ORIGINAL ARTICLE

Changes in copper speciation and geochemical fate in freshwaters following sewage discharges

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Abstract The main factors determining the geochemical fate of copper in urban freshwaters affected by raw sewage discharges were investigated in this work. Water samples from the Iraí and Iguaçu rivers were collected monthly during a 1-year period at two points located upstream and downstream from the city of Curitiba, in Brazil. Results revealed that raw sewage discharges from the heavily urbanized area caused an enhancement of humic-coated suspended solids in the Iguaçu River. In these waters copper is predominantly associated with the humic-coated particles whereas in the Iraí River copper was found primarily in the aqueous phase. The transfer of copper from the aqueous to the solid phase changed its physical speciation along the watercourse. Thus, aspects related to the overall transport of trace metals in watercourses become an important issue to be considered in further studies concerning the effect of sewage discharges on the geochemical speciation and fate of trace metals in urban rivers.

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1. Introduction

The speciation of trace metals plays a critical role in their distribution and behavior in natural aquatic environments (Luoma, 1983). It is an important issue to consider when assessing possible biological and environmental impact in terms of metal bioavailability, fate, and water quality criteria (Allen and Hansen, 1996). These aspects are recognized to be ruled by the physicochemical form in which trace metals are present in the sample (Templeton *et al.* 2000).

The central role of speciation in dictating the fate and effects of trace metals in natural waters has been well established in the past few decades (Florence, 1982; Florence *et al.*, 1992; Campbell, 1995; Łobiński, 1998). Results have shown that physical speciation, i. e. the distribution of an analyte according to physical properties such as size or solubility controls the overall physical transport of trace metals, while the chemical speciation of dissolved metals, i. e. the distribution of an element amongst defined chemical species in a system, governs its effects on aquatic biota. Therefore, the most important process controlling trace metal effects and fate in aquatic systems is the partitioning between the solid and the aqueous phase (Kunz and Jardim, 2000). When this competition favors the aqueous phase, metal bioavailability and toxic potential tend to increase. When adsorption predominates, particulate matter acts as the major carrier of trace metals, thus reducing metal toxicity on a short-term basis and changing the ultimate fate of these species.

Trace metal contamination of aquatic systems is a critical concern due to the potential detrimental effects both directly within food chains of impacted systems, as well as linked to public health (Warren and Haak, 2001). Furthermore, in urban agglomerations there is a permanent concern regarding trace metal loads and speciation (Goonetilleke *et al.*, 2005).

The effect of heavy metals on the biota in urban catchments has been considered worldwide as a very important non-point source pollution issue (Cole *et al.*, 1984; Tsihrintzis and Hamid, 1997; D'Arcy and Frost, 2001, Yuan *et al.*, 2001). However, many of these studies were conducted in developed countries under mostly temperate conditions. Much less is known about the relationship between watercourse conditions and land use in tropical areas of developing countries.

In the developing countries, it is estimated that more than 90 percent of sewage has been directly discharged without treatment of any kind into rivers, lakes, and coastal waters that are also frequently sources of drinking water (UNEP, 2002). According to the latest National Survey on Basic Sanitation (IBGE, 2002), 82 percent of Brazilian cities discharge their raw sewage into natural aquatic systems. In the city of Curitiba, where this work was carried out, approximately 150 000 m^3 of raw sewage are released daily in rivers located in the urban area. Raw sewage laced with heavy metals remains the principal contributor to the deterioration of aquatic systems in developing countries. Consequently, trace metal concentration and speciation are also affected by changes in water quality due to sewage inputs (Williams *et al.*, 2001). Variations in some physico-chemical parameters such as pH, dissolved oxygen, organic matter and suspended solids are able to modify trace metal speciation in urban aquatic systems (Cabaniss and Shumann, 1988; Alonso *et al.*, 2004). The importance of raw sewage discharges in providing a pool of organic binding sites was evaluated by Kunz and Jardim (2000). These authors pointed out that particulate organic matter may control the fate of copper in receiving waters by changing its speciation and, consequently, its effect to the biota.

