SPATIAL VARIATION OF TRACE ELEMENTS IN THE TIETÊ RIVER BOTTOM SEDIMENTS (SÃO PAULO, BRAZIL): ENRICHMENT FACTORS AND ANTHROPOGENIC CONTRIBUTIONS

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ABSTRACT

The spatial variation of some trace elements (Ni, Cr, Zn, Cu, Sc, Co, Rb, Sr, Cs, Pb, Th and U) was studied in the bottom sediments of the Tietê river in São Paulo, Brazil. The main objective was to identify the enrichment factors and possible anthropic contributions to the observed high toxicity of these chemical elements in this drainage basin, which crosses the metropolitan area of São Paulo city with about 20 millions people and receives a large load of domestic and industrial wastes. The chemical analyses were performed after the chemical extraction procedure using alkaline fusion with Lithium tetraborate. An Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) and a Neutron Activation Analysis (NAA) were used for the analytical purposes. The enrichment factor was calculated by the relationship between the concentration of each trace element in the bottom sediment and the natural soil background in the drainage basin, weighted by the conservative Sc.

1. INTRODUCTION

Metallic trace elements mainly the heavy metals are present in different forms in the environment (atmosphere, water, soil, sediments and living organisms). These forms are controlled by the physic and chemical conditions of the environment and in terms of the main elements constituting the ecosystem. The toxicity of some heavy metals in the fluvial ecosystems is related not only to the observed high concentrations but also with their chemical form presents in the water/sediment interface and represent a high sanitary risk for the population and other living organisms by the consume of polluted water and/or food.

According to the literature the high concentrations observed in the main polluted fluvial ecosystems are from domestic and industrial wastes [1,2,3] but also from the agriculture [4,5]. This is the case of the Tietê river basin located in the São Paulo State, Brazil, which crosses the metropolitan area of São Paulo which is one of the most industrialized and largest urban centers of South America. The whole drainage basin comprises about 20 million people and receives a large load of industrial and mostly domestic wastes.

Hydrogeochemical studies in drainage basins are very important nowadays to understand the behavior of the metallic trace elements in fluvial ecosystems in order to identify and control the critical level of toxicity and to promote the right activities for the agricultural soil management and mainly for the domestic and industrial waste treatment.

The aim of this paper was to know the spatial variation of some trace elements (Ni, Cr, Zn, Cu, Sc, Co, Rb, Sr, Cs, Pb, Th and U) in the bottom sediments of the Tietê river in order to identify the enrichment factors and possible anthropic contributions to the observed high toxicity of these chemical elements in the drainage basin.

2. STUDY AREA

The Tietê River basin is a unit of the Paraná basin consisting of sub-basins including the Piracicaba, Atibaia, Jaguari, Sorocaba, and Corumbataí river basins, and extends over an area of about 32930 km^2 with regard to the Barra Bonita reservoir. It lies between 21^{o}30' and 24^{o}00' S and 46^{o}00' and 48^{o}00' W, being about 260 km west from the Atlantic Ocean coast (Fig. 1).

