COMPARISON BETWEEN SOME TRACE AND HEAVY METALS CONCENTRATIONS IN SEDIMENTS OF A RIVER AND A NATURAL WETLAND SYSTEM IN RIBEIRA DO IGUAPE BASIN, SÃO PAULO STATE, BRAZIL

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ABSTRACT

The sediment is an integrator site of many processes that take place in the water column. Its study is extremely important for the assessment of environmental impacts to which aquatic ecosystems are subordinated, since the sediments are able to accumulate nutrients and pollutants. The aim of this research was to compare copper, lead, manganese and mercury concentrations in the sediments of Jacupiranguinha River and of a natural wetland, observing the spatial-temporal variation of these concentrations in two sampling periods: October, 2004 and January, 2005. The study area is located in one of the most miserable regions in Brazil, Ribeira do Iguape Basin, whose economy is based on banana cultivation and mining activities. The obtained results contributed to better understand the differences in contaminants´ dynamic for lotic and lentic biological systems. Copper, lead and manganese concentrations were higher in the natural wetland sediment when compared to the river, probably due to the variability of processes in one and other ecosystem. It was possible to observe temporal variation, since the highest concentrations of these three metals were obtained in the sampling during the rainy period. Mercury, however, presented a different behavior. The highest concentrations were obtained in Jacupiranguinha River, reaching 0.8 mg kg^{-1}, painting a deep and serious public health problem. Besides, mercury concentrations during the rainy period were lower in comparison with the period with less intense precipitation, pointing the possibility of this metal's transportation from Jacupiranguinha river to the other rivers located in the basin.

Key-words: trace-metals; heavy metals; rivers; natural wetlands; Ribeira do Iguape Basin.

COMPARAÇÃO ENTRE AS CONCENTRAÇÕES DE ALGUNS ELEMENTOS-TRAÇO E METAIS PESADOS NOS SEDIMENTOS DE UM RIO E DE UMA ÁREA ALAGADA NATURAL NO VALE DO RIO RIBEIRA DE IGUAPE, ESTADO DE SÃO PAULO, BRASIL

RESUMO

O compartimento sedimento é o sítio integrador de diversos processos que ocorrem na coluna de água. O seu estudo é importante na avaliação das formas de impactos a que os ecossistemas aquáticos estão ou estiveram submetidos, além da intensidade dessas alterações, já que os sedimentos têm a propriedade de acumular nutrientes e poluentes. O objetivo desta pesquisa foi comparar as concentrações de cobre, chumbo, manganês e mercúrio nos sedimentos do rio Jacupiranguinha e de uma área alagada natural, observando a variação espaço-temporal em amostragens realizadas em outubro de 2004 e janeiro de 2005. A área estudada se localiza em uma das regiões mais pobres do Brasil, o Vale do Ribeira, cuja economia se baseia no cultivo de banana e na mineração. Os resultados obtidos contribuíram para melhor compreender as diferenças na dinâmica de contaminantes em ambientes lênticos e lóticos. As concentrações de cobre, chumbo e manganês foram superiores no sedimento da área alagada, em comparação com o sedimento do rio, em razão dos diferentes processos predominantes em um e outro ambiente. Observou-se variação temporal, uma vez que as maiores concentrações destes metais foram verificadas no mês chuvoso. Já o mercúrio apresentou comportamento diferenciado. As maiores concentrações foram verificadas no rio Jacupiranguinha, atingindo 0,8 mg kg^{-1}, configurando um sério risco à saúde pública. Além disso, as concentrações de mercúrio no período chuvoso foram menores em comparação ao período de menor precipitação, indicando o possível transporte do metal ao longo do eixo longitudinal do rio até outros rios da bacia hidrográfica estudada.

Palavras-chave: elementos-traço; metais pesados; rios; áreas alagadas; Vale do Ribeira de Iguape.

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1. INTRODUCTION

The studies and researches about the environment have been using the investigation of aquatic ecosystems sediments as an important tool, since the sediments congregate physical, chemical and biological processes. Through sediments´ chemical and biological composition, it's possible to study the historic evolution of the aquatic ecosystem as well as the adjacent land ecosystems. The sediments are also indicators of the kind of activities that occur around the study area. They are in charge of stocking nutrients and, in case of pollution, storing persistent substances, such as heavy metals, for instance. According to Nilsson et al (2005), this accumulation is a result of physical, chemical, and biological processes (e.g., settling, precipitation, complexation, bioaccumulation), some of which are influenced by inundation, flow manipulation, and channel fragmentation imposed by impoundments.

It's important to clarify some differences between rivers and natural wetlands. Rivers are systems with permanent circulation, in which there are three vital processes: erosion, transport and sedimentation. They are opened ecosystems with permanent interaction with the terrestrial ecosystem and with the atmosphere. According to Tassaduqe et al (2003), the physical and chemical characteristics of river waters show seasonal fluctuations, interacting with one another and having a combined effect on animals and plants. Rivers are an important sensor of the kind of human activities that are developed around. Nicolau et al (2006) remember that rivers are a dominant pathway for metals transport and that the existence of heavy metals in aquatic environments has led to serious concerns about their influence on plant and animal life.

Differently, natural wetlands are, as their name expresses, wet habitats, subordinated to permanent or periodic floods. According to EPA (2006), wetlands are lands where saturation with water is the dominant factor determining the nature of soil development and the variety of plant and animal communities living in the soil on its surface. Wetlands can be identified by the presence of hydrophytes, plants that are adapted to life in the soils that form under flooded or saturated conditions (hydric soils). Thus, natural wetlands are valuable as sources, sinks, and transformers of a multitude of chemical (including heavy metals), biological, and genetic materials (MITSCH and GOSSELINK, 2000). Besides, wetlands generally include swamps, marshes, bogs and similar areas (CLEAN WATER ACT, 2002).