While raw sewage discharges from urban areas remain the most important source of pollution in developing countries, little is known on how the discharge of these effluents could affect trace metal partitioning and speciation in receiving waters. This lack of information, along with the key role played by trace metals, led us to evaluate the main factors governing the geochemical
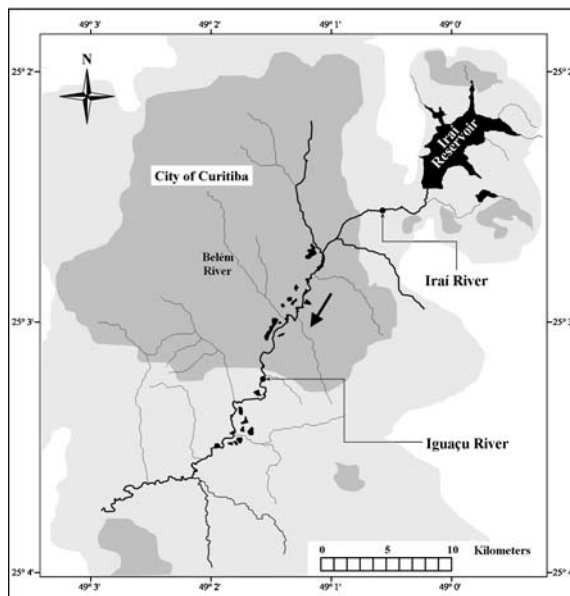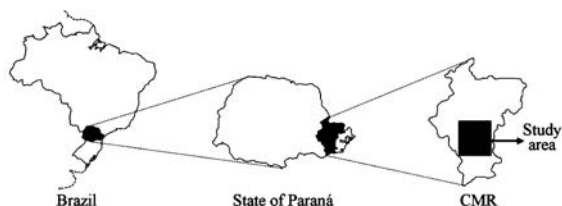

Fig. 1 Location of the sampling sites in the Metropolitan Region of Curitiba, Brazil. The light gray region on the map is a sparsely populated area and the darker gray regions represents the heavily urbanized areas. The arrow indicates direction of the water flow.

speciation of copper in rivers located in the Metropolitan Region of Curitiba (Brazil), in order to assess the influence of raw sewage discharges on the behavior and fate of copper.

2. Materials and Methods

2.1. Study sites

Two sampling sites were selected to assess copper behavior under different ranges of geochemical regimes and levels of watershed occupation. The sites were located in the Metropolitan Region of Curitiba (MRC), in the south of Brazil as shown in Fig. 1. The MRC is located in the State of Paraná and has an average air temperature ranging from 13 to 23 °C and annual rainfall of 1400 mm (Simepar, 2002). About 2.5 million inhabitants live in the MRC, while most of its urban area

is developed in the Upper Iguaçu River Basin which has a total basin area of 1000 km^2. There are a number of tributaries with basin areas of about 100 km^2 and the highest urban concentration is in the Belém River Basin (Tucci, 2002).

The first sampling site was located in the Iraí River (25°26′40″S, 49°08′34″W, 890 m elevation). This site is situated in a sparsely populated area upstream from the city of Curitiba. It has a substantially lower human impact and is considered a less polluted site where water quality is generally good, except for small discharges and some limited diffuse source pollution (Sodré *et al*., 2005). The second sampling site was placed in the Iguaçu River (25°32′16″S, 49°13′32″W, 865 m elevation), downstream from the City of Curitiba. At this sampling location, the Iguaçu River receives water from the Belém River and effluents drained from the heavily urbanized area which has a population of approximately one million people. Consequently, this river is a polluted anoxic body of water receiving discharges from sewage treatment works (STW) and raw sewage inputs from combined and sanitary sewers as well as from individual residences along the stream (Sodré *et al*., 2005). This transition from a less polluted upstream river to a heavily polluted system downstream from the city of Curitiba provides a suitable outlook to assess the influence of urbanization processes, such as raw sewage discharges, on copper behavior and fate in this watershed.