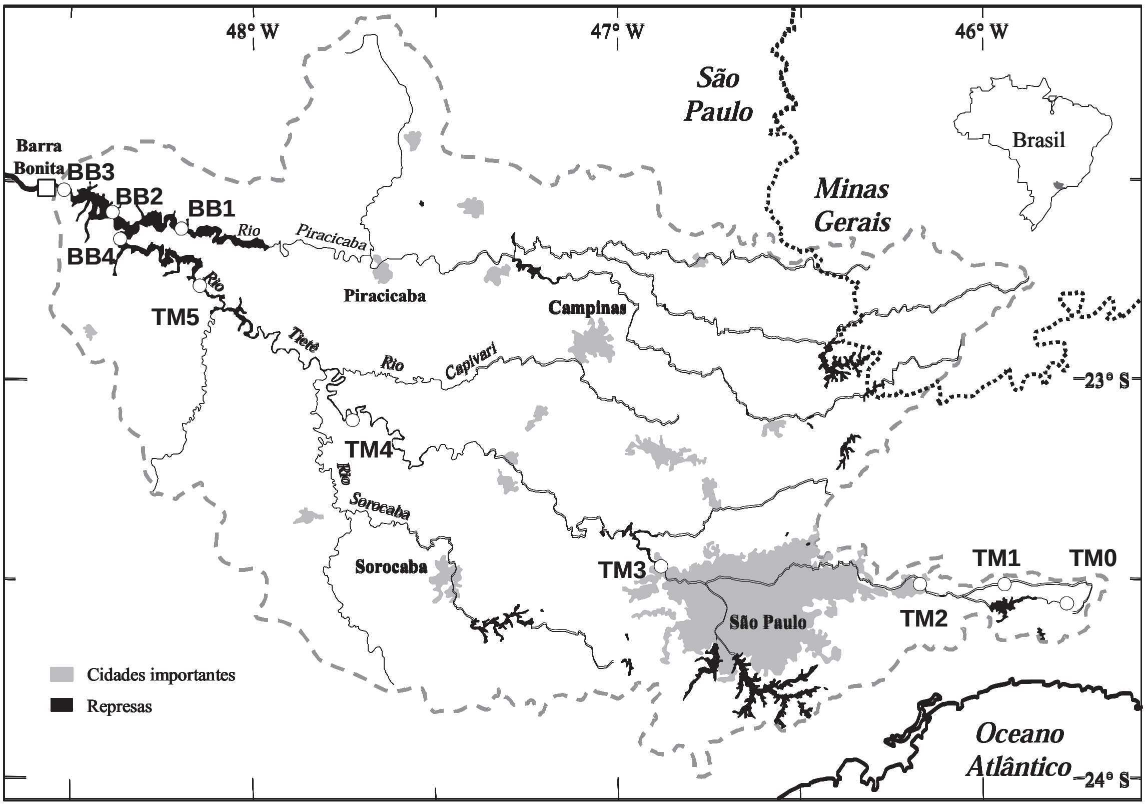

Figure 1. Location map of the Tietê River basin including the sampling stations along of river to the Barra Bonita reservoir.

The Tietê River crosses the metropolitan area of São Paulo which is one of the most industrialized and largest urban centers of South America. The basin under study comprises about 20 million people and receives a large load of industrial and mostly domestic wastes.

The main geological domain is formed by rocks of the crystalline plateau and sedimentary basin, represented basically by granites, gneisses, and basalts mainly in the middle part of the basin along the Depressão Periférica zone. Among the major types of soils that occur in the Tietê River basin, ultisols (55.4 %) and oxisols (28.3 %) cover about 84% of the entire basin area [6]. The Tietê River basin is characterized by a Cwa climate type according to Köppen's classification, with tropical rainy weather characterized by a wet summer. Soil use in the basin comprises an area of intense agricultural (sugarcane and citrus) and industrial occupation (paper, cellulose, textile products, and oil refinery).

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3. MATERIALS AND METHODS

The bottom sediments were sampled during January to May 2004 period, a long of the Tietê river, from the headwaters to the mouth using a classical grab sampler and storaged at 4 ^{o}C in plastic bags until the chemical analysis. The sediment was sieved (63µm) and for total trace element extraction the alkaline fusion procedure was used with lithium tetraborate and lithium metaborate (3:1) in a platinum crucible under 1000 ^{o}C during 30 minutes. The residual phase was taken in 100 mL HNO_3 2N. The chemical analyses were performed using an Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) and a Neutron Activation Analysis (NAA) for Ni, Cr, Zn, Cu, Sc, Co, Rb, Sr, Cs, Pb, Th and U in the bottom sediments of the Tietê river basin. For the natural background chemical signal, the main soil types of the basin were sampled at different depths ((0-10 cm, 40-50 cm e 90-100 cm) and the same procedure was followed.

Trace element concentrations of Tietê River bottom sediments (X) in the samples (S) were weighted by the conservative Sc of the samples (Y_S) and the natural background soil Sc (Y_R) in order to know the enrichment factor (EF) according to equation 1:

$$EF = (X_S / Y_S) / (X_R / Y_R) \qquad (1)$$

The enrichment factor values placed between 0.5 and 2.0 must be considered as part of the natural variability that occurs in the studied ecosystem [7]. EF values higher than 5 must be considered critical for possible disponibilities and for the incoming risks.

4. RESULTS AND DISCUSSION

It can be observed in Table 1 the main results of trace element concentrations in the bottom sediments of Tietê River basin.

Table 1. Trace element concentrations (mg/kg) for the Tietê River bottom sediments in the main sampling stations a long of the drainage basin, for the studied period.