Metals are either necessary in low concentrations to the human beings (trace-metals) or extremely toxic for them in any concentration (heavy metals). High concentrations may cause many diseases and injuries to the human beings health. Besides, they tend to bioaccumulate in upper levels of the food chain. Bioaccumulation means an increase in the concentration of a chemical compound in a biological organism over time, compared to the chemical's concentration in the environment. According to WRI (2006), humans are exposed to metals through inhalation of air pollutants, consumption of contaminated drinking water and food and exposure to contaminated soils or industrial waste. Food sources, such as vegetables, grains, fruits, fish and shellfish may become contaminated by accumulating metals from surrounding soil and water. Therefore, Davydova (2005) considers that metals can exert detrimental effects not only on human health but on the whole environment.

These are some of the factors that justify the importance and relevance of this research. Sediments are important sources for the assessment of man-made contamination in aquatic systems (GAUR et al, 2004). Moreover, sediments´ contamination causes very noxious effects to the whole ecosystem, according to Jardim (2004). The comparison between some trace and heavy metals concentrations in aquatic systems that present different dynamics, prime aim of this study, may help to better understand the processes involved in these ecosystems and significantly help in the context of environmental management plans´ establishment.

The main aim of this research was to determine the concentrations of copper, lead, manganese and mercury in sediments of Jacupiranguinha River and of a natural wetland system, both located in Ribeira do Iguape Basin, São Paulo state, Brazil. Besides, other aim was to analyze the spatial distribution of the metals in the river longitudinal axle and in the natural wetland. It’s important to mention that it was also possible to observe the temporal distribution variation, since there were two sampling periods: October, 2004, between 14th and 16th, and January, 2005, between 24th and 26th, with different levels of precipitation.

2. MATERIAL AND METHODS

a) Study area

The limit geographic coordinates of Ribeira do Iguape Basin are 23º30’ and 25º30’S (latitude) and 46º50’ and 50º00’W (longitude). Despite of its localization, in two very developed states in Brazil, São Paulo and Paraná, Ribeira do Iguape Basin owns a significant environmental patrimony, Mata Atlântica Tropical Forest. This environmental richness, however, contrasts with severe social and economical problems.

The economy of Ribeira do Iguape Basin is based on tea and banana cultivation. Mining activities are also extremely important there, with a great variety of ferric and non-ferric minerals. The intense minerals exploration was the motivation of this research, since it was possible to evaluate some environmental impacts derived from this activity.

Figure 1 shows an aerial photo of part of Jacupiranguinha River and of the whole natural wetland system.

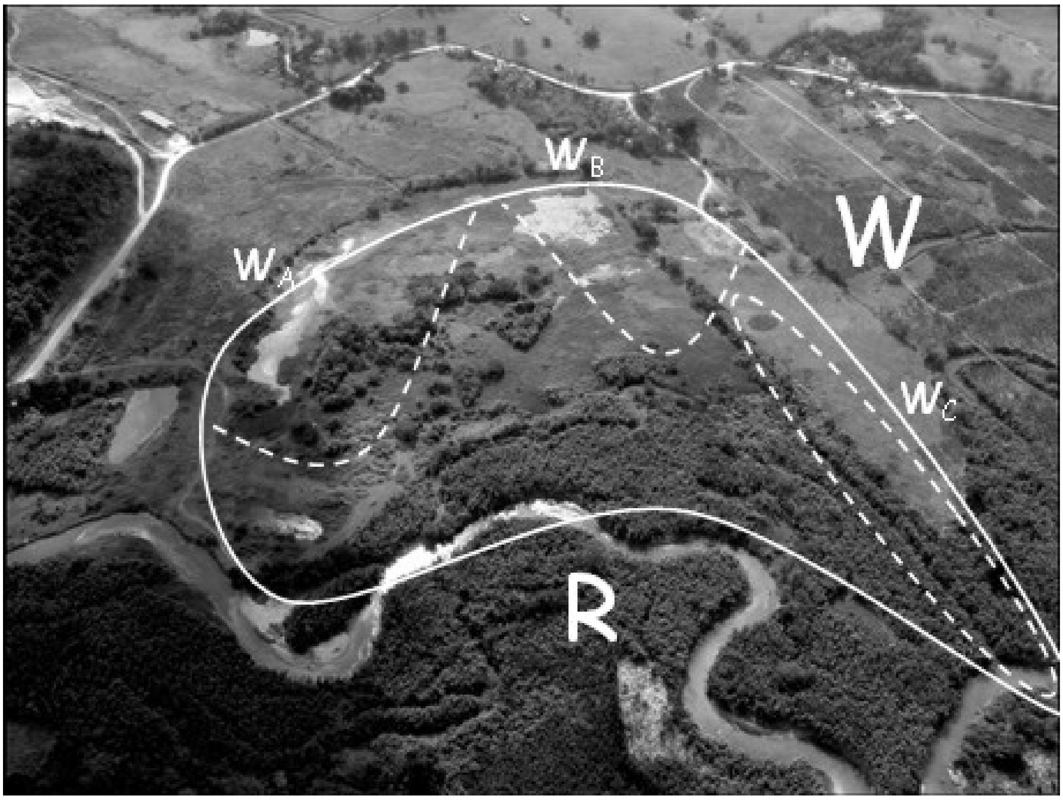

Figure 1. The whole Natural Wetland System (W); Wetland I (W_A); Wetland II (W_B); Canal which connects the natural wetland system with Jacupiranguinha River during the rainy period (W_C); Jacupiranguinha River (R).

b) Sampling

Ten points were demarcated in Jacupiranguinha River and four points were determined in the natural wetland. The localization of the fourteen points is showed in Table 1. It´s important to mention that Jacupiranguinha River provides water for Cajati city: R3 is the point of impounding of water.

Table 1. Localization of the sampling points in Jacupiranguinha River and in the natural wetland system.