2.2. Sampling and sample preparation

Freshwater samples from both rivers were collected monthly from March 2002 to February 2003 using a pre-cleaned plastic bailer. The samples were transferred to acid-washed polyethylene bottles and kept on ice until analysis. Just after transport to the laboratory an aliquot of the sample was acidified to pH 2 with suprapure HNO$_3$. Another aliquot was filtered through 0.45 μm pore size membranes (Schleicher & Schuell) and collected into pre-cleaned polyethylene bottles. Prior to analyses all labware and sampling bottles, as well as the filtration devices were carefully washed, soaked in a 5% detergent bath, rinsed with distilled water, and soaked in 1 mol L^{-1} HNO$_3$ solution before they were thoroughly rinsed with Milli-Q type water (Milipore). Deionized water was also used in all experiments, for all dilutions and blanks. To avoid trace metal contaminations, all procedures were performed using clean techniques described elsewhere (U.S.EPA, 1996).

2.3. Copper speciation

Copper speciation analyses were performed by differential pulse anodic stripping voltammetry (DPASV) and involved the determination of total recoverable copper (TRCu), total dissolved copper (TDCu), and labile Cu concentrations. TRCu determinations were carried out in acidified unfiltered samples (pH 2) after a microwave-assisted photochemical digestion step (Sodré *et al*., 2004). TDCu and labile Cu concentrations were assessed by a method based on the medium exchange principle using ethylenediamine (EN) as competing ligand (Scarano *et al*., 1990, 1992).

The use of medium exchange in DPASV was advocated as a means of reducing interference in the stripping step (Batley *et al*., 2004). In addition, EN eliminates interference in samples containing up to 30 mg L^{-1} of organic matter (Labuda *et al*., 1994), which was expected in waters affected by raw sewage discharges (Stumm and Morgan, 1996; Vega *et al*., 1998). The competing ligand equilibrium between EN and natural strong Cu-binding ligands is established by adding EN to the sample at an appropriate concentration. When high concentrations of EN are added prior to electrolysis, EN competes for copper with the natural ligands and ligand-exchangeable copper is obtained. In order to evaluate the efficacy of EN as a competing ligand we prepared a set of samples containing up to 20 mg L^{-1} of humic acid (Aldrich) and Cu concentrations ranging between 5.00 and 10.0 mg L^{-1}. In these samples the EN-exchangeable fraction at pH 8 was identical with the acid-exchangeable fraction at pH 2. In the presence of EN, the stripping reaction becomes Cu(Hg) $\rightarrow$ Cu(EN)$_2^{2+}$ + 2e$^-$ and the stripping peak is doubled in sensitivity with the two-electron oxidation in the presence of EN (Scarano *et al*., 1991). Because the Cu(EN)$_2^{2+}$ complex is electroactive, it can be detected by DPASV during the titration of the sample with Cu, in an approach analogous to adsorptive cathodic stripping voltammetry (Bruland *et al*., 2000). At low concentrations of EN the Cu peak current reflects the proportion of labile species in the sample by the electro-deposition of the ionic and labile Cu complexes in the untreated sample at natural pH, followed by the stripping in a more suitable EN electrolyte. Medium exchange was achieved by adding a suitable amount

of EN a few seconds before the end of the deposition period (Scarano *et al.*, 1990).

For TDCu and labile Cu determinations, filtered samples at natural pH were split into two sub-samples. The first sub-sample was acidified, digested, treated with a solution of double distilled EN (Sigma) to a final ligand concentration of 1.0 mmol L^{-1}, and then allowed to equilibrate for a 12 h period. This equilibration period is sufficient for reaching a maximum *ip* value which remains constant for the following 48 h (Scarano *et al.*, 1990). DPASV of this sub-sample provided the ip^0 related to the EN-exchangeable copper. This peak was finally quantified by standard additions to produce the TDCu concentration in the sample. The second sub-sample, not treated with EN, was electrolyzed under the same voltammetric parameters used for TDCu determinations, but EN was added no more than 15 s prior to the stripping step. The current peak ip^* was a measure of the labile Cu in the sample. The ratio ip^*/ip^0 was used to quantify the concentration of labile Cu in the sample.

