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Abstract - The sediments carried by runoff water are an important part of this process because their presence in the bodies of water not only cause sedimentation problems but, mainly, they contaminate the water due to the presence of the pollutants found associated with sediments. The urban sub-watershed under study is located in the metropolitan region of Porto Alegre city, Brazil. This paper aims to present the relation between pollutants on the street sediments and in suspended sediment sampled in the river. The collections of suspended sediment samples begun in the end of 2003 and finished in the end of 2006. Collections of urban dust samples (47 samples per km²) were taken in the main diffuse sources of the urban environment, represented by paved and non-paved streets, beyond the area with remaining vegetation, in some points of the bed river and in its margins. During these analyses, it was studied 29 samples of fluvial suspended sediments. The elements selected for this study are some of the most frequently found in high concentrations in urban areas (Zn, Pb and Cu). The results suggest it is occurring a high enrichment of the local sediment with these metals. The concentrations of these elements vary temporally during storms due the input of road runoff containing elevated concentrations of elements associated with vehicular traffic and other anthropogenic activities. In general, they have their most concentrations on the streets but they are carried to the channel during the storms.

Keywords - Suspended sediments, metals, urban dusts.

INTRODUCTION

The permeable soil is replaced by impermeable surfaces such as roads, roofs, parking lots, and sidewalks that store little water, reducing infiltration of water into the ground, and accelerating runoff to ditches and streams (USGS, 2003). The sediments are an important part of this process because their presence in the bodies of water not only cause sedimentation process problems but, mainly, they contaminate the water due to the presence of the pollutants found associated with sediments. Horowitz (1991) clearly shows that as suspended sediment concentrations increase, the percentage contribution of suspended sediment-associated trace elements also increases.

The sediments contaminated with heavy metals have been considered as one of the biggest environmental problems. While many metals are required nutrients, others are toxic to living organisms (Dahl, 2005). In this sense, the studies on quality of sediments are having an important focus in environmental assessments, protection and management of aquatic ecosystems.

There are many causes that can increase the production of sediments in urban areas, however, the most important ones are related to the little vegetal covering, the lack of urban infrastructure (paved streets, sewer and draining system), the absence of a rigid control on the civil labor and the lack of works to store the sediments from the pavements (restrainer boxes).

OBJECT OF INVESTIGATION

The urban sub-watershed under study is located at Vila Santa Isabel, located in the city of Viamão, metropolitan region of Porto Alegre city, capital of the state of the Rio Grande do Sul, southern Brazil (Fig. 1). The area of study is a non-industrial urban watershed which according to Poleto *et al*. (2005) can be considered a representative watershed of the Brazilian peripheral regions and this area presented in 2005 approximately 42% of its entire surface covered by impermeable coverings.

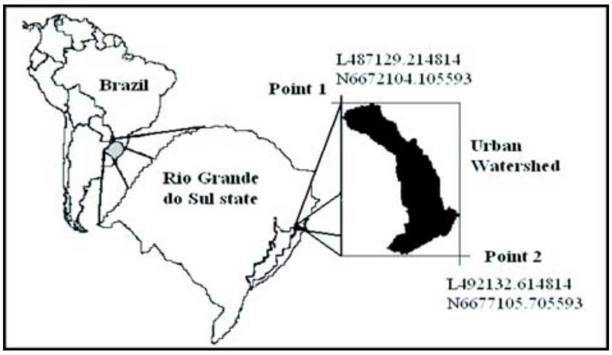

Figure 1 - Localization of the studied area in Brazil and in the state of Rio Grande do Sul. Modified from Poleto *et al*. (2005).

The studied area has its watershed limits inside the spindle 22S, point 1: L487129.214814 and N6672104.105593, point 2: L492132.614814 and N6677105.705593, and has an approximated area of 0.83 km².