Sample	Ni	Cr	Zn	Cu	Sc	Co	Rb	Sr	Sb	Cs	Pb	Th	U
TM1	43	60	88	41	16	8.72	146	119	0.075	7.67	46.1	163	42.0
TM1b													
TM2	31	114	266	53	19	7.16	92.0	115	0.136	6.06	47.5	37.1	11.5
TM3	92	183	648	200	19	15.9	95.2	134	0.269	5.02	76.5	26.8	7.60
TM4	60	133	360	79	16	13.7	121	78	0.196	6.06	44.3	24.7	6.78
TM5	67	127	381	97	14	11.9	91.8	84	0.126	5.10	36.0	21.4	6.28
BB1	41	96	210	45	20	19.3	85.8	62	0.335	6.81	28.0	15.4	3.57
BB2	70	94	163	39	12	14.3	38.1	43	0.233	5.76	17.9	22.3	5.59
BB3	51	262	514	55	14	14.3	56.6	69	0.152	2.90	18.5	30.0	7.81
BB4	80	132	266	46	15	19.4	69.1	42	0.259	5.88	30.3	15.6	5.29
BB5	237	111	126	109	32	26.0	49.5	56	0.159	5.37	31.2	16.8	3.95

The spatial distributions of the main trace elements in the bottom sediments of the Tietê River can be observed in Fig. 2 and 3.

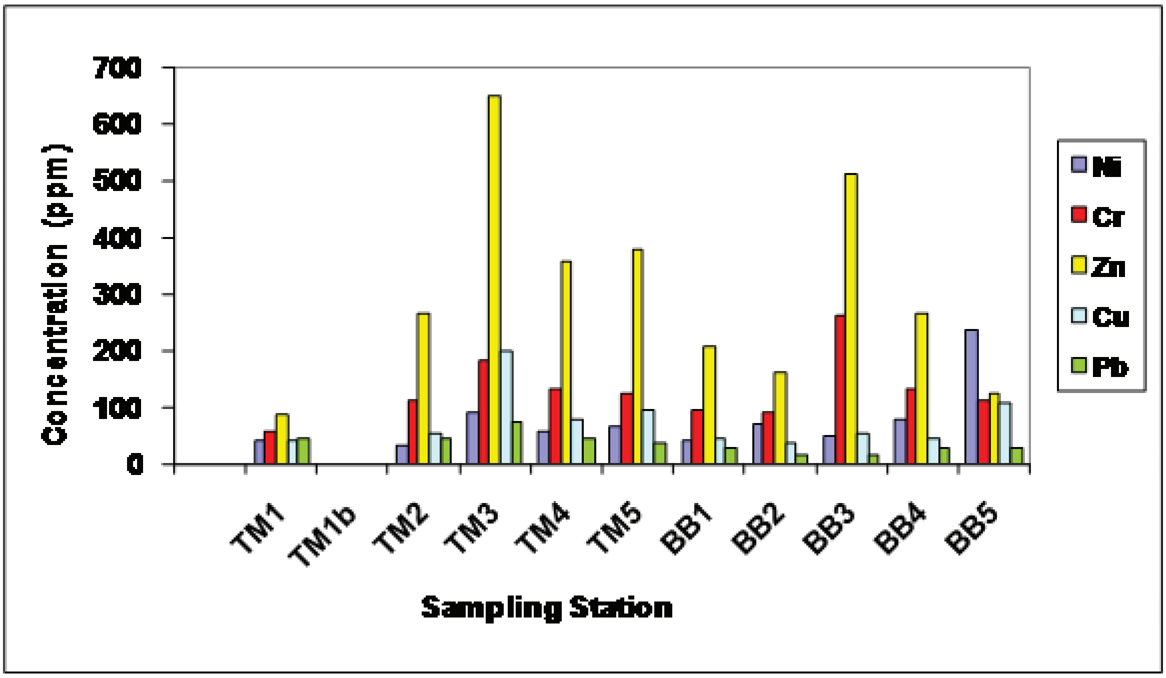

Figure 2. Concentration of Ni, Cr, Zn, Cu and Pb in the bottom sediments along of the Tietê River basin, for the studied period.