Point	Latitude	Longitude	Reference/Localization
R1	24° 43' 11"	48° 10' 26"	Jacupiranguinha River
R2	24° 43' 56"	48° 08' 49"	Jacupiranguinha River, before Cajati city
R3	24° 43' 51"	48° 07' 57"	Sabesp (water supply for the population)
R4	24° 43' 47"	48° 06' 44"	New bridge, already in Cajati city
R5	24° 43' 38"	48° 05' 55"	Before WTP (Wastewater Treatment Plant)
R6	24° 43' 22"	48° 05' 37"	WTP effluent
R7	24° 43' 05"	48° 05' 10"	Fertilizer Factory effluent
R8	24° 43' 02"	48° 04' 55"	Near the natural wetland system
W1	24° 42' 55"	48° 04' 59"	Natural Wetland I
W2	24° 42' 47"	48° 04' 53"	Natural Wetland II
W3	24° 42' 47"	48° 04' 53"	Natural Wetland II
W4	24° 42' 50"	48° 04' 52"	Connecting Canal
R9	24° 42' 59"	48° 04' 41"	Connecting Canal
R10	24° 43' 02"	48° 03' 00"	The end of Jacupiranguinha River

Another characteristic is the lack of original vegetation in the riversides, which is substituted by banana and tea cultivation. When it comes to the natural wetland system, there is a diversity of aquatic macrophytes, showed in Table 2. Water variables, like pH and dissolved oxygen were measured, in order to better understand the interaction between the water column and the sediment compartment. In this context, it’s necessary to mention that there is a strong relationship between the water column and the sediment, that is, water characteristics influence the sediment ones, as remembered by Isidori et al (2004).

Table 2. Diversity of aquatic macrophytes found in the natural wetland system

Point in the natural wetland system	Aquatic macrophyte (s) observed
W1	*Eichhornia crassipes; Azolla spp.; Pistia stratiotes.*
W2	*Pistia stratiotes; Eicchornia crassipes; Eicchornia azula; Nynphaeia spp.*
W3	*Nynphaeia spp.*
W4	*Pistia stratiotes.*

c) Physical and Chemical Analysis

When it comes to the methodologies adopted, copper, lead and manganese concentrations in sediment were determined using Inductively Coupled Plasma (ICP). Mercury's ones were obtained by Cold-Vapor Atomic Absorption Spectrometric. Bioagri Ambiental, a laboratory in São Paulo state, Brazil, was in charge of the analysis. Besides, water variables, like pH and dissolved oxygen (mg L^{-1}) were sub-surfaced measured using a Yellow Spring® 556 MPS Multi-Sond.

d) Statistical analysis

All the results obtained were analyzed using correlation matrices in Microsoft Excel for Windows®, in order to verify correlations between water's and sediment's results.

3. RESULTS AND DISCUSSION

Figure 2 presents precipitation data, according to CIIAGRO (2006). The measurements were done in CIIAGRO/IAC – Jacupiranga sampling unit (Latitude: 24°41´; Longitude: 48°00´; Altitude: 59m).

The total precipitation for October and for January was 113.1 mm and 377.0 mm, respectively. During the October sampling days, it rained just 24.9 mm, while during the January sampling days, it rained 91.6 mm. The different patterns of precipitation determined different characteristics and answers of the river and wetland water and sediment.

Figure 3 presents an important water variable for all sampling points: pH. It's possible to observe that the highest pH values were found in January sampling, reaching 10.71 (R6). The lowest pH in Jacupiranguinha River was detected in R10, during October sampling, 7.04. For the wetland, it´s possible to notice that pH variation between the sampling periods was less accented than it was in the river.

