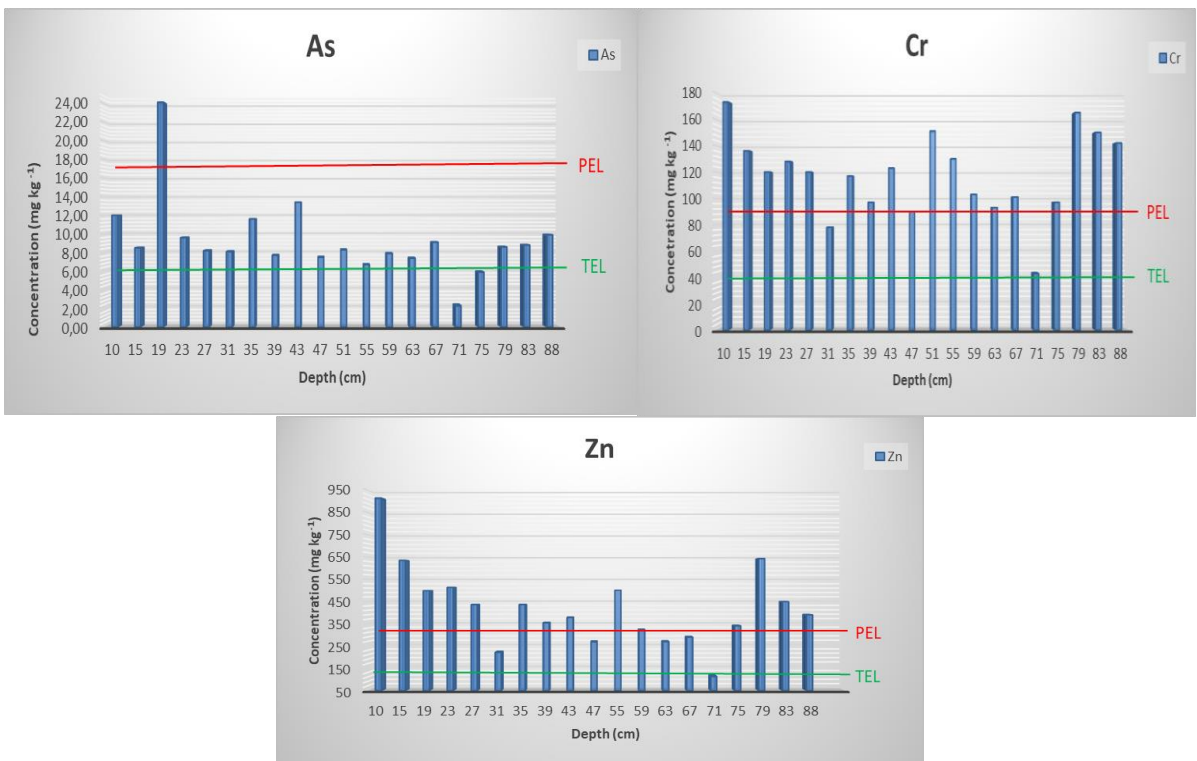

Figure 6: Concentration values for As,Cr and Zn (mg/kg^{-1}) in comparison with TEL and PEL values, Core 6

3.2 Results for sediment analysis by ICP OES

3.2.1 Validation of the ICP OES methodology

The validation of analytical methodology was carried out through the analysis of Sandy Clay1 reference material – CRM049 (Trace Metal). This certified reference material presents concentration for the elements, for digestion made according to the USEPA 3051a procedure. Sandy Clay Soil reference material presented satisfactory results for most elements analyzed, with recovery of 70 to 120%, attesting the accuracy of the method. (Table 4)

Table 4: Concentration values obtained for the reference material analyses by ICP OES