The little stream located in the studied area (Fig. 2), in which was built the section to sample of suspended sediment samples, is located in the hydrographical watershed Arroio Mãe d'Água stream, and it contributes to the main hydrographical watershed of Arroio Dilúvio stream.

Although the climate of the region is subtropical, the substitution of a tropical air mass for a polar air characterizes the meteorological weather that generates abrupt falls in the temperature. The borderline between them is called cold front. And after the cold front installs the cold air mass in the region, its permanence can continue for several days.

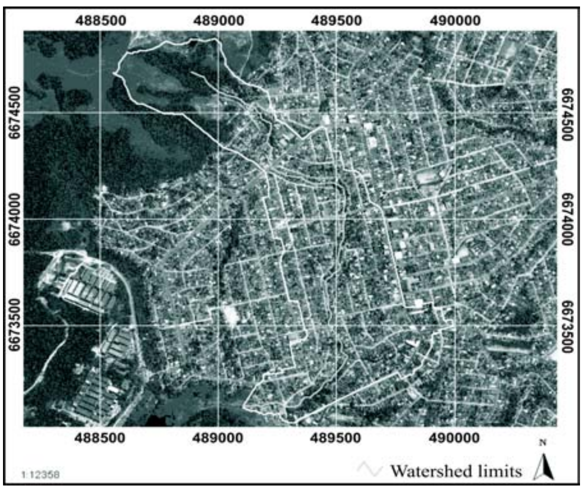

Figure 2 - Watershed limits and its stream. Font: Cardoso *et al*. (2006).

METHODS

Collection of Suspended Sediment, Urban Dust and Background Samples

The collection of the samples of suspended sediments begun in the end of 2003, yet as a staff training and equipment test stage and finished in the end of 2006. As most of the load of sediments in this area is carried through during the outflows generated by precipitations, the collections of samples of suspended sediments were accomplished during rainy days, in the section located in the outlet of the studied area, in two points of the transversal section, at 0.60 m and 1.20 m of the stream's left edge, with an US DH-81 equipment. The total of suspended sediment samples studied was 29 samples.

The samples had been collected in polypropylene gallons of 20 liters, where they had been stored for 24 hours to be initiated its centrifugation, facilitating the concentration of the sediments. The centrifuged samples were dried at maximum temperature of 40ºC per, approximately, seven days. The dry samples were transferred to polypropylene bottles of 50 mL and frozen, preventing the contact with metal implements so that the samples could not be contaminated, according to a procedure suggested by Horowitz (1991) and Mudroch *et al*. (1997).

Collections of urban dust samples (47 samples per km²) were done in the main diffuse sources of the urban environment, represented by paved and non-paved streets, beyond the area with remaining vegetation, in some points of the bed river and in its margins. This sampling looked for representative areas (composed samples) and was conducted to cover all watershed area. Every sample was composed by 100 m² (minimum). The particulated material was collected by vacuum and plastic bags to avoid contamination.

To obtain background values of the samples to the hydrographical watershed, the collection of samples were accomplished in the soil of the region next to the stream (inside the studied area), the place that presents fragments of the original vegetation, still without human alterations. Some samples were obtained at different points of this area, dividing it in three regions. After that, the samples were separated by its respective areas of collection, joined and homogenized to get three compounding samples that could represent the place.

All the gallons, baskets and glassware involved in the collection procedure and concentration of the sediments for posterior freezing were washed with distilled water and stayed in nitric acid solution of 14% (v/v) for 24 hours and later they were again rinsed with deionized water.

Characterization of Suspended Sediments and Background Samples

Mineralogical analyses had been done to verify if the samples obtained with background values presented similar mineral characteristics of the samples of fluvial suspended sediments and the kinds of mineral. These analyses were carried out in four phases (natural, powder, glycol and calcined) for diffraction by D5000 from SIEMENS.

Acid Digestions of Samples

During these analyses, it was studied 29 samples of fluvial suspended sediments. Regarding the background samples, three compounding samples of the soil were digested (after bolted), and later a grain sized factor of correction to the results was applied, enabling the equalization of the concentrations with the ones obtained in the studies of the suspended sediments.