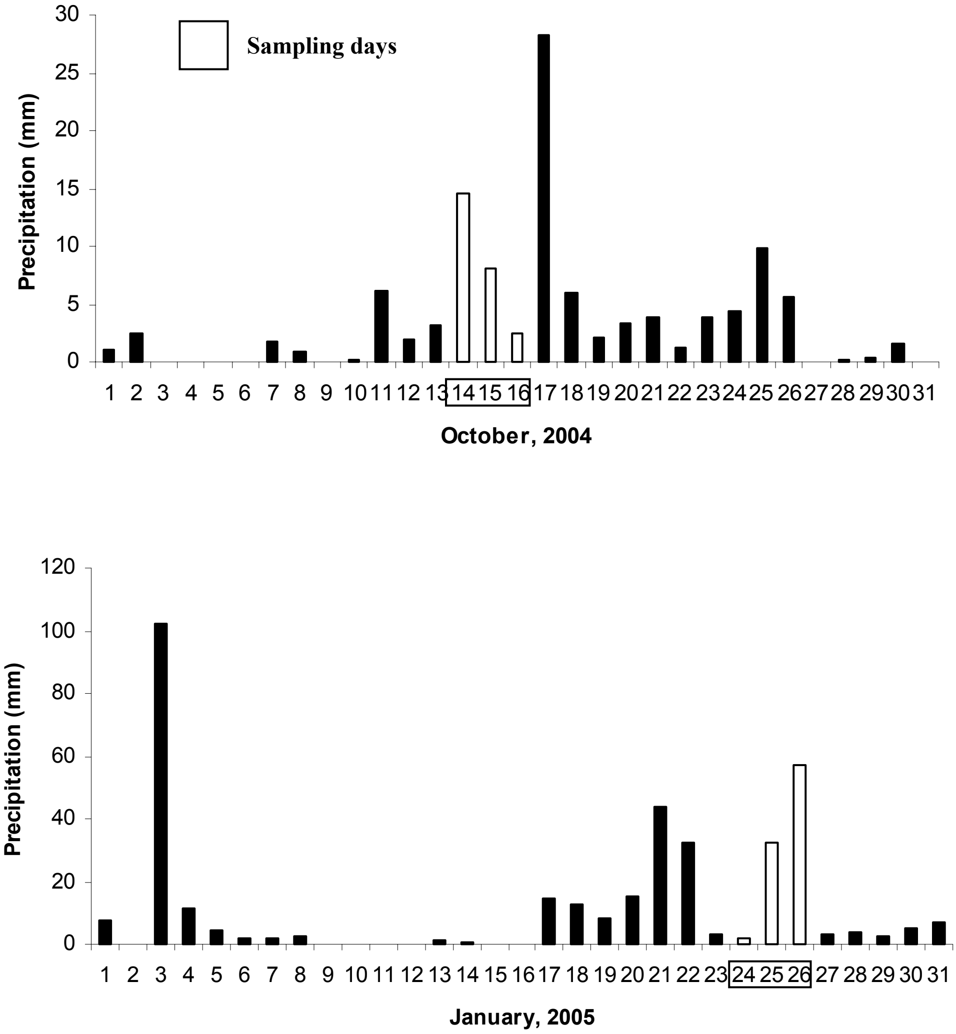

Figure 2. Daily precipitation (mm) for both sampling months: October, 2004 and January, 2005.

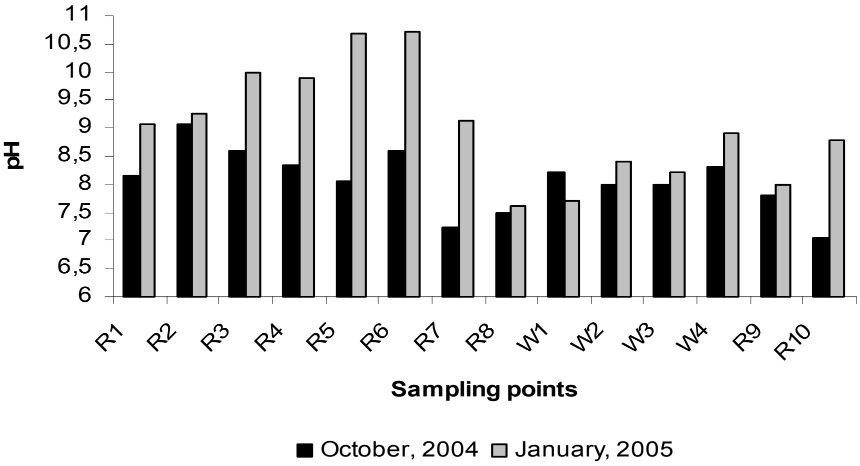

Figure 3. pH for all sampling points in Jacupiranguinha River and in the natural wetland system.

The pH values ranged from 7.7 (January sampling), in W1, to 8.9 (January sampling), in W4. The temporal variation was clear, since the pH values during the rainy month, January, were higher.

Figure 4 shows dissolved oxygen concentrations. The highest concentration was observed in October, 2004, in R4, 7.3 mg L^{-1} and the lowest was detected in W4, 0.1mg L^{-1}, also during the first sampling.

The dissolved oxygen concentrations presented a strong decrease in the wetland, almost reaching anaerobic conditions. This must be associated with the innumerous degradation reactions which occur in the natural wetland system. Natural wetlands play an important role in biochemical cycles and the consumption of oxygen, expressed by the significant reduction in oxygen concentrations, corroborates the importance of these wet areas in the nutrient's cycles, as observed by many other authors (Richardson, 1996; Walker and Hurl, 2002; Watras et al., 2005).

Figure 5 shows copper concentrations in Jacupiranguinha River and in the natural wetland, for both samplings. The highest concentration in Jacupiranguinha River sediment was 22.0 mg kg^{-1}, in R7, during January sampling, and the lowest was found in October sampling, 3.1 mg kg^{-1} (R10). The highest copper concentration in the wetland sediment was 32.0 mg kg^{-1}, in W4, in the second sampling, and the lowest concentration was found in W1, 9.3 mg kg^{-1}, during the first sampling.

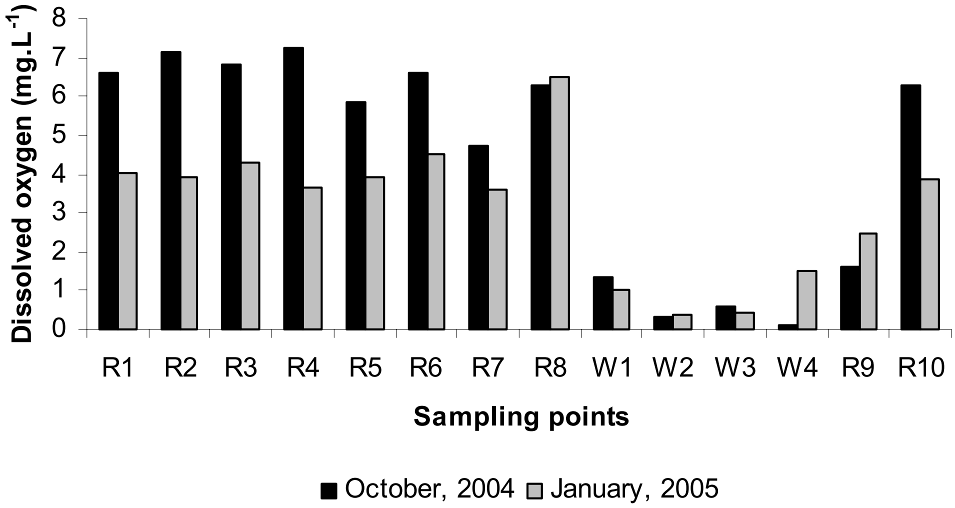

Figure 4. Dissolved oxygen (mg L^{-1}) for all sampling points in Jacupiranguinha River and in the natural wetland system