All voltammetric determinations were carried out in an EG&G Princeton Applied Research 394 Electrochemical Trace Analyzer coupled with an EG&G PAR 303A Static Mercury Drop Electrode in the HMDE mode. The instrument settings were as follows: 10 min purge with purified N_2, 15 min electro-deposition at -0.6 V vs. Ag/AgCl followed by the anodic scan from -0.6 to 0 V at 4 mV s^{-1}, with modulation amplitude of 50 mV. A constant stirring rate was maintained during the determinations.

2.4. Analytical methods

A set of aquatic parameters was determined during the sampling period. pH was measured as soon as the samples were brought to the laboratory. Dissolved chloride, total alkalinity, and suspended solids (SS) were determined by methods 4500B, 2320B, and 2540D described elsewhere (APHA, 1995). Dissolved organic carbon (DOC) determinations (method SM5310B) were performed on a Shimadzu TOC 5000 Analyzer.

To assess copper partitioning under controlled conditions, sediment samples from both rivers were collected at the same locations as water samples using a PVC cylindrical corer (50 cm tube; 10 cm inner diameter) and polystyrene bags. In the laboratory, the first 3 cm of the sediment cores were air-dried at room temperature and then passed through a 390 mesh nylon sieve to produce a fine-sized solid fraction. Simulated suspensions were prepared in aliquots of pre-filtered water collected in each river. Sediment was added to 100 mL samples of the filtered water to achieve solid concentrations of 5.00, 10.0, 25.0, 50.0 and 100 mg L^{-1} for each of the two river samples. Suspensions were shaken for 24 h and then fortified with copper to reach a metal concentration of 10 μg L^{-1}. The pH of the suspensions was adjusted to 6.8 and the samples were shaken for another day. Determinations of total recoverable and dissolved copper were performed via DPASV after the filtration and digestion steps.

Suspended solids from bulk samples of both rivers were separated by centrifugation at 2000 rpm for 2 h. The resulting pellet was air-dried at room temperature and passed trough a 390 mesh nylon sieve. Both sediment and SS samples were characterized by electron spin resonance (ESR). ESR spectra were recorded at 77 K on a Bruker ESP 300E spectrometer using Wilmad suprasil tubes with the X-band frequencies of about 9.5 GHz. The observed ESR signals were first-derivative and also signed by their spectroscopic splitting factors (g-values) by means of $\Delta E = g\beta H$, where ΔE is the net absorption energy, *g* represents a parameter describing the interaction of the paramagnetic centre with the external magnetic field, β is the Bohr magneton, and *H* is the intensity of the resonance magnetic field. The magnetic field was calibrated using DPPH (α-diphenyl-β-picryl hidrazyl), which has a *g* factor of 2.0036 ± 0.0003.