The total concentrations of metals had been determined by acid digestion (HCl - HF - $HClO_4$ - HNO_3) for total destruction of the minerals aggregated to the sediments (Horowitz *et al*., 2001). This analysis was conducted in duplicated and the metals determinate by ICP-OES. The detection limits can be observed in table 1.

Tabela 1 - Detection limits to ICP-OES for studied metals

Metals	Detection limit ICP-OES (mg L^{-1})	Detection limit ($\mu g g^{-1}$ for sediment)
Zn	0.030	3.0
Pb	0.020	2.0
Cu	0.004	0.4

The analytical reagents and the extracting solutions used in the analyses are Merck®, which have a high degree of pureness. The water used for the dilutions is a Milli-Q type (extra-pure), for a simple distillation water could present organic complexes of metallic ions. All the glassware involved in the procedure of acid digestion had been washed with distilled water and stayed in nitric acid solution of 14% (v/v) for 24 hours and later rinsed with deionized water. Ten reference materials for quality control were used (NIST 2709, NIST 2711 MT. Soil, NIST 1646a, USGS MAG-1, USGS STM-1, USGS SDO-1, USGS SGR-1, USGS SCO-1, USGS QLO-1 and USGS GSP-2).

Studied Metals

The elements selected for this study are some of the most frequently found in high concentrations in urban areas. So, it was determined during the total acid digestions and sequential extractions the lead (Pb), copper (Cu) and zinc (Zn).

RESULTS AND DISCUSSION

Assessment of Potential Environmental Risks from Sediments

To evaluate the metal concentration in the sediment and thus enable a first analysis in its possible ecological impact on the environment, it is common to use tool as the guidelines or Background concentrations. Therefore, for the studies on the concentrations of Pb, Cu and Zn in suspended sediment samples, Background concentrations as a minimum limit or reference value in relation to the local studies were used, as presented in figures 3, 5 and 7. The distribution of the three metals concentrations in the urban area can be observed in figures 4, 6 and 8.

Despite the guidelines are “site specific” (Poleto & Gonçalves, 2006), it was used the resolution CONAMA (2004) as reference parameters to compare the analysis results with the local background values.

The Pb concentrations (Fig. 3) presented in the analyzed suspended sediment samples had an average of 52 $\mu g\ g^{-1}$, standard deviation of 12.33 and all samples exceeded the background value and the Level I determinated by CONAMA (2004). It means that the ecosystem is in great risk. In another study in Australia, the researchers Simonovski *et al.* (2003) found concentrations three times higher than the background value and they considered the area was contaminated for industrial activities.

The distribution of this metal in the area can be observed in the figure 4. The major Pb concentrations appeared on the paved streets and in the downstream. It occurs because during the storms the metals associated with the sediments in the streets are lead to the stream.

The results of Zn studies had shown that 100% of the suspended sediment samples have its concentrations above the reference value (background) as presented at the figure 5. The concentrations are so high that more than 50% are above the Level II from CONAMA (2004), what represents great damages for the aquatic life. The concentrations found in the samples had presented an average of 326.16 µg g^{-1} and a standard deviation of 108.64, what was similarly found in studies accomplished in urbanized areas in Hawaii by De Carlo *et al*. (2004). These results suggest it is occurring a high enrichment of the local sediment with Zn. Guéguen *et al*. (2000) found similar concentrations in Poland and considered the place very contaminated. The distribution of this metal in the area can be observed in the Figure 6. The Zn appeared in elevated concentrations all over the watershed then it is almost impossible to distinguish the different values presented in this figure.