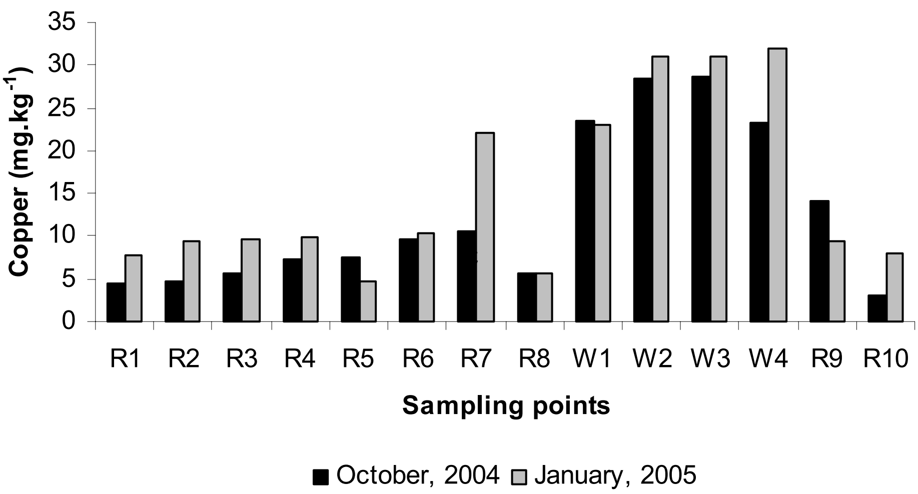

Figure 5. Copper concentrations in Jacupiranguinha River and in the natural wetland system sediments for all sampling points. Quantification limit: 0.5 mg kg^{-1}

All the concentrations obtained in this research were lower than copper concentrations in Tubarão river (Santa Catarina state, Brazil) sediment, whose highest copper concentration was 72.2 mg kg^{-1} (LIMA et al, 2001). Gaur et al (2004) studied Gomti River (India) sediment and obtained even higher concentrations. The maximum concentration found was 91.2 mg kg^{-1}. For the wetland, comparing with the research of Cardwell et al (2002), the concentrations obtained in the wetland of this present work were lower. The maximum copper concentration obtained by Cardwell et al (2002), who studied the sediment of a natural wetland in Southeast Queensland, Australia, was 49.6 mg kg^{-1}, which is higher than copper concentrations obtained in this work for the wetland in Ribeira do Iguape Basin.

In a general way, it's possible to observe that the sediment of the wetland presented higher copper concentrations, compared to the river sediment. According to Richardson (1996), wetlands perform many activities inside the ecosystems. One of them, for instance, is the great importance that these wet areas have in the biochemical cycles. Thus, wetlands play an important part in nutrients and trace-metals cycle. Besides, due their own water flow characteristics, like the low velocity of the water, wetlands tend to accumulate more nutrients and substances in the sediment, when compared to rivers, which have a different kind of flow and a lower water retention time.

According to Wen et al (2001), adsorption and desorption play a dominant role in the transformation process and in the concentrations of trace and heavy metals in natural waters. Copper concentrations in sediments are highly affected by the physical and chemical conditions of the water column. In this context, Wen et al (2001) studied the adsorption and desorption behavior of copper on polluted sediments taken from the Le An river (China) and concluded that the adsorption behavior of the polluted samples is dependent on pH and polluted ion concentration in the water column. In this present research, the importance of pH in copper concentrations in sediment could be evaluated. For the river and for the wetland, higher pH values determined higher copper concentrations in the sediments, since the highest copper concentrations, detected in January, coincided with the higher pH values observed in this sampling.

Also, it's important to observe that the spatial-temporal distribution variation was pronounced in copper concentrations in the river sediment. The higher concentrations were detected during January sampling, in which it rained more than in October sampling, as already shown in Figure 1. Diffuse pollution sources have to be considered to explain this concentration increase during the rainy month, like agriculturist activities and cattle breeding in small properties around the study area. For the wetland, this variation was not too evident, but also happened, since the highest concentrations were also observed for samples of October, 2004.

Copper contamination is frequently studied and there are many researches about it. Copper pollution studies are extremely important due the existence of several sources of copper contamination to the environment, mainly by anthropogenic activities, like domestic wastewaters, industrial effluents, pesticides, and so on (RASHED, 2001). Moreover, copper pollution causes damages to the human-beings´ health. According to EPA (2006), the symptoms of high copper exposure (more than 10 mg per day) are: headaches, hypoglycemia, increased heart rate, nausea, anemia and so on. Besides, copper deposits in the brain and liver causing damage. High copper interferes with zinc, which is needed to manufacture digestive enzymes. Many high copper people dislike protein and are drawn to high-carbohydrate diets because they have difficulty digesting protein foods. Excessive copper in children is associated with hyperactive behavior, learning disorders such as dyslexia and infections, such as ear. The acceptable levels for copper in river sediments are, according to Cetesb (2005), up to 60.0 mg kg^{-1}.

Lead concentrations in sediment are showed in Figure 6. It's possible to observe that the highest lead concentration in the river sediment was 7.4 mg kg^{-1}, in R7, while R10 presented the lowest concentration, 1.6 mg kg^{-1}. For the wetland, the highest lead concentration was detected in W4, 15.0 mg kg^{-1}. The lowest one, 9.3 mg kg^{-1}, was observed in W1.

Tomazelli (2003), who studied Piracicaba River (São Paulo state, Brazil), obtained higher lead concentrations in the sediment of this river. The concentrations ranged between 80.0 mg kg^{-1} and 233.0 mg kg^{-1}. When it comes to lead, the acceptable levels for river sediments are, according to Cetesb (2005), up to 72.0 mg kg^{-1}. The sediment of the wetland in Ribeira do Iguape Basin presented higher concentrations than those obtained by Aksoy et al (2005), who studied Sultan Marsh, a natural wetland in Turkey. The highest concentration in the Turkish wetland sediment was 7.9 mg kg^{-1}.