Sandy Clay- Extraction					
Certified value				**Result Obtained**	
Element	Unit	Certificate		Obtained	Recovery rate (%)
Al	%	1.01 ± 0.15		0.22 ± 0.02	22
Fe		0.66 ± 0.03		0.58 ± 0.08	88
Ba	mg/kg^{-1}	549 ± 11		528 ± 85	96
Cd		88 ± 2		88 ± 12	100
Co		218 ± 5		219 ± 33	100
Cr		135 ± 2		134 ± 20	99
Cu		134 ± 3		127 ± 17	95
Mn		1110 ± 36		1212 ± 400	109
Na		1500 ± 48		1154 ± 171	77
Ni		288 ± 6		282 ± 38	98
Pb		340 ± 7		296 ± 49	87
Ti		67 ± 6		61 ± 30	92
V		148 ± 2		144 ± 21	97
Zn		433 ± 8		426 ± 58	98

3.2.2 ICP OES sediment analysis results and comparison with TEL and PEL guideline values

Tables 5 and 6 present the results for Core-4 and Core- 6, respectively, by ICP-OES.

For metals Al, Ba, Co, Mn, Ti and V, in general, a concentration decrease from the top to the bottom of the profile was observed.

Table 5: Results (mg kg^{-1}) for the sediment samples from Core 4 (T-5), by ICP-OES

depth. (cm)	Unit Element	%		mg kg^{-1}										
		Al	Fe	Ba	Cd	Co	Cr	Cu	Mn	Ni	Pb	Ti	V	Zn
0	C4-1	1.2 ± 0.1	2.5 ± 0.2	180 ± 7	1.9 ± 0.2	10 ± 1	83 ± 6	104 ± 8	630 ± 35	39 ± 3	33 ± 4	123 ± 3	34 ± 2	432 ± 31
3	C4-2	0.8 ± 0.2	1.2 ± 0.1	119 ± 10	0.9 ± 0.3	6 ± 1	53 ± 1	75 ± 5	423 ± 7	29 ± 1	22 ± 5	100 ± 24	23 ± 1	297 ± 11
6	C4-3	0.8 ± 0.1	1.9 ± 0.3	123 ± 19	1.6 ± 0.8	7 ± 1	54 ± 6	78 ± 12	460 ± 66	26 ± 5	28 ± 2	117 ± 12	26 ± 3	299 ± 41
9	C4-4	1.1 ± 0.3	2.3 ± 0.4	150 ± 27	1.9 ± 0.4	6 ± 1	67 ± 9	95 ± 12	483 ± 62	26 ± 3	36 ± 8	122 ± 36	34 ± 7	324 ± 45
12	C4-5	1.1 ± 0.2	2.2 ± 0.1	182 ± 1	2.2 ± 0.7	7 ± 1	74 ± 3	109 ± 2	430 ± 12	31 ± 4	39 ± 11	113 ± 30	33 ± 1	351 ± 6
15	C4-6	0.8 ± 0.1	2.0 ± 0.1	133 ± 5	1.8 ± 0.4	6 ± 1	58 ± 1	84 ± 5	387 ± 17	28 ± 1	32 ± 6	107 ± 3	26 ± 1	280 ± 14
18	C4-7	0.6 ± 0.3	1.4 ± 0.3	94 ± 7	1.3 ± 0.4	6 ± 1	41 ± 3	50 ± 2	386 ± 14	24 ± 6	26 ± 5	79 ± 18	20 ± 4	189 ± 9
21	C4-8	0.8 ± 0.2	1.9 ± 0.1	95 ± 8	1.5 ± 0.4	7 ± 1	54 ± 2	48 ± 1	522 ± 12	20 ± 1	33 ± 3	88 ± 31	26 ± 2	157 ± 4
23	C4-9	0.8 ± 0.2	1.9 ± 0.2	95 ± 12	1.2 ± 0.4	7 ± 1	50 ± 6	41 ± 5	585 ± 52	20 ± 2	34 ± 6	91 ± 9	28 ± 4	143 ± 16
26	C4-10	0.9 ± 0.2	2.1 ± 0.1	105 ± 10	1.7 ± 0.9	7 ± 1	55 ± 4	46 ± 3	700 ± 36	23 ± 1	34 ± 2	93 ± 16	29 ± 2	178 ± 13
29	C4-11	0.7 ± 0.1	2.0 ± 0.1	72 ± 3	1.1 ± 0.1	7 ± 1	37 ± 1	32 ± 1	585 ± 5	18 ± 1	23 ± 1	70 ± 16	22 ± 1	116 ± 2
31	C4-12	0.9 ± 0.6	2.0 ± 0.3	108 ± 14	1.6 ± 0.8	7 ± 1	49 ± 5	30 ± 2	685 ± 11	18 ± 2	43 ± 2	77 ± 7	27 ± 5	113 ± 13
33	C4-13	1.1 ± 0.3	2.3 ± 0.6	124 ± 33	3.0 ± 0.7	9 ± 2	66 ± 7	38 ± 1	775 ± 34	23 ± 4	50 ± 12	96 ± 4	32 ± 5	151 ± 14