The Cu concentrations presented in the analyzed suspended sediment samples had an average of 53.52 µg g^{-1} and a standard deviation of 17.58, sometimes exceeding up to eight times the background values. All samples were almost above the Level I from CONAMA (2004). No samples were below the base value, as shown in figure 7, what it indicates a new source of this metal in this area. Only studies in the Northern of France carried out by Vdovic *et al*. (2006) indicate 15 times higher than the background value.

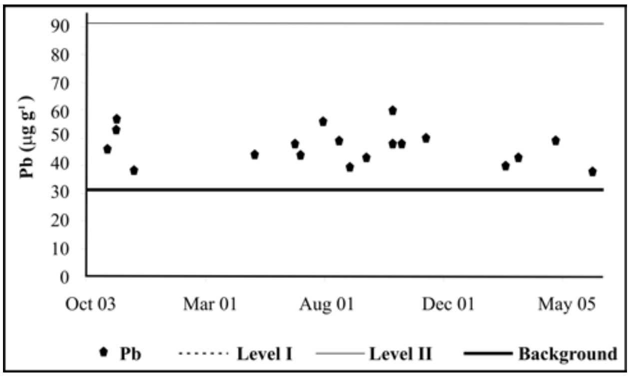

Figure 3 - Frequency of the Pb concentrations in suspended sediments compared with the background value and the limits or levels established by CONAMA (2004).

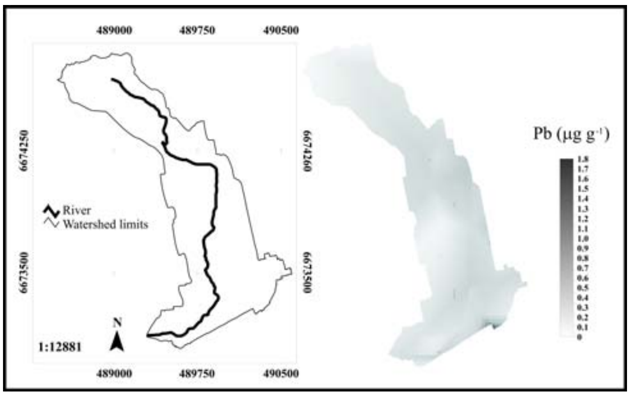

Figure 4 - Distribution of Pb concentrations in urban dusts inside the studied area.

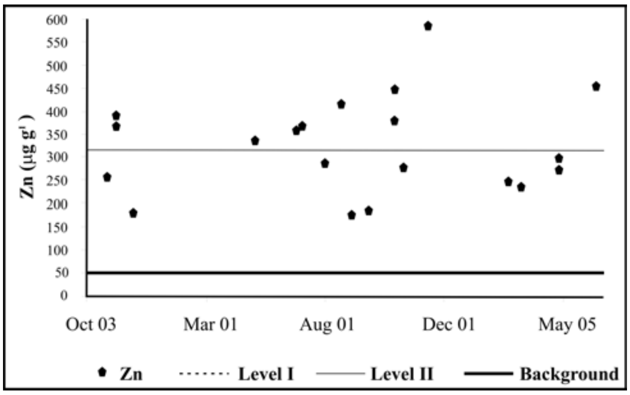

Figure 5 - Frequency of the Zn concentrations in suspended sediments compared with the background value and the limits or levels established by CONAMA (2004).

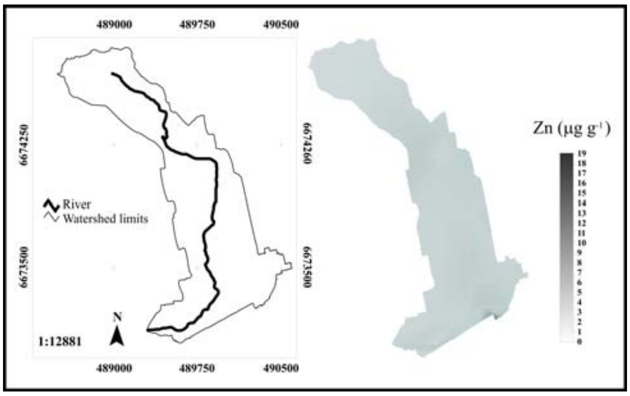

Figure 6 - Distribution of Zn concentrations in urban dusts inside the studied area.