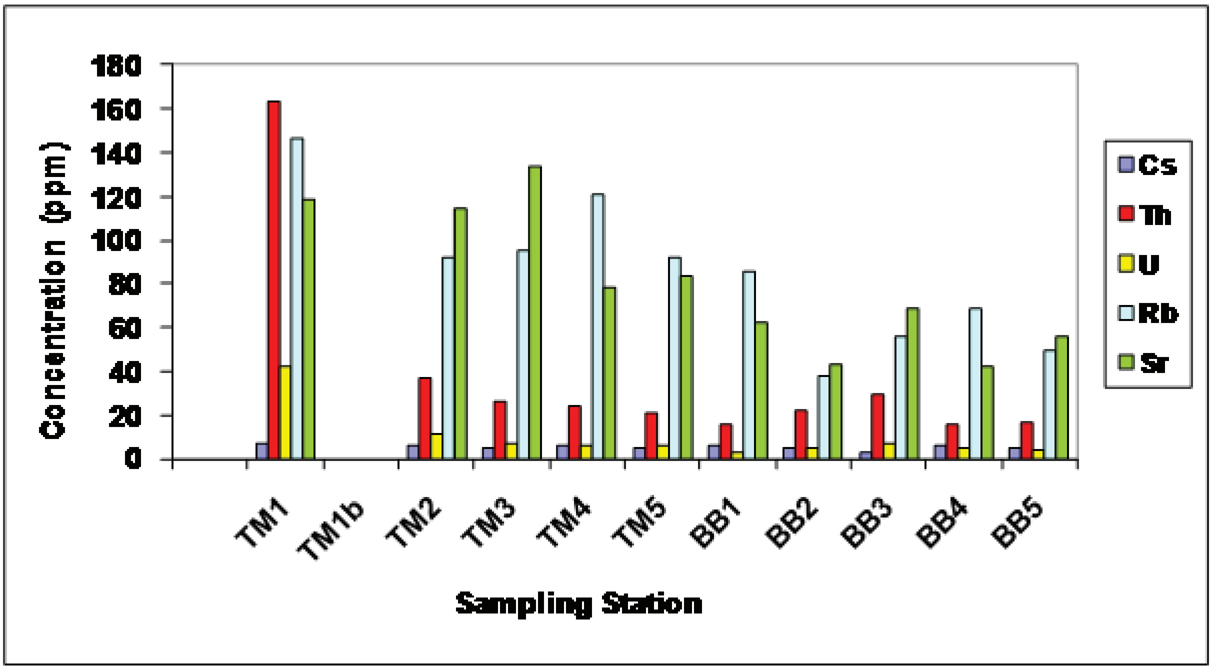

Figure 3. Concentration of Cs, Th, U, Rb and Sr in the bottom sediments along of the Tietê River basin, for the studied period.

According to the observed in Fig. 1, Ni, Cr, Zn, Cu and Pb concentrations in the bottom sediments of the Tietê River, have been increased from headwaters (TM1) to Santana do Parnaíba sampling station (TM3), with respectively 648 mg/kg of Zn and 183 mg/kg of Cr, decreasing after in direction to the Barra Bonita reservoir (BB2), with 163 and 94 mg/kg for Zn and Cr respectively. In downstream direction to the sampling station BB3, the Zn and Cr concentrations have been increased again with values of 514 and 262 mg/kg respectively. These values were higher than the observed in the literature for the same reservoir [8].

High Th and U concentrations were verified in the bottom sediments of the Tietê River near the headwater sampling station at Salesópolis (TM1), showing a natural occurence possibility. The concentrations obtained for Th (163 mg/kg) and U (42 mg/kg) were 10 times higher than the world mean value (14 and 3 mg/kg, respectively) [9]. For Cs, the observed concentration (7.7 mg/kg) was similar to the world mean value of 6.0 mg/kg. For Rb and Sr, the same behavior could be observed.

For all trace elements, it was possible to observe the same behavior of increase concentration near the TM3 and TM4 sampling stations (more populated zone of the basin) and consequently downstream decrease to the Barra Bonita reservoir. It seems to be evident the anthropogenic influences in this área, mainly with respect to the domestic and industrial effluent releasing without any previous treatment.

Table 2 shows the calculated enrichment factors for the main trace elements verified in the bottom sediments a long of the Tietê River basin.

Table 2. Enrichment factors (EF) for the main trace elements occurring in the bottom sediments of the Tietê River, weighted in terms of Sc, for the studied period.