3. Results

3.1. Aquatic parameters

The results of the aquatic parameters for samples of both Iraí and Iguaçu rivers are displayed in Fig. 2. In general, for all parameters higher values were observed for the Iguaçu River samples. The higher oscillation in pH levels for the Iraí River is, possibly, a result of the lower alkalinity, which provides buffer capacity to natural waters. The higher concentrations of dissolved chloride in Iguaçu River samples can be used as a tracer to recognize raw sewage discharges in receiving waters, especially in tropical and subtropical regions. In these regions chloride can occur as a consequence of its presence in human urine (Guyton, 1986). DOC
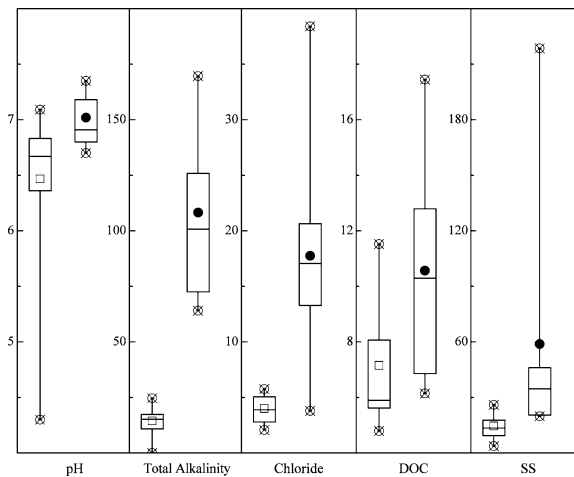
Fig. 2 Aquatic parameters determined in samples from both rivers during a 1-year sampling period. Open squares represent the arithmetic mean for the Iraí River samples; Full circles represent the arithmetic mean for the Iguaçu River samples. The large box represents the 25th percentile, median, and 75th percentile; error bars indicate the 5th and 95th percentiles; X-symbols represent the 1st and 99th percentiles; open circles symbolize the minimum and maximum values. Chloride, Dissolved organic carbon, and suspended solids, are given in mg L^{-1}; total alkalinity is given in mg CaCO$_3$ L^{-1}.

concentrations were systematically greater in Iguaçu River waters during the whole sampling period. A pronounced difference is observed for SS concentrations from both river samples. Despite the fact that SS levels were also systematically higher in Iguaçu river samples during the sampling period, extremely high SS levels were observed in two months when sampling took place immediately after a long rainy period. Thus, an increase in the water flow affected the particles' residence time in the water column, which also increased. Detailed considerations of the parameters described here can be found elsewhere (Sodré *et al.*, 2005).

3.2. ESR measurements

According the Curie law, maximum sensitivity for paramagnetic species will be attained at the lowest possible sample temperature (Senesi, 1990). Therefore, spectra were often recorded at 77 K using liquid nitrogen. For the ESR measurements the solid powders were packed into quartz ESR tubes with an inside diameter of a few millimeters.

Fig. 3 displays the first derivative mode EPR spectra over a magnetic field range of 5000 Gauss obtained for the sediment samples as well as from typical SS samples from both rivers. Both Iraí River spectra from SS and sediment samples showed pronounced six-line resonance, centered on 3500 G, resulting from Mn^{2+} ions

within the solid mineral matrix. It is also possible to observe a resonance line at 1500 G probably related to Fe^{3+} ions localized in dilute domains which are incorporated as impurities within minerals such as gibbsite, kaolinite or quartz (Crook *et al.*, 2002). Both spectra from Iguaçu River solids presented a large and intense resonance line at 3300 G related to a more symmetrical Fe^{3+} center in concentrated domains. In general, it is possible to observe that there is a similarity between SS and sediment spectra obtained from each river. The only exception was the presence of a single-line with a g-value of 2.0038 in the Iguaçu River suspended solids spectrum as can be seen detailed in Fig. 3.

3.3. Copper speciation

During the sampling period TRCu, TDCu and labile Cu concentrations were systematically higher in Iguaçu River samples with average values of 9.17, 3.66, and 0.62 μg L^{-1}, respectively. Average copper levels for the Iraí River samples were 4.10, 2.19, and 0.47 μg L^{-1}, respectively. A ternary plot for Cu speciation in both rivers is shown in Fig. 4. The particulate copper was obtained by the difference between TRCu and TDCu concentrations, and dissolved complexed copper means the difference between TDCu and labile Cu levels.

