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Characteristics of heavy metals and their evaluation in suspended sediments from Piracicaba river basin (São Paulo, Brazil)

Jefferson Mortatti¹ & Jean-Luc Probst²

Abstract Fluxes of the particulate heavy metals like chromium (Cr), copper (Cu), cobalt (Co), nickel (Ni), zinc (Zn) and lead (Pb) were determined along the Piracicaba River basin. Suspended sediments from the main channel and tributaries were sampled during January 2005 (high water period) and analyzed for total concentrations after extraction by alkaline fusion procedure. The average concentrations showed a significant increase pattern from upstream to downstream for Zn, Cr, Ni, Cu and Pb, except for Co, in which only a small variation was noted. The specific fluxes of Zn, Cr and Ni were slightly higher (79.9, 33.3 and 20 kg km⁻² yr⁻¹, respectively) in comparison to other industrialized regions in Asia, Europe, North and South America. Significant correlations between organic matter and Cr, Cu and Co, observed in the suspended sediments along the Piracicaba River basin, revealed that heavy metals were adsorbed or complexed by the organic matter, while Ni and Pb were significantly correlated with Fe oxide. The geo-accumulation index (I_{geo}) used to evaluate the pollution degree of the Piracicaba River sediments, revealed a medium to strong pollution for Zn in the entire basin and moderate pollution for Cr and Ni at downstream direction around an important area covered by sugar cane plantations and urban areas influenced by domestic sewage.

Keywords: riverine transport, heavy metal, Piracicaba River, suspended sediment, geo-accumulation index.

Resumo *Características dos metais pesados e sua avaliação nos sedimentos em suspensão da bacia de drenagem do rio Piracicaba (São Paulo, Brasil).* Foram determinados os transportes dos metais pesados cromo (Cr), cobre (Cu), cobalto (Co), níquel (Ni), zinco (Zn) e chumbo (Pb) nos sedimentos em suspensão ao longo da bacia do rio Piracicaba. Os sedimentos foram amostrados na calha principal dos rios estudados durante o período de cheia (Janeiro de 2005) e analisados após abertura total das amostras pelo processo da fusão alcalina. As concentrações médias obtidas ao longo da bacia do rio Piracicaba apresentaram um padrão de aumento significativo das nascentes até a foz para Zn, Cr, Ni, Cu e Pb, exceto para o Co, que pouco variou ao longo da bacia. Os transportes sólidos específicos de Zn, Cr e Ni nos sedimentos estudados foram relativamente altos (79,9, 33,3 e 20 kg km⁻² a⁻¹, respectivamente) em comparação com outras regiões industrializadas da Ásia, Europa, América do Norte e América do Sul. Correlações lineares significativas puderam ser observadas entre as concentrações da matéria orgânica e Cr, Cu e Co nos sedimentos em suspensão, evidenciando a complexação desses metais na fase orgânica, enquanto que Ni e Pb se mostraram correlacionados com a fração dos óxidos de Fe. O índice de geoacumulação (I_{geo}) usado para a avaliação das classes e do grau de poluição dos metais pesados presentes na carga sólida da bacia do rio Piracicaba evidenciou uma poluição de média à forte para Zn em toda a bacia e uma poluição moderada para Cr e Ni em direção à foz, no entorno da zona agriculturável com cana-de-açúcar e sob influencia urbana.

Palavras-chave: transporte fluvial, metais pesados, Rio Piracicaba, sedimentos, índice de geoacumulação.

INTRODUCTION Heavy metals are present in various environmental compartments (atmosphere, water, soil, sediments and living organisms) and these forms are controlled by physical and chemical conditions as well as by biological processes. The toxicity of some heavy metals in fluvial ecosystems is related not only to the observed high concentrations but also with the weathering process. In this way, several data focus on heavy metal concentrations in dissolved and particulate river loads (Elderfield *et al.* 1990; Goldstein & Jacobsen 1988; Sholkovitz 1992). However, river suspended matters, consist of two major phases: the residual and labile fractions. According to Leleyter & Probst (1999) met-

als from labile fractions are participating in liquid-solid adsorption-desorption, surface reaction and co-precipitation with different solid fractions such as clay minerals, carbonates, oxides and organic matter. Thus, the study in order to quantify the major trace elements partitioned between labile and residual fractions in fluvial sediments is very important for local and regional settings.