Table 6: Results (mg kg^{-1}) for the sediment samples from Core 6 (T-18), by ICP-OES

depth. (cm)	Unit Element	%		mg kg^{-1}										
		Al	Fe	Ba	Cd	Co	Cr	Cu	Mn	Ni	Pb	Ti	V	Zn
0-10	C6-1	2 ± 1	4.0 ± 0.1	269 ± 30	3 ± 1	19 ± 1	139 ± 5	190 ± 2	714 ± 15	62 ± 3	47 ± 4	157 ± 39	60 ± 4	878 ± 8
17-19	C6-3	1.6 ± 0.3	4.0 ± 0.1	211 ± 12	2.0 ± 0.1	17 ± 1	100 ±1	139 ± 2	717 ± 15	48 ± 3	38 ± 4	134 ± 19	55 ± 1	621 ± 5
25-27	C6-5	2 ± 1	4.0 ± 0.4	208 ± 43	2.0 ± 0.1	17 ± 1	89 ± 10	118 ± 10	831 ± 73	43 ± 9	34 ± 2	164 ± 74	51 ± 8	486 ± 4
33-35	C6-7	1.6 ± 0.5	4.0 ± 0.4	218 ± 19	2.0 ± 0.1	17 ± 1	95 ± 6	138 ± 6	830 ± 35	50 ± 5	38 ± 5	139 ± 7	60 ± 8	529 ± 19
41-44	C6-9	1.6 ± 0.5	4.0 ± 0.3	234 ± 9	2.0 ± 0.1	17 ± 1	89 ± 4	114 ± 1	1253 ± 29	42 ± 3	35 ± 3	137 ± 17	60 ± 7	449 ± 5
49-51	C6-11	1.0 ± 0.1	2.0 ± 0.1	120 ± 13	1.0 ± 0.1	9 ± 1	44 ± 3	56 ± 7	560 ± 67	23 ± 3	17 ± 7	82 ± 7	31 ± 2	233 ± 26
57-59	C6-13	1.2 ± 0.2	3.0 ± 0.3	189 ± 16	2.0 ± 0.4	13 ± 1	81 ± 7	121 ± 12	731 ± 19	47 ± 5	32 ± 6	115 ±14	40 ± 5	493 ± 26
65-67	C6-15	0.9 ± 0.3	2.2 ± 0.1	145 ± 5	2.0 ± 0.4	9 ± 1	65 ± 3	97 ± 9	545 ± 100	37 ± 1	36 ± 1	106 ±19	33 ± 4	391 ± 36
73-75	C6-17	1.2 ± 0.4	2.4 ± 0.1	153 ± 41	2.0 ± 0.6	10 ± 1	67 ± 16	97 ± 21	460 ± 78	36 ± 7	31 ± 10	116 ± 45	43 ± 14	367 ± 7,7
81-83	C6-19	1.0 ± 0.1	2.1 ± 0.1	135 ± 9	1.0 ± 0.4	8 ± 1	55 ± 5	82 ± 7	405 ± 32	27 ± 1	25 ± 4	120 ±28	36 ± 2	289 ± 19

The results obtained for metal concentration of Cd, Cr, Cu, Ni, Pb and Zn determined by ICP OES, were compared with VGQS values (Table 1) and are presented in Figures 7 and 8, to Co re-4 and Core-6, respectively.