A significant difference can be noticed when the two aquatic environments are compared. On a relative
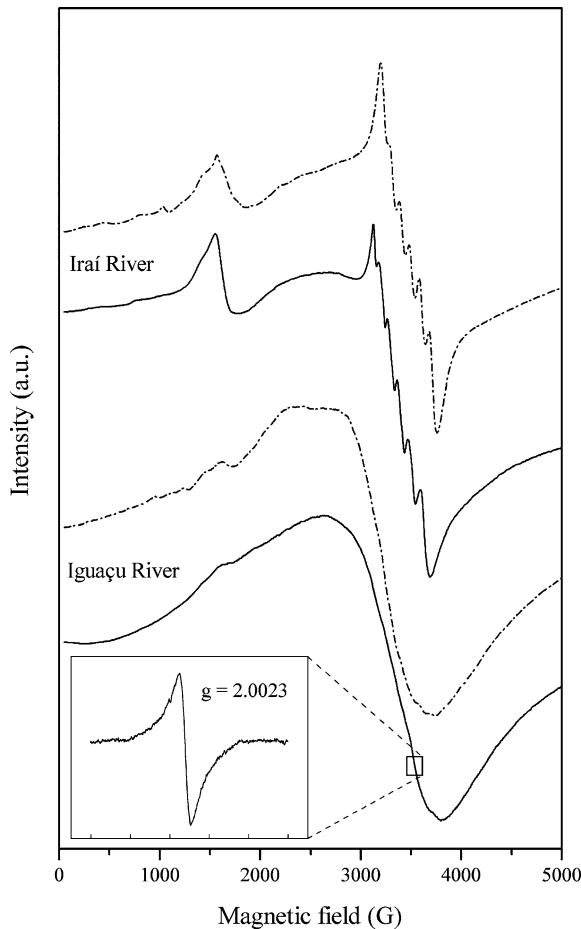
Fig. 3 Electro spin resonance spectra for suspended solids samples from Iraí and Iguaçu rivers (full lines) as well as for sediments collected in both rivers (dashed lines).

basis, higher percentages of copper were found in the particulate fraction in Iguaçu River samples, whereas in the Iraí River copper was preferably complexed in the aqueous phase. This copper distribution pattern was observed for more than 90% of the samples collected during the whole sampling period. For both river samples copper in the labile form corresponded to about 10 percent of the TRCu concentration. However, in some cases, the labile concentration determined in the Iraí River reached 20–30% of the total copper content in the sample.

3.4. Copper partitioning from Iguaçu and Iraí rivers and from simulated samples

Partition coefficients (K_D) were computed for both river water samples as well for the simulated samples by the

quotient between the copper concentration in the particulate matter in mg kg^{-1} and the TDCu concentration in μg L^{-1}. Therefore, the unit for K_D is L kg^{-1}. Fig. 5 shows Log K_D values as a function of total suspended solids concentrations. For both river samples, represented by open symbols, Log K_D values were similar to those reported elsewhere (Shi *et al.*, 1998; Benoit and Rozan, 1999; Lu and Allen, 2001) ranging from 4.4 to 5.0, excluding values of about 5.3 determined in two samples from Iraí River.

It is possible to observe that there is a decrease in K_D values as the SS concentrations increase for both rivers. For both simulated samples from Iraí and Iguaçu rivers, there is an exponential decrease in the K_D values as the SS concentration increases. Simulated Iraí samples presented systematically higher K_D values than simulated Iguaçu samples for all SS concentrations tested. As a matter of fact, only simulated and real samples from the Iraí presented similarities between each other concerning the K_D evaluation. For SS concentrations up to 30 mg L^{-1}, the values for Log K_D obtained in simulated samples are scattered over the same range as values corresponding to river samples. In contrast, Log K_D values from simulated Iguaçu samples are lower than those obtained for the river samples over the entire SS concentration range.
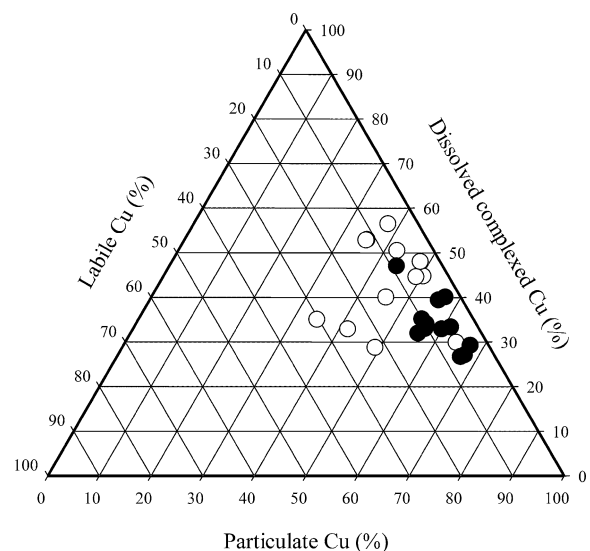