Fluvial transport estimates of particulate heavy metals along the drainage basin are usually based on metal concentrations measurements on the sediment loads. However, it provides inadequate information about the potential toxicity of these chemical species when the natural background of major heavy metals is

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not considered (Kersten & Forstner 1995). The degree of particulate heavy metal pollution can be evaluated in terms of the element geochemical background value in a drainage area, normally obtained in the headwater region without anthropogenic influences, according to Salomons & Forstner (1984) using an geo-accumulation index (Müller 1979; Yan *et al.* 2007; Audry *et al.* 2004; Simonovski *et al.* 2003).

This study aimed to estimate the fluvial transport of particulate heavy metals along the Piracicaba River basin (a medium-scale watershed in southeast Brazil under anthropogenic influences). Intensity quantification of the metal pollution occurring in the particulate load during a high water period, specifying characteristics, distributions and heavy metal sources of in the suspended sediments along the Piracicaba River basin, allowed an assessment of the factors controlling bioavailability of these chemical species in river waters and sediments.

STUDY AREA The Piracicaba River basin is located in a subtropical climate zone ranged from 45°51' to 48°24' W and a latitudinal extent ranging from 22°05' to 23°16' S draining an area of 12,400 km². The Piracicaba River is formed by the confluence of Atibaia and Jaguari rivers flowing from east to west receiving the Corumbataí River waters after cross the urban area of Piracicaba city (Fig. 1).

According to Krusche *et al.* (1997) the upper part to the center of the basin is occupied by degraded forest and pasture, while the other part is supplied by sugarcane culture. This region contains about 61 municipal districts with over 3,000,000 inhabitants where only 10% of the urban sewage is treated. The total load of the urban sewage generated along the basin was calculated to be 120 t B.O.D. (biochemical oxygen demand) per day (Favaro *et al.* 2004).

The eastern headwaters of Piracicaba River basin are relatively unpolluted, whereas the central and western sub-basins, which have higher population densities, are polluted mainly for having domestic effluents and industrial discharges into the river. In this catchment, two major rock types are outcropping: crystalline rock, in the upper part of the basin, and, carbonate sedimentary rock in the lower part of the basin. The weathering profiles are mainly represented by red lateritic soils that are composed of kaolinite and iron oxides.

METHODOLOGY The suspended sediments were sampled during January 2005 (flood period), along Piracicaba River basin, in the sampling stations: Atibaia River (P1A and P2A), Jaguari River (P1J and P2J), Piracicaba River (P1P and P2P) and Corumbataí River (P1C). The river water, at 2 m depth, was pumped into polyethylene bottles (30 L) and let to decant the particulate phase in the laboratory. After a calcination period at 1000 °C in order to eliminate organic matter, 100 mg of fine sediment (< 63µm), was carried out to alkaline fusion procedure with lithium tetraborate and lithium metaborate (2:1) in a platinum crucible under 1000 °C during 30 minutes. The residual phase was taken in 100 mL HNO₃ 2N.

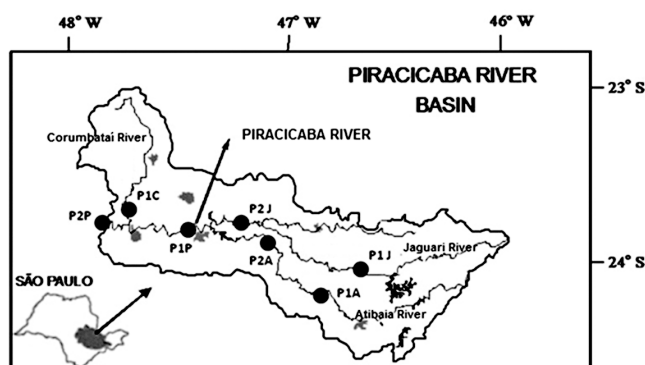


Figure 1 - Location of the Piracicaba River basin including the sampling stations along the river and main tributaries.