From the data presented in Figure 7, it was found that Cd concentration values were between TEL (0.6 mg kg^{-1}) and PEL values (3.5 mg kg^{-1}), so the sediment being classified as good quality for this metal. For Cr, Cu, and Ni, all concentration values were between TEL and PEL, also with good sediment quality classification for these metals. For Pb, most concentration values were below TEL value (35 mg kg^{-1}), with very good classification for this metal. For Zn, most values were between TEL and PEL (good Classification). However, C4-1 (0 cm), C4-4(9 cm) and C4-5 (12 cm) exceeded PEL value (315 mg kg^{-1}), with the sediment being classified as very poor quality according to criteria adopted by CETESB (Table 1).
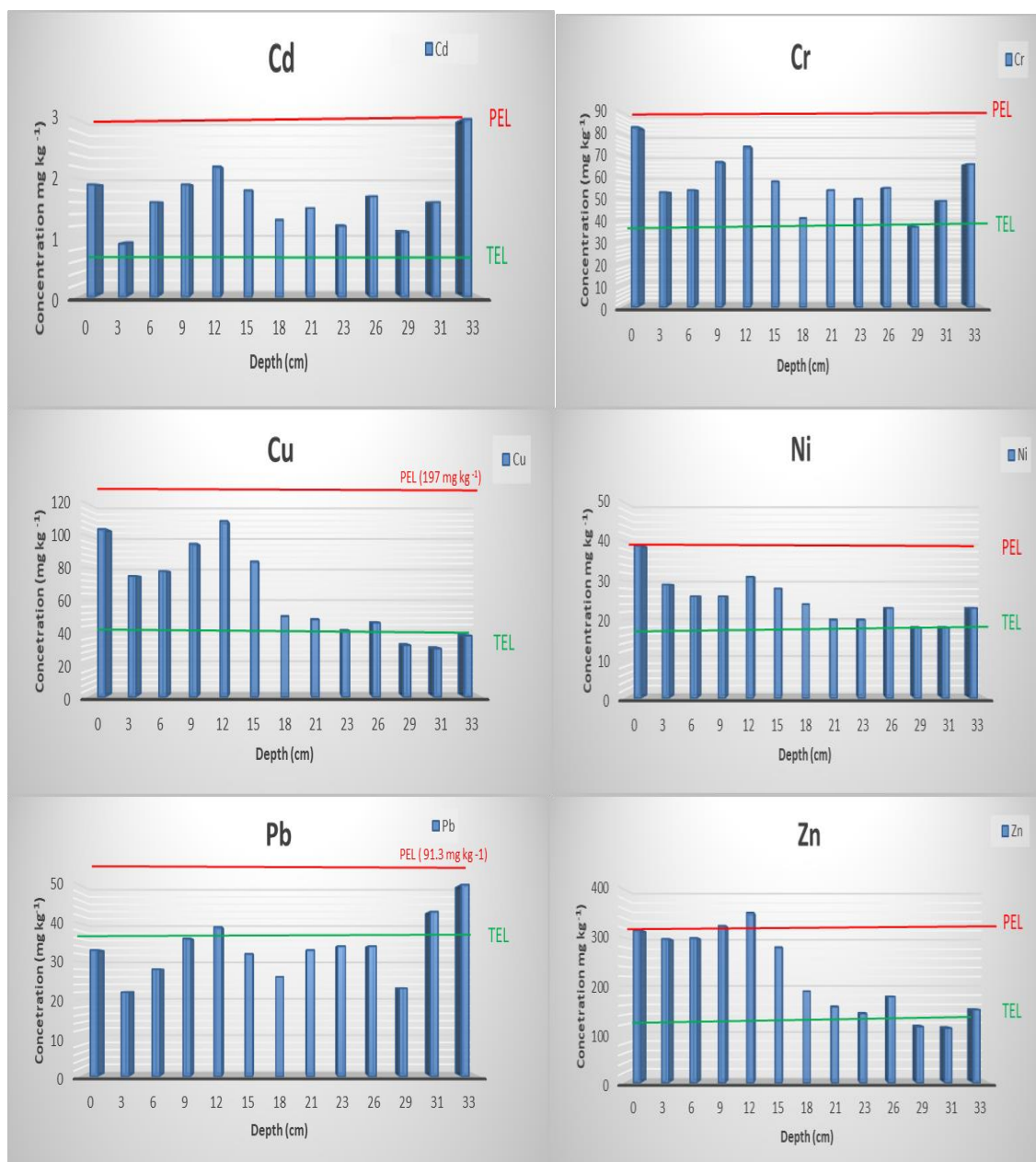
Figure 7: Concentration values for Cd, Cr, Cu, Ni, Pb, and Zn (mg kg⁻¹) in comparison with TEL and PEL values, Core 4