Fig. 4 Relative concentrations for the particulate dissolved complexed and labile copper for the Iguaçu River (solid circles) and Iraí River (open circles) samples during a 1-year period.
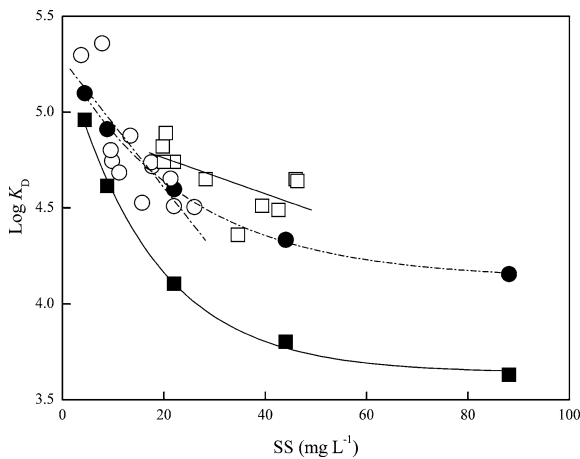
Fig. 5 Copper partition coefficients (K_D/L kg^{-1}) as a function of total suspended solids for samples collected in Iguaçu (open squares) and Iraí (open circles) rivers as well as for simulated samples from Iguaçu (solid squares) and Iraí (solid circles). Dashed lines represent tendency correlations for the Iraí samples and solid lines for Iguaçu samples.

4. Discussion

A critical evaluation of all aquatic parameters determined in both rivers revealed a strong influence of the urbanization process mainly on the Iguaçu River water quality. In this river, total alkalinity, Suspended solids, dissolved chloride, and DOC exhibited not only greater values, but also greater oscillations reflecting the intensity of human activities (Perona *et al.*, 1999). As a matter of fact, in an earlier study (Sodré *et al.*, 2005) it was demonstrated that raw sewage discharges are the main source of pollution in the MRC and the most important aspect for the variations of the water characteristics in the Iguaçu River. In contrast, the Iraí River is certainly a less polluted environment.

The changes in water chemistry due to raw sewage discharges also affected the composition of the SS in the Iguaçu River. The sewage discharges in rivers from the city of Curitiba contributed to the enrichment of a pool of organic matter that may alter the characteristics of the water constituents at the sites downstream. During the entire sampling period, ESR spectra (Fig. 3) from Iguaçu river suspended solids revealed a well-defined signal in $g = 2,0038$. This resonance line reflects the presence of organic free radicals from semiquinone moieties possibly conjugated to various extended aromatic ring systems in fulvic acids structures (Senesi, 1990). Thus, the g-value measured in the Iguaçu River

SS indicates that the particulate matter from this river was coated with humic substances. Stumm (1992) and Zachara *et al.* (1994) reported that humic substances with high molecular mass are more readily adsorbed at the existing mineral surface in freshwaters than less aromatic and low-weight organic matter. Au *et al.* (1999) verified that the charge of a hematite surface was deeply affected by the adsorption of humic acid (HA). The hematite-HA surface had an overall negative charge at all pH values examined indicating that the adsorption of the humic acid on the hematite caused an exchange on the surface charge of the mineral at pH below 8.1 (pH$_{zpc}$ for hematite), and enhanced the negative charge on the surface at higher pH values. Furthermore, enhanced negative charges on the mineral surface have important implications for metal sorption to humic-coated minerals in natural aquatic systems (Warren and Haack, 2001).