In order to determine the amount of fine suspended sediment, a single stage sampler was used at 2 m depth. About 300 mL of river water were filtered, dried at 60 °C and weighed again. The organic matter content was calculated after particulate organic carbon determination (1.72 POC) directly in tin capsule using an ANCA-SL mass spectrometer coupled with a gas chromatography.

All chemical analyses were performed using an Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES). Samples were analyzed in triplicate, including the reactive blank. The accuracy of the heavy metal analysis was performed using Soil-7 (IAEA reference standard). Percentages of recovery were as follows: Cr (92.3%), Cu (94.1%), Co (95.3%), Ni (97.4%), Zn (103%) and Pb (107.1%).

RESULTS AND DISCUSSION

Chemical Characteristics Suspended sediments from the upper part of the basin, mainly for Atibaia River (P1A) and Jaguari River (P1J), exhibited a combined silt and clay fractions of more than 75%, while at downstream sampling stations the suspended sediments were classified as sandy (> 60% sand).

The low SiO₂ concentrations verified in the upper part of the basin for P1A and P1J, 35.1 and 37.0 % respectively, with an increasing of Al₂O₃ (27.2 and 26.6%, respectively), are in agreement to the granulometric observations (Tab. 1). The suspended sediments for all sampling stations present in average, very low base cation content (CaO+MgO+Na₂O+K₂O < 4) and high chemical maturity index of about 10.4, calculated according to the equation (1) defined by Konta (1985) as follows:

$$\text{ChM} = \text{Al}_2\text{O}_3 (\%) / (\text{Na}_2\text{O} + \text{MgO} + \text{CaO}) (\%) \quad (2)$$

The elevated ChM index verified in the suspended sediment is associated to the high rock weathering process occurring in Piracicaba River basin. High concentrations of Fe and Mn oxides confirm the predominance of lateritic soils in the drainage basin.

Particulate Heavy Metal Transport Fine suspended sediment contents (FSS) along Piracicaba river basin were ranged from 35.4 and 19.2 mg L⁻¹ from upper basin (P1A and P1J) to 172.5 mg L⁻¹ near the mouth (P2P). This behavior was associated with the runoff increase along the basin, 47 to 376 m³ s⁻¹, giving a spatial variation in the particulate load of about 190 t km⁻² y⁻¹ (Tab. 2). The specific load carried out by the Piracicaba River at mouth (P2P) during the high water period (190 t km⁻² y⁻¹) could be classified as high transport according to the classification proposed by Meybeck *et al.* (2003) based on global variability of daily total suspended solids and their fluxes in rivers (73 to 365 t km⁻² y⁻¹). This behavior could be justified by agricultural practices associated to sugarcane plantations along the year over the basin, which increase the soil remobilization to streams.

The specific transports estimated for the particulate heavy metals were calculated considering the instantaneous discharge and the influence drainage area for each sampling point. The observed particulate heavy metal specific transports were relatively high at downstream direction, with important Zn, Cr, Ni and Cu contributions (79.86, 33.27, 19.96 and 18.63 kg km⁻² yr⁻¹, respectively).

At upper basin, high specific transport of Zn (6.65 kg km⁻² yr⁻¹) was observed mainly for Atibaia River (P1A). When compared with other world rivers, the observed specific transports for Zn, Cr, Ni and Cu were higher than Mississippi, St. Lawrence, Rhone and Madeira rivers (Guyot 1993; Zhang & Liu 2002; Radakovitch *et al.* 2008).

Correlation Analysis The correlation coefficient matrix between heavy metals in the suspended sediments of Piracicaba River basin is presented in table 3.

It can be observed that all particulate heavy metals were positively correlated with each other and most correlations were statistically significant (p<0.01) showing similar geochemical features, except for the relations between Co-Ni, Co-Zn and Pb-Zn.

Positive correlations between organic matter and Cr, Cu and Co were observed in the suspended sediments along Piracicaba River basin, which indicates that these metals are associated with the organic matter. According to Kabata-Pendias & Pendias (1991), Gaiero *et al.* (1997) and Leleyter & Probst (1999) the metals associated with the labile organic fraction could be degraded under oxidizing conditions on aquatic sedi-

Table 1 - Distribution of major elements in the suspended sediments along Piracicaba River basin during January 2005 (flood period).