From the data in Figure 8 (core 6), concentration values were between TEL and PEL values for Cd and Cu, with a good quality sediment classification for these metals. For Cr and Ni, the concentration values were between TEL and PEL values, but with some fractions exceeding PEL value, with bad sediment quality classification for these metals. For Zn, practically all the fractions exceeded the PEL value, with poor sediment quality classification for this metal. For Pb, the concentration values were at the TEL limit for most fractions and then with good sediment quality classification according to the CETESB criteria. In this core, it was observed that all surface fractions (0 to 10 cm) showed higher concentration values for all of these metals analyzed, indicative of recent contamination in this location.
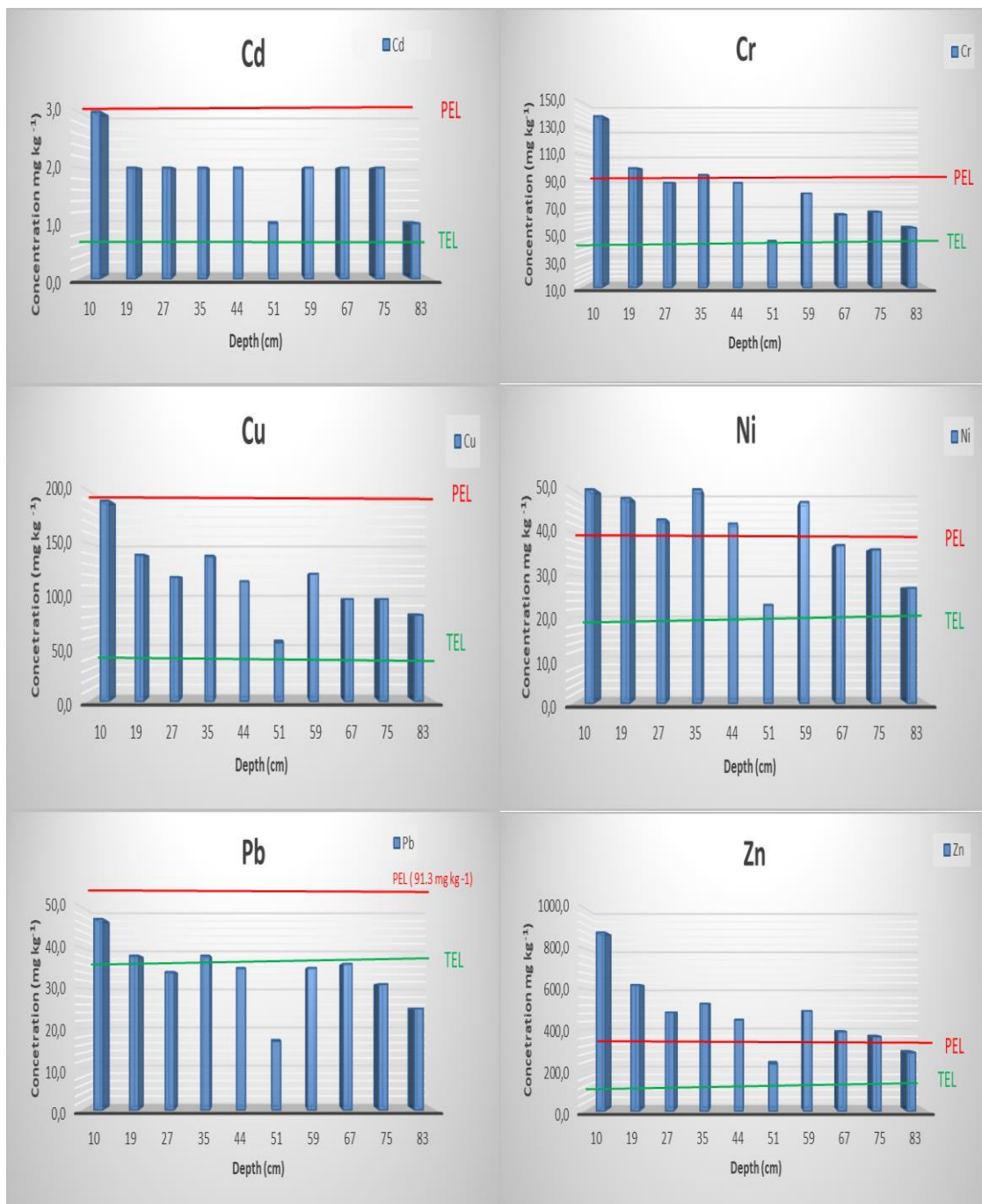
Figure 8: Concentration values for Cd, Cr, Cu, Ni, Pb, and Zn (mg kg^{-1}) in comparison with TEL and PEL values, Core 6