EF	Ni	Cr	Zn	Cu	Sc	Co	Rb	Sr	Cs	Pb	Th	U
TM1	1.0	1.8	2.2	3.8	1.0	2.3	5.7	7.6	5.8	0.6	1.7	5.5
TM1b												
TM2	0.6	2.9	5.7	4.1	1.0	1.6	3.0	6.2	3.9	0.6	0.3	1.3
TM3	1.8	4.5	13.6	14.9	1.0	3.4	3.1	7.0	3.2	0.9	0.2	0.8
TM4	1.4	3.9	8.9	7.0	1.0	3.5	4.6	4.8	4.5	0.6	0.2	0.9
TM5	1.7	4.2	10.7	9.7	1.0	3.4	4.0	5.9	4.3	0.6	0.2	0.9
BB4	2.0	4.2	7.2	4.5	1.0	5.4	2.9	2.8	4.8	0.4	0.2	0.7
BB2	2.1	3.6	5.4	4.6	1.0	4.9	1.9	3.6	5.7	0.3	0.3	1.0
BB3	1.3	8.8	14.8	5.6	1.0	4.2	2.5	5.0	2.5	0.3	0.3	1.2
BB1	0.8	2.3	4.3	3.2	1.0	4.0	2.7	3.1	4.1	0.3	0.1	0.4
BB5	2.8	1.7	1.6	5.0	1.0	3.4	1.0	1.8	2.1	0.2	0.1	0.3
soil nat	50	39	45	13	18	4.4	29.5	18.2	1.5	83.0	112.4	8.8

The behavior of the enrichment factors a long of the Tietê river basin calculated for Ni, Cr, Zn, Cu and Pb verified in the bottom sediments, for the studied period, can be observed in Fig. 4. Considering the classification proposed by Sposito [7] it was used in this paper the enrichment factor 2 to separate the natural contribution from the anthropogenic influences.

High enrichment factors associated with Cu and Zn present in the bottom sediments were verified a long of the Tietê River basin. In the headwaters only Zn was higher than 2. After this point the EF values increase until Santana do Parnaíba station (TM3) that involves the urban zone of São Paulo, with values of 15 for both Cu and Zn showing contaminated bottom sediments. This critical situation remains a long of the basin including the Barra Bonita reservoir where Cr shows to be more important with an enrichment factor of 9.

The enrichment factors calculated for Ni and Pb seems to be from natural occurrence and remained constant a long of the basin.

Fig. 5 illustrate the behavior of the enrichment factors calculated a long of the Tietê river basin for Co, Rb, Sr, Cs, Th and U observed in the bottom sediments during the studied period.