Sampling site	OM	SiO ₂	Al ₂ O ₃	MgO	CaO	Fe ₂ O ₃	Mn ₃ O ₄	TiO ₂	Na ₂ O	K ₂ O	P ₂ O ₅
P1A	8.83	35.10	27.20	0.57	0.76	7.90	0.32	1.20	0.40	1.41	0.47
P2A	10.00	45.80	25.20	0.75	0.45	8.00	0.15	1.05	0.30	2.30	0.40
P1J	9.45	37.00	26.60	0.75	1.00	6.30	0.36	1.28	0.49	1.50	0.62
P2J	7.50	46.90	24.90	0.85	0.80	7.20	0.15	1.00	0.42	1.99	0.26
P1P	9.15	50.30	19.04	0.90	0.79	8.20	0.23	1.25	0.60	1.60	0.25
P1C	7.20	65.30	8.50	1.28	0.85	8.20	0.21	1.30	0.40	1.56	0.20
P2P	10.70	60.50	17.28	0.77	0.55	8.90	0.20	1.17	0.35	1.40	0.32

Table 2 - Content and transport of suspended sediments (FSS and Tss) and heavy metals, including organic matter concentration (OM) along Piracicaba River basin during January 2005 (high water period).

Sampling Site	Basin Area km ²	Runoff m ³ s ⁻¹	OM %	FSS mg L ⁻¹	T _{FSS} t km ² y ⁻¹	Cr		Cu		Co		Ni		Zn		Pb	
						μg g ⁻¹	kg km ² y ⁻¹	μg g ⁻¹	kg km ² y ⁻¹	μg g ⁻¹	kg km ² y ⁻¹	μg g ⁻¹	kg km ² y ⁻¹	μg g ⁻¹	kg km ² y ⁻¹	μg g ⁻¹	kg km ² y ⁻¹
P1A	1813	47	8.8	35.4	28.7	143 ± 8	4.1	70 ± 5	2.0	23 ± 1	0.7	62 ± 3	0.7	230 ± 9	6.7	35 ± 2	1.0
P2A	2621	68	10.0	125.6	102.6	165 ± 11	17.0	85 ± 5	8.7	30 ± 3	3.1	70 ± 4	7.2	250 ± 14	25.7	40 ± 3	4.1
P1J	1931	52	9.5	19.2	16.1	115 ± 9	1.9	50 ± 2	0.8	12 ± 1	0.2	41 ± 2	0.7	210 ± 15	3.4	14 ± 1	0.2
P2J	3380	161	7.5	108.6	163.0	120 ± 9	19.6	60 ± 4	9.8	12 ± 1	2.0	50 ± 1	8.2	240 ± 12	39.2	18 ± 2	2.9
P1P	8626	304	9.2	100.0	111.2	153 ± 6	11.1	95 ± 7	6.9	19 ± 2	1.4	90 ± 6	6.5	390 ± 18	28.2	45 ± 3	3.3
P1C	1627	70	7.2	99.3	134.6	120 ± 8	16.2	80 ± 5	10.8	20 ± 1	2.7	85 ± 6	11.5	180 ± 12	24.3	42 ± 4	5.7
P2P	10758	376	10.7	172.5	190.1	175 ± 15	33.3	98 ± 7	18.7	25 ± 1	4.8	105 ± 5	20.0	420 ± 15	79.9	50 ± 3	9.5

Table 3 - Correlation coefficient matrix between the major heavy metals in the suspended sediments along Piracicaba River basin during January 2005 (high water period).

Correlation coefficient	Cr	Cu	Co	Ni	Zn	Pb	Fe oxide	Organic matter
Cr	1							
Cu	0.843	1						
Co	0.840	0.704	1					
Ni	0.691	0.950	0.575	1				
Zn	0.756	0.737	0.279	0.702	1			
Pb	0.765	0.963	0.770	0.948	0.586	1		
Fe oxide	0.753	0.930	0.729	0.935	0.596	0.960	1	
Organic matter	0.977	0.879	0.875	0.782	0.693	0.855	0.861	1

ments, causing the release of soluble metals.