CONCLUSIONS

INAA and ICP OES analytical techniques used in the present study showed to be excellent tools for toxic metal, major and trace element monitoring sediment assessment, with high precision and accuracy.

In general, Br, Cs, Rb, Ta, Hf, Th, U and Zn determined by INAA, presented EF > 1.5 values, indicating a likely anthropogenic contribution, for all the fractions in both Core 4 and 6.

When As concentration values determined by INAA and toxic metals Cd, Cr, Cu, Ni, Pb and Zn determined by ICP OES, were compared to the VGQS values adopted by CETESB, values were between TEL and PEL, for most of the fractions analyzed, in both profiles, with good classification and/or regular quality of sediments. In general, the Core-6 sediment quality classification was worse for these metals and semi-metal As, than samples from C-4 profile. Core-6 showed higher concentration values for all of these metals in the surface fraction (0 to 10 cm), indicative of recent contamination in this location.

Comparing the sites of the present study, it was verified that Core-4 (Point T-5), from Salto de Itu to Porto Feliz Counties, seemed to have less impact in relation to toxic metals than Core-6 (Point T-18), from Laras to Anhembi Counties. In this region, there are agricultural, mining, industrial, manufacture of metallic structure and chemical activities that possibly may be contributing.to the concentration increase of the elements analyzed. The Tietê River in this segment, also receives a load of tributaries that may also be contributing to the pollution of the sediments analyzed. In addition, high concentrations of trace elements and metals in the deepest fractions of the two profiles analyzed was observed, indicating past contamination.

This study brings to light a series of important indicators, which made possible the study of the anthropic influence for the elements analyzed in the sediment profiles of the studied regions.

ACKNOWLEDGMENTS

REFERENCES

1. J. Mortatti, G.M. Morais, J.L. Probst, "Heavy Metal distribution in recent sediments along the Tietê River basin (São Paulo, Brazil)". *Geochemical Journal*, **46**, pp. 13-19 (2012).
2. M.R.L Nascimento, A.A. Mozeto, "Reference value for Metals and Metalloids concentrations in bottom sediments of Tietê River Basin, Southeast of Brazil". *Soil and Sediment Contamination*, **17**, pp. 269-278 (2008).
3. J. Mortatti, C. Hissler, J.L. Probst, "Distribuição de metais pesados nos sedimentos de fundo ao longo da bacia do Rio Tietê". *Geologia USP. Série Científica*, **10** (2), pp. 3-11 (2010).