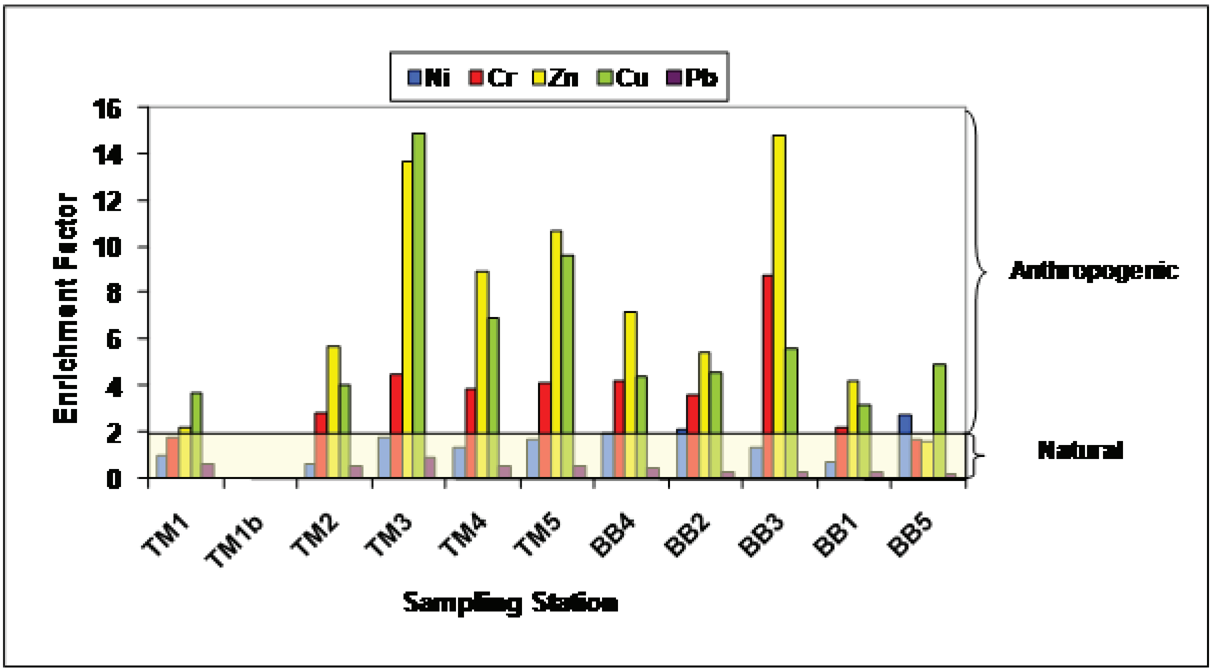

Figure 4. Enrichment factors (EF) calculated for Ni, Cr, Zn, Cu and Pb in the bottom sediments a long of the Tietê River basin during the studied period.

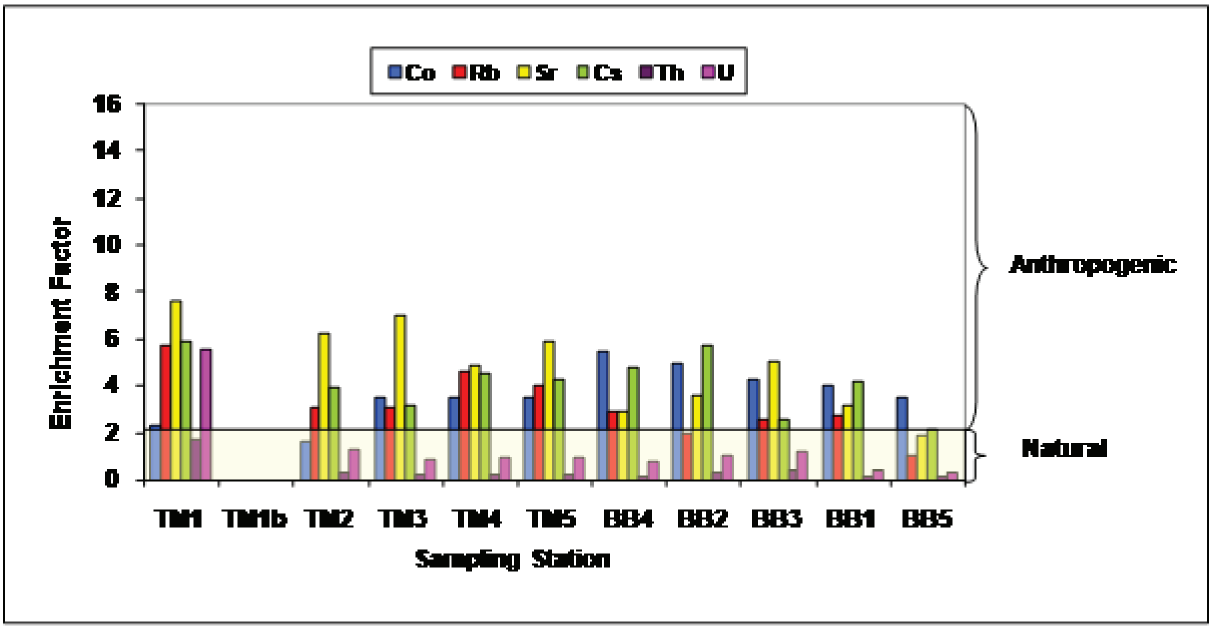

Figure 5. Enrichment factors (EF) calculated for Co, Rb, Sr, Cs, Th and U in the bottom sediments a long of the Tietê River basin during the studied period.

According to the observed for the headwater sampling station (TM1) at Salesópolis, Rb, Sr, Cs and U shows a significative enrichment factors in comparison to the natural background, but it seems to be localized. The distributions observed for Co and Th could be considered normal at this sampling point. The high value observed for U at headwater decrease a long of the basin and remains constant under natural occurrence. The Co distributions increase a long of the basin with an enrichment factor of 6 in the sampling station near of the Barra Bonita reservoir (BB4).

The behavior observed at TM1 sampling station was justified in terms of the organic soils that occur in this region with shows high concentration of this trace elements.

5. CONCLUSIONS

The results observed a long of the Tietê River basin for the distribution of trace elements in the bottom sediments shows to be preoccupant because it was possible to verify critical points in the basin where anthropogenic influences seems to be very important mainly around the great São Paulo with release of domestic and industrial effluents without previous treatment. The monitoring of the river waters and sediment loads must to be implanted for a better control of the water quality and effluent released and to improve the treatment plants a long of the river.

6. REFERENCES

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