Cu, Ni and Pb were positively correlated with Fe oxide. The metals associated with this fraction could be mobilized under anoxic conditions on aquatic sediments (Tessier & Campbell 1987).

The results obtained by the inter-element correlations about common metal sources in suspended sediments along the Piracicaba River basin are in accordance with the previous results verified in the same river basin, using sequential extraction procedure of fine sediments. Considering the Pb, about 90% was linked with Fe oxide, while for Co only 40% shown to be related with this fraction. In terms of bioavailability, 40% of the Pb was in non-residual phase, while for Co this value was about 60%.

Intensity of Heavy Metal Pollution The geo-accumulation index was used to evaluate the degree of heavy metal pollution in the suspended sediments

along the Piracicaba River basin during the high water period. The geo-accumulation index (I_{geo}) introduced by Müller (1979) is shown as follows (equation 2):

$$I_{geo} = \log_2 [Me]_{sed} / 1.5 [Me]_{background} \quad (2)$$

where $[Me]_{sed}$ is the concentration of a given heavy metal and $[Me]_{background}$ is the geochemical background value of the element in the reference site.

The index I_{geo} is associated with a qualitative scale of pollution intensity and is divided into 7 degrees (0 to 6) which reflects the conditions ranging from zero pollution to very strong pollution.

The geochemical background values for the studied heavy metals were obtained from the riverbed sediments of Piracicaba River at the upper part of the basin by Falótico (2001) and Favaro *et al.* (2004). The mean background concentrations used to calculate the geo-accumulation index for Cr, Cu, Co, Ni, Zn and Pb were 40, 50, 7, 28, 50 and 30 $\mu\text{g g}^{-1}$, respectively.

According to the calculated I_{geo} , along of Piracicaba river basin and main tributaries (Tab. 4), there were no large differences for the sampling stations located at the upper part of the basin (P1A, Atibaia River and P1J, Jaguari River), corresponding to none pollution for Cu and Pb, none to medium pollution for Ni and medium pollution for Cr and Zn. Downstream, at the main channel of Piracicaba River (P2P) the pollution degree seems to be more serious, with medium to strong pollution for Zn and medium pollution for Cr, Co and Ni.

CONCLUSION The results of medium to strong heavy metal pollution along Piracicaba River basin, observed in terms of the high metal transport, correlation analysis and geo-accumulation index, could be severely detrimental to aquatic biota with the sediment remobilization occurrences during flood events, oxidizing particulate heavy metals from the labile fraction of the sediment. Other activities related to the agricultural practices could increase the mechanical erosion along the basin elevating the transport of the suspended sediment in the basin. The domestic untreated sewage released to the riv-

Table 4 - Geo-accumulation index (I_{geo}) and pollution degree along Piracicaba River basin during January 2005 (flood period).

Sampling site	Cr	Cu	Co	Ni	Zn	Pb	I_{geo}	Degree of pollution
P1A	1-2	<0	1-2	0-1	1-2	<0	<0	none
P2A	1-2	0-1	1-2	0-1	1-2	<0	>0-1	none to medium
P1J	0-1	<0	0-1	<0	1-2	<0	>1-2	medium
P2J	1-2	<0	0-1	0-1	1-2	<0	>2-3	medium to strong
P1P	1-2	0-1	0-1	1-2	2-3	0-1	>3-4	strong
P1C	1-2	0-1	0-1	1-2	0-1	<0	>4-5	strong to very strong
P2P	1-2	0-1	1-2	1-2	2-3	0-1	>5	very strong

er water increases the degraded organic matter causing anoxic conditions in depth, changing the oxy-reduction conditions in the sediment labile fractions. The observed severe heavy metal pollution indicates that the studied catchment is affected by anthropogenic activities, which contribute to the input of particulate metals increasing concentrations above background levels.

The results of this scientific investigation can be helpful to understand the behavior of the heavy metals and their relationships with the labile fraction

of the fluvial sediments in order to control possible toxicity occurrences.

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