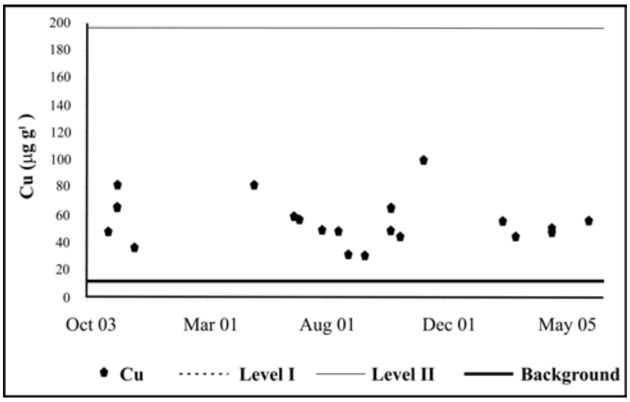

Figure 7 - Frequency of Cu concentrations in suspended sediments compared with the background value and the limits or levels established by CONAMA (2004).

The distribution of Cu in the urban area is shown in figure 8, and it can be observed that the major concentrations are in some paved streets with more movement of cars and near by the watershed outlet (there is a deposition of one part of the sediment discharge in this lower area). The concentrations of these elements vary temporally during storms due to input of road runoff containing elevated concentrations of elements associated with vehicular traffic and other anthropogenic activities.

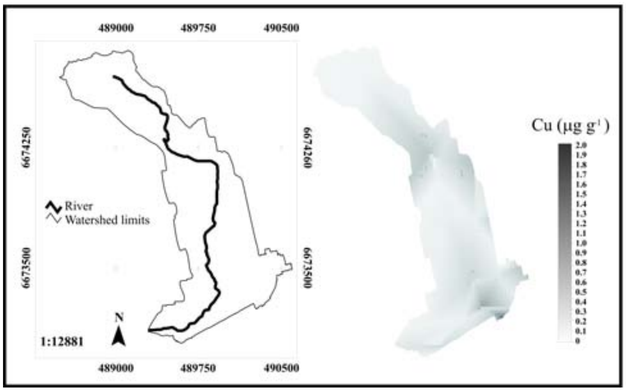

Figure 8 - Distribution of Cu concentrations in urban dusts inside the studied area.

To understand the influence of the diffuse sources of these pollutants in the results of suspended sediments, table 2 presents these three main sources in an urban watershed. The three metals presented the major concentrations in the paved streets. These results are the same presented in other studies, as De Miguel *et al*. (1997), Charlesworth *et al*. (2003) and Taylor (2007), and those paved streets were considered as the major source of metals and other contaminants.

Table 2 - Average concentrations (µg g-1) of Zn, Pb and Cu in urban dusts in the three main sources.

Metals	**Paved streets**	**Unpaved streets**	**Stream**
Zn (µg g^{-1})	377.64	139.95	201.73
Pb (µg g^{-1})	79.66	36.45	49.78
Cu (µg g^{-1})	98.81	17.27	57.79

CONCLUSIONS

From the three elements studied (Cu, Pb and Zn) in samples of fluvial suspended sediments in this urban watershed, all of them presented signals of anthropogenic enrichment two or more times bigger, above the background values and the CONAMA (2004) levels even it is a non-industrial area. The results suggest a high enrichment of the local sediment with these metals. The concentrations of these elements vary temporally during storms due to input of streets runoff containing elevated concentrations of elements associated with vehicular traffic and other anthropogenic activities. In general, they have their most concentrations on the streets but they are carried to the channel during the storms. Then, it is possible to say that the contamination of the urban area reflected in the results obtained in the fluvial suspended sediments.

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