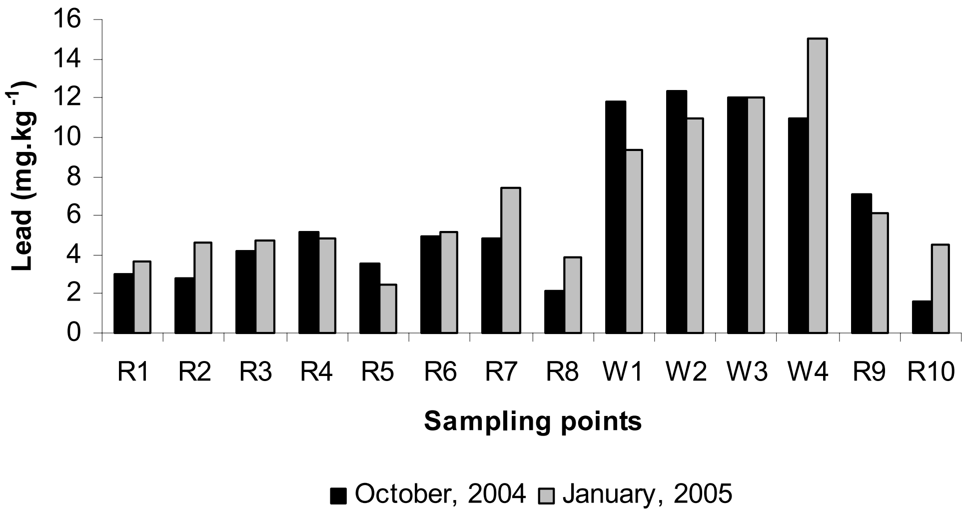

Figure 6. Lead concentrations in Jacupiranguinha River and in the natural wetland system sediments for all sampling points. Quantification limit: 0.5 mg kg^{-1}

Comparing the results for lead concentrations in sediments obtained in this research, the wetland sediment presented, like it was observed for copper, higher concentrations than the river sediment.

In this context, it’s important to recognize the importance of wetlands in water filtration. According to EPA (2006), after being slowed by a wetland, water moves around plants, allowing the suspended sediment to drop out and settle the wetland floor. Thus, many contaminants may go to the sediment, cleaning the water column, by storing the trace-metal in the sediment, like the lead, for instance. In other words, sedimentation has long been recognized as the principal process in the removal of heavy metals from the water not only in natural wetlands, but also in constructed ones (WALKER and HURL, 2002).

Especially for Jacupiranguinha River, the spatial-temporal distribution variation of lead was very clear. The higher concentrations were observed during the second sampling. It’s probably associated to the transport of particles as a consequence of the intense precipitation. The sources of these particles include areas with erosive problems, like the banana and tea plantations around the river, and urban areas, since the river crosses Cajati city. Diffuse pollution must also be cited as an important source of this lead increment.

Lead pollution is extremely common in aquatic ecosystems, since there are many sources of contamination by this metal, as it was already observed by many authors (Lima et al, 2001; Silva, 2002; López-Flores et al, 2003). According to EPA (2006), lead has a wide variety of uses due to its properties of high density, softness, low melting point, resistance to corrosion, and ability to stop gamma and x-rays. Lead is commonly used in storage batteries for automobiles and industry; electrical and electronic equipment; machine bearings; cable coverings; and in pipes, traps, solder, and sheets for building construction.

According to EPA (2006), the health effects of lead exposure have been extensively studied. When lead enters the body, it travels through the blood to the soft tissues, such as brain, liver, and kidneys. In adults, most lead taken into the body is excreted, with a small amount stored in bones and teeth, where it may accumulate with repeated exposure. Chronic exposure to lead may cause a variety of adverse health effects in adults, including brain and kidney damage, poor reaction time, joint weakness, anemia, memory impairment, and possibly increased blood pressure. These effects may persist long after lead exposure ends. Lead can be released from the bones into blood under certain circumstances, such as during pregnancy and breastfeeding. These releases can potentially expose the developing fetus or nursing infant. Lead is classified by EPA as a probable human carcinogen, based on evidence from rodent studies. Large doses of lead have caused tumors in rats and mice. Nevertheless, there is not yet enough information to determine whether lead causes cancer in humans.

Manganese concentrations in sediment are showed in Figure 7 for Jacupiranguinha River and for the wetland. On one hand, the highest concentration in Jacupiranguinha River was 551 mg kg^{-1}, detected in R7, and the lowest was 95 mg kg^{-1}, in R8. On the other hand, for the wetland, manganese concentrations in sediment ranged between 310 mg kg^{-1} (W2 and W4) and 543 mg kg^{-1} (W1). Brigante et al (2003), who studied Mogi-Guaçu river sediment (São Paulo state, Brazil), obtained extremely diverse manganese concentrations: from 51 mg kg^{-1} to 1,324 mg kg^{-1}. Mansour and Sidky (2003), who studied Wadi El-Rayan natural wetland (Egypt), obtained 394 mg kg^{-1} as the highest manganese concentration. Thus, this concentration is lower than many concentrations found in the wetland sediment of this present research. It was possible to observe higher manganese concentrations in the wetland sediment, compared to the river sediment.