Speciation analyses (Fig. 4) showed that in the Iguaçu River copper was preferably found in the solid phase, while in the Iraí River this metal was mostly in the aqueous phase. We believe that the organic matter arising in Iguaçu River from raw sewage discharges causes an enhancement of humic-coated particulate matter in this river which may be responsible for the conveyance of copper from the aqueous to the solid phase, thus changing the metal speciation in the watercourse. Peart and Walling (1986) verified that the enrichment of the particles with organic matter in the Devon River Basin, England, was responsible for the removal of various elements from the water column.

The distribution of copper between the solid and aqueous phases (Fig. 5) shows that K_D decreases as the SS concentrations increase for all samples. Although K_D is a conditional constant there is no reason to expect it to vary as a function of partitioning phases, solid and solution. However, this inconsistency may be explained by two major aspects. The first is the change in the adsorption surface area of the particles per mass of suspended solids causing the enrichment of metal in fine-sized solids at low SS concentrations and, at the same time, the decrease of the particulate metal content at high SS levels. The second aspect is caused by the particle concentration effect (Benoit *et al.*, 1994; Martin *et al.*, 1995) which may be attributed to the occurrence of colloids in the aqueous phase due to the sample filtration through 0.45 μm pore size membranes.

The partition for the simulated samples of Iraí River shows a strong connection with the original distribution of copper for this river mostly due to the similarities between the sediment and the suspended solids (Fig. 3). In contrast, results for copper partitioning in the Iguaçu River samples reveal a strong difference between simulated and real samples. Higher K_D values were determined in the river samples indicating that copper was preferably in the solid phase in the original Iguaçu River solids, more so than in the simulated samples. This dissimilarity occurs due to characteristics of the solids from both samples. ESR spectra revealed that organic free radicals were found only in the Iguaçu River samples and not in the sediment samples collected in this river. Thus, the absence of humic-coated particles in the simulated samples produced lower K_D values for copper in all SS concentrations evaluated (Fig. 5) This result corroborates the assumption that humic-enriched solids were the most important aspect in dictating the speciation of copper. Shi *et al.* (1998) demonstrated that copper adsorption by the solids is strongly correlated to the particulate organic matter content. Grassi *et al.* (2000) confirmed that copper adsorption tends to increase as the concentration of particulate organic carbon becomes greater.

The changes in copper speciation in rivers located in the MRC, throughout the city of Curitiba, will also affect the ultimate fate of copper in this urban catchment. While no reliable differences were observed in the labile Cu levels, on a relative basis (Fig. 4), the most important aspect in controlling copper behavior in the watershed is the physical speciation. Thus, aspects related to the overall transport of copper in the streams become an important issue to consider in further studies concerning the effect of sewage discharges on trace metals speciation in freshwaters.

5. Conclusion

The results show a strong influence of the urbanization process on copper dynamics at the Upper Iguaçu River Basin. While the Iraí River is found to be a less affected water body, the Iguaçu River presents a high level of pollution, especially associated with the discharge of raw sewage from the city of Curitiba. Iguaçu River waters always presented higher levels of suspended solids, dissolved organic carbon, chlorides, and total alkalinity. Moreover, the qualitative characterization of the particulate matter by electron spin resonance revealed that the organic matter arising in the Iguaçu River, mainly from raw sewage discharges, caused an enhancement of humic-coated suspended solids in water samples collected downstream the city. These humic-coated particles were responsible for the transfer of copper from the aqueous to the solid phase, thus changing aspects such as physical speciation, transport and fate. These aspects must be taken into account in predicting the overall behavior of trace metals in urban rivers located in aquatic systems affected by sewage discharges.

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