4. C.A. Almeida, O. Rocha,"Estudo comparativo da Qualidade dos Sedimentos dos Reservatórios do Rio Tietê (SP)". *J. Braz. Soc. Ecotoxicol*., **1** (2), p. 141-145 (2006).
5. D.I.T. Favaro, G.F. Alegre, S.I. Borrely, W. Vukan, A.S. Vieira, S.M.O. Oliveira, "Metal, major and trace elements assessment of Tietê River sediments, São Paulo, Brazil". *J. Radioanal. Nucl. Chem*., **299** (1), p. 797-805 (2014).
6. F. Rocha, P.S.C. Silva, Paulo , L.M. Castro, I.C.C.L Bordon, Isabella , S.M.B. Oliveira, D.I.T. "NAA and XRF technique bottom sediment assessment for major and trace elements: Tietê River, São Paulo State, Brazil". *J. Radioanal. Nucl. Chem.*, **306** (3), pp. 655-665 (2016).
7. U. Forster, "Metal pollution assessment from sediment analysis, in: Forstner, G.T.W. Wittman (Eds)'. Metal Pollution in the Aquatic Environment, Springer, Berlin, 1983, pp. 110-193.
8. E. Bostelmann, "Avaliação da concentração de metais em amostras de sedimento do Reservatório Billings, Braço Rio Grande", São Paulo, Brasil. 2006. Dissertação (Mestrado) – Instituto de Pesquisas Energéticas Nucleares, São Paulo.
9. USEPA. Method 3051a.*Microwave Assisted Acid Digestion of Aqueous Samples and Exctrats*.2007. https://www.epa.gov./sites/production/files/2015-12/documents/3015a.pdf. Accessed in 20 July 2017.
10. P. Bode, *Instrumental and organizational aspects of a neutron activation analysis laboratory*, Delft, Interfaculty Reactor Institut, Netherlands, pp.147 (1996).
11. M. L. T. G. de Mendonça, "Metodologia para determinação de metais em sedimentos utilizando micro-ondas com frasco fechado e análise estatística multivariada das concentrações de metais em sedimentos da Bacia de Campos". Tese (Doutorado), Pontifícia Universidade Católica, Departamento de Química, Rio de Janeiro-RJ, pp. 90-92(2006).
12. F. C. Gomes, J. M. Godoy, M. L. D. P. Godoy, Z. L. Carvalho, R. T. Lopes, J. A. SanchezCabeza, L. D. Lacerda, J. C. Wasserman, "Metal concentration, fluxes, inventories and chronologies in sediments from Sepetiba and Ribeira Bays: A comparative study", *Marine Pollution Bulletin*, **59**, pp. 123-133 (2009).

13. CCME – Canadian Council of Ministers of the Environment, Canadian Environmental Quality Guidelines. Canadian Sediment Quality Guidelines for the Protection of Aquatic Life – Protocol for the Derivation of Canadian Sediment Quality Guidelines for the Protection of Aquatic Life, (1999) http://ceqg-rcqe.ccme.ca/download/en/317, Accessed in 20 July 2017.
14. CETESB- Cia Ambiental do Estado de São Paulo Relatórios. Disponível em https://www.cetesb.sp.gov.br/agua-superficiais/35-publicacoes-/-relatorios.(2013) , Accessed in 20 July 2017.
15. H. R.A. Henrique, L. L. Turushima, F.R. Rocha, D.I.T. Fávaro. Avaliação da Concentração de Elementos Traço e Metais em Sedimento Superficial do Rio Tietê, Estado de São Paulo pela técnica de Ativação Neutrônica. *Proceedings of the International Nuclear Atlantic Conference* – INAC, São Paulo, 04 – 08 October, 2015.