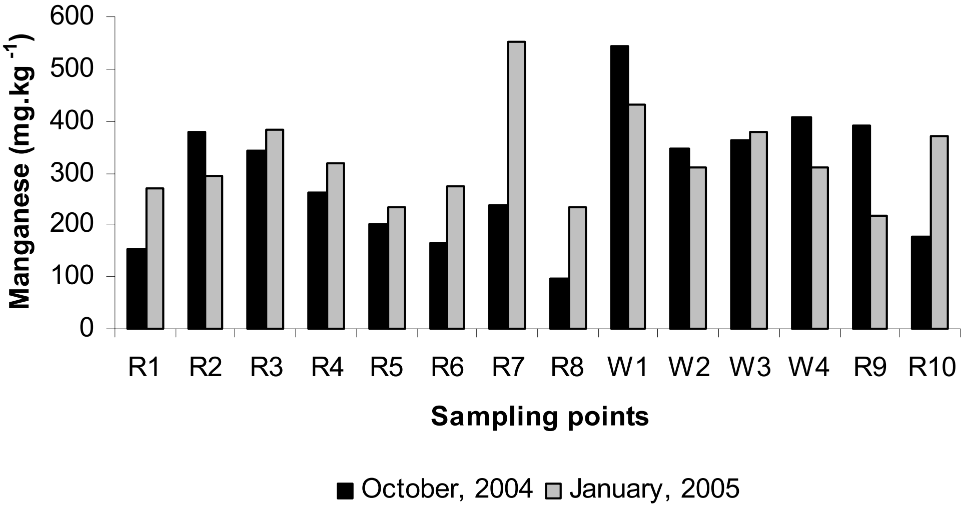

Figure 7. Manganese concentrations in Jacupiranguinha River and in the natural wetland system sediments for all sampling points. Quantification limit: 0.5 mg kg^{-1}

Besides, the spatial-temporal distribution variation was pronounced in Jacupiranguinha River again, with higher concentrations in January sampling. In the wetland, however, there was a pattern of reduction in manganese concentrations in January.

When it comes to water parameters interference in sediment characteristics, the answers of the river and the wetland for the water conditions were different. On one hand, for the river, the increase of pH values and the decrease of dissolved oxygen concentrations in January determined the increase of manganese concentrations in the sediment. On the other hand, for the wetland, the increase of pH values and the decrease of dissolved oxygen concentrations caused a reduction in manganese concentrations in its sediment.

Scientific concern about manganese contamination has arisen due to its widespread use in ceramics, the manufacture of matches, glass, solder, metal alloys, batteries, aluminum cans, electronic components and, for over 20 years, in gasoline additive compounds, such as methylcyclopentadienyl manganese tricarbonyl, MMT (Burgoa et al, 2001). Moreover, world production has increased by 30-fold through-out this century due to industrial use.

According to Burgoa et al (2001), the most important manganese health end point is the neuropsychological, including the cognitive, motor and sensory areas. Some symptoms of manganese exposure could include compulsive or violent behavior, emotional instability, and hallucinations. Other early manifestations of manganese neurotoxicity include fatigue, headache, muscle cramps, loss of appetite, apathy, insomnia, and diminished libido (ASCHNER et al, 2005). Fraga (2005) also remembers that, in brain, manganese may cause a Parkinson-type syndrome. Thus, it's alarming that R3 presented the third highest manganese concentration in Jacupiranguinha river sediment, since this point corresponds to the place where the impounding of water for the population occurs and the risk associated is high.

Mercury concentrations in sediment are showed in Figure 8, for the river and for the wetland sediments. The highest mercury concentration in Jacupiranguinha river sediment was 0.80 mg kg^{-1}, in R7. R2, R4, R5 and R9 presented concentrations below the detection limit, 0.1 mg kg^{-1}, during the second sampling. For the wetland, mercury concentrations ranged between the detection limit (W4), during the second sampling, and 0.63 mg kg^{-1} (W1), during October sampling. Mascarenhas et al. (2004), who studied Acre River, in Acre state, Brazil, obtained 0.2 mg kg^{-1} as the highest mercury concentration in sediment. Mehotra and Sedlak (2005), who studied a natural wetland system around San Francisco Bay, USA, obtained 1 mg kg^{-1} as the highest mercury concentration in the sediment.

Comparing mercury concentrations in the sediment of the river and of the wetland, it´s possible to verify that the former presented the highest concentrations, reaching 0.8 mg kg^{-1}, which is a different pattern, compared to the other trace metals quantificated in this research. It does not corroborate the work of Kamman et al (2005), who compared mercury concentrations in sediments of different ecosystems and obtained the highest total mercury concentrations in lakes and reservoirs, ecosystems with a lower water velocity, when compared to rivers.

Besides, the spatial-temporal distribution variation was also different when compared to the other metals ones. The highest mercury concentrations were detected during the first sampling, when the precipitation was lower than during the second sampling.

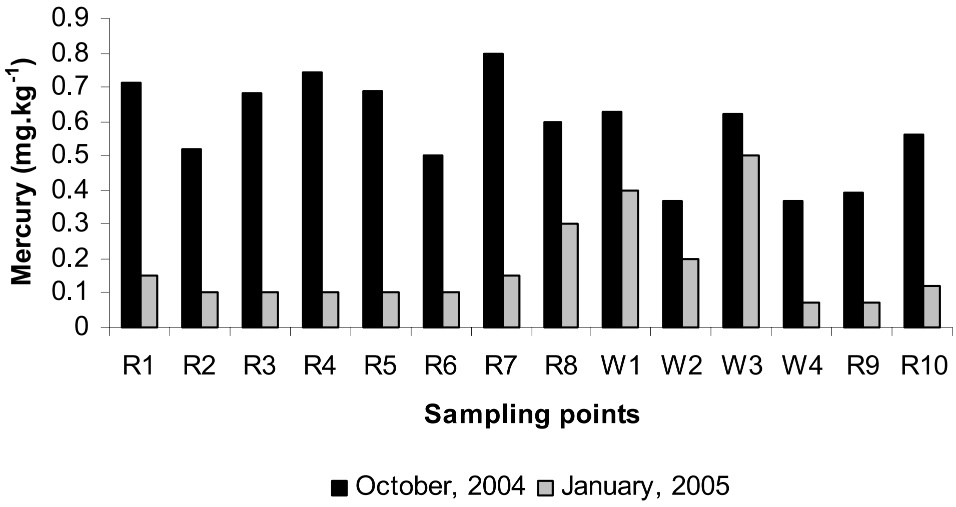

Figure 8. Mercury concentrations in Jacupiranguinha River and in the natural wetland system sediments for all sampling points. Quantification limit: 0.1 mg kg^{-1}

The higher precipitation amount in January may have transported the mercury from Jacupiranguinha sediment to other rivers´ sediments.

Recent studies (Machado et al., 2002; Marins et al., 2004) have been showing the increase of mercury concentration in the sediment of Ribeira do Iguape river, which is the main river of the basin in which Jacupiranguinha river is located. It indicates that metals transportation from Jacupiranguinha River and other tributaries to Ribeira do Iguape River may have been occurring.

According to Kamman et al (2005), environmental mercury contamination is an issue of global importance. In the past two decades, the concentration of mercury has been determined in numerous environmental matrices, including air, water, sediment, and biota. As sediments serve as the ultimate repository for much of the particulate matter that moves through watersheds, sediments are a well-studied environmental matrix. Mercury concentrations in the river and the wetland sediments both were pretty high. Cetesb (2005) establishes 0.5 mg kg^{-1} as an acceptable mercury concentration in freshwater sediments. Thus, many concentrations obtained in this work are above. This is such a hard public health problem.

According to EPA (2006), mercury enters humans' lives more frequently than someone may imagine. It may be in the fluorescent lights in offices, in old cans of latex paint, in batteries, in dental fillings, and numerous other sources. Nevertheless, mercury does not degrade easily, it´s not destroyed by combustion and therefore it's extremely dangerous to the human health.

Watras et al (2005) emphasizes that several lines of evidence suggest that wetlands may be a major source of methylmercury (MeHg) environment. Therefore, the concentrations of mercury in the wetland sediment of this work are extremely preoccupying, since the synthesis of methylmercury may happen and the toxicity of this compound is extremely high. Mehrotra and Sedlak (2005) emphasize that MeHg poses a significant risk to humans and wildlife due to its neurotoxicity and tendency to accumulate in aquatic food chains. Azevedo (2003) considers methylmercury as the most dangerous specie of mercury, considering that its physical and chemical properties make it easy to be introduced in the human organism and absorbed by the humans. Thus, considering that Jacupiranguinha River and the wetland are used as sources of fish by the local population, it's possible to paint a deep public health problem. Moreover, up-to-date researches have been showing that about 60-95% of total mercury fish (muscular tissue) is in methylmercury form (WHO, 1990; Akagi et al, 1996; Burger and Gochfeld, 2005).

Table 3 shows a correlation matrix among all metals in sediment and the water characteristics, pH and dissolved oxygen for the October sampling. It's important to observe the significant correlation between lead and copper, following Eggleton and Thomas (2004) considerations. Besides, during this sampling, dissolved oxygen played an important role in lead and copper concentrations in sediment. The inverse correlations reached -0.9 for these metals.

Table 4, on the other hand, shows the matrix for January sampling period. Again, a significant correlation was observed between lead and copper. Dissolved Oxygen also played an important role in this sampling, determining an increase in lead and copper concentrations.

Finally, the comparison between trace metals concentrations in sediments of ecosystems with different dynamics was extremely important and it may encourage other researches that establish this comparison, in order to better understand the processes involved and the difference in metals concentrations in sediments of rivers and natural wetlands.

Table 3. Correlation matrix among metals concentrations in sediment and water characteristics of the studied ecosystems for October sampling.

	Lead	Copper	Manganese	Mercury	pH	Dissolved Oxygen
Lead	1					
Copper	**0.982997**	1				
Manganese	**0.730323**	**0.648624**	1			
Mercury	-0.4236	-0.44896	-0.3329618	1		
pH	0.122186	0.030337	0.3731229	-0.15388	1	
Dissolved Oxygen	**-0.91635**	**-0.93866**	**-0.6610617**	0.552355	0.128159	1

Table 4. Correlation matrix among metals concentrations in sediment and water characteristics of the studied ecosystems for January sampling.

	Lead	Copper	Manganese	Mercury	pH	Dissolved Oxygen
Lead	1					
Copper	**0.961946**	1				
Manganese	0.309742	0.44725	1			
Mercury	0.364594	0.443602	0.28148736	1		
pH	-0.41279	-0.37839	-0.0891859	-0.59643	1	
Dissolved Oxygen	**-0.81418**	**-0.84453**	-0.2658064	-0.39238	0.355503	1

4. CONCLUSIONS

The quantification of copper, lead, manganese and mercury in sediments of Jacupiranguinha River and of the wetland, for samples collected in October, 2004, and in January, 2005, enables to conclude that:

It was possible to observe the interdependence between water and sediment characteristics. Dissolved oxygen concentrations in water have decisively intervened in metals concentrations in the sediment, for both river and wetland. As shown by correlation's matrices, the lower dissolved oxygen concentrations found in January have determined an increase in lead and copper concentrations, associated with other factors, like the diffuse pollution;

Copper, lead and manganese concentrations were higher in wetland sediment than in Jacupiranguinha River sediment, for both sampling periods. This difference is probably associated to the variability of processes that occur in one and other ecosystem. Water velocity, for instance, may be considered as an important factor in this context. High velocities, commonly found in rivers, may transport the sediments and the trace metals as well, consequently;

Mercury presented a different pattern. The highest concentrations were observed in the river sediment. The high concentrations in the natural wetland system sediment are also very dangerous, since the formation of methylmercury in the wetland may happen, causing the liberation of this mercury specie to the water column. The high concentrations, both in the river and the natural wetland system may be associated to the mining activities;

The spatial-temporal distribution variations were clearer in the river sediment. Copper, lead and manganese concentrations were higher during the second sampling, the rainy one. Mercury, however, was detected in higher concentrations during October sampling.

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