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The distribution of metals (Co, As and Zn) in a residential urban watershed, typical of the Brazilian suburbs

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Abstract Environmental contamination by heavy metals has been a constant concern in areas with industrial activity. However, little research has been devoted to the presence of metals in residential areas, especially in the urban periphery. In Brazil, these areas are characterized by disordered urban development and mixed land use, including homes, businesses and services. There is normally no control over point source pollution (domestic sewage, motor oils) in these areas, much less non-point source pollution (sediment from paved and unpaved roads). This study seeks to investigate the concentrations of Co, As and Zn in soil and aquatic environments in a 0.83 km^2 urban watershed in the metropolitan region of Porto Alegre, in southern Brazil. Forty-seven samples per km^2 were collected from paved and unpaved roads, vegetated areas, the riverbed and its banks. The presence of metals in suspended fluvial sediment was also studied, and sequential extraction was performed to evaluate the geochemical fractions occupied by these metals. Analysis indicates that the metals in question are widely distributed throughout the study area, with higher concentrations in streets with more intense automobile traffic. The metals were found in concentrations above the background values in fluvial sediment; however, sequential extractions showed that both Co and As are found mainly (>50%) in the crystalline phase, offering little risk to the aquatic environment. On the other hand, Zn was distributed among the easily reducible (12%), oxides (41%) and carbonates (20%), representing greater mobility in the aquatic environment in the event of changes in the pH and/or Eh of the water. This non-industrial study area presented high concentrations of the three metals studied, but only Zn poses significant risk of contaminating the aquatic environment.

Key words urban sediments; metals; sequential extraction

INTRODUCTION

The increase in the frequency of pollution and flooding in streams and rivers, in addition to gulley erosion and health problems, are part of the disorganized occupation of the urban space. Sediment in the hydrological cycle of urban watersheds represents the consequences of unsustainable urban growth characterized by population increase, disordered growth of the urban environment and damage to the natural environment, especially the channel and riparian zones. The permeable soil is replaced by impermeable surfaces such as roads, roofs, parking lots, and sidewalks that store little water, reduce infiltration of water into the ground, and accelerate runoff to ditches and streams (USGS, 2003). The sediments are an important part of this process through not only problems of sedimentation, but also contamination by sediment-associated pollutants. Horowitz (1991) clearly shows that as suspended sediment concentrations increase, the percentage contribution from suspended sediment-associated trace elements also increases.

There are many causes that can generate sediments in urban areas, but the most important are related to sparse vegetation cover, the lack of urban infrastructure (street pavement, network of sewers and drains, retention basins), and the failure to enforce planning controls. 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). Therefore, studies of sediment quality represent an important focus in environmental evaluation, protection and management of aquatic ecosystems.

Generally, most of the studies of sediment-associated heavy metals in suspension and/or in the streambed have been concerned with evaluating only the total concentration of these metals, which is not always sufficient to indicate their pollution potential (Poleto & Teixeira, 2006). Many studies (e.g. Hursthouse, 2001) have observed that these pollutants can be found in many forms, and the use of total concentrations as a criterion for evaluation of potential effects implies different forms have the same impact, which is unsustainable (Tessier *et al.*, 1979). Therefore, it is of great importance that the studies of metal contamination in aquatic ecosystems take into consideration not only the total metal concentration but also the geochemical fractions where these metals are found.

OBJECT OF INVESTIGATION

This study evaluates the concentration and geochemical fractions of metals, such as cobalt, arsenic and zinc, in order to infer the conditions that will allow the release of these metals adsorbed onto suspended sediments in aquatic environments.

The urban sub-watershed under study is located at Vila Santa Isabel in the city of Viamão, which lies within the metropolitan region of Porto Alegre city, capital of the state of the Rio Grande do Sul, in the south region of Brazil (Fig. 1). The study area is a non-industrial urban watershed with an approximate area of 0.83 km^2 and, according to Poleto *et al.* (2005), can be considered representative of peripheral regions in Brazil. The relief is nearly gently sloping and parent material is granite-gneiss. The predominant soil units are a complex Humic Hapludult and Umbric Dystrochrept and Humic Hapludult Umbric Dystrochrept and Udarent (DNPEA, 1973).

Although the climate of the region is generally subtropical, the substitution of polar for tropical air masses generates abrupt falls in the temperature, which may continue for several days. The long-term averages (1912–1997) of selected climatic parameters are presented in Table 1 (Livi, 1999).

The study stream (Fig. 2) instrumented for the collection of suspended sediment samples is located in the Arroio Mãe d'Água watershed, which contributes, in turn, to the main watershed of the Arroio Dilúvio. The latter includes the barrage of the Hydraulic Research Institute at UFRGS. According to Poleto *et al.* (2005), ~42% of the study area had an impermeable cover in 2005.

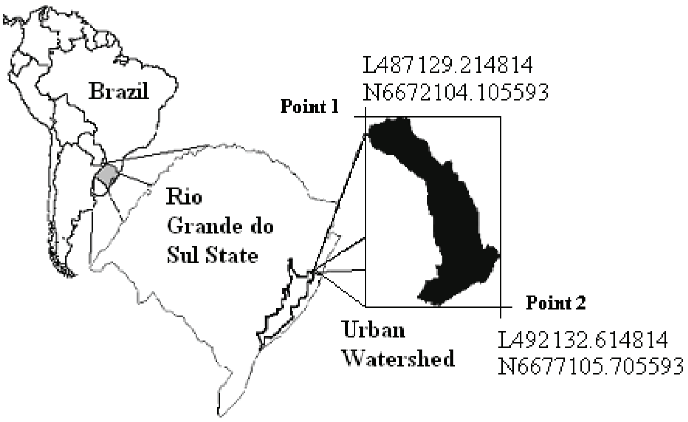

Fig. 1 Location of the study area in Brazil and in the state of Rio Grande do Sul. Adapted from Poleto *et al.* (2005).

Table 1 Climatic parameters for the metropolitan region of Porto Alegre.

Average air temperature	19.4°C
Maximum air temperature	24.9°C
Minimum air temperature	15.2°C
Mean annual maximum absolute air temperature	37.8°C
Mean annual minimum absolute air temperature	1.4°C
Annual sunshine (duration)	76%
Average annual precipitation	1310 mm
Average number of rain days during the year	135

Adapted from Livi (1999).

Collection of suspended sediment, urban dust and background samples

The collection of suspended sediment samples began at the end of 2003, as part of a programme of staff training and equipment testing, and finished at the end of 2006.

As most of the sediment load is transported by outflows generated by precipitation, sample collection was undertaken during rainy days at the outlet of the study catchment. Samples were taken using an US DH-81 sampler from two verticals located at 0.6 and 1.2 m from the left bank. The samples were collected in 20-litre polypropylene containers and were stored for 24 hours before centrifuging to concentrate the sediment. The centrifuged samples were dried at a maximum temperature of 40°C for approx. 7 days. The dry samples were transferred to 50-ml polypropylene bottles and frozen. Contact with metal implements was avoided to prevent contamination (Horowitz, 1991; Mudroch & Azcue, 1995; Mudroch *et al.*, 1997).

Collection of urban dust samples (47 samples per km^2) was undertaken to sample the main diffuse sources of the urban environment, including paved and non-paved streets, unvegetated areas, and river bed and banks. The aim was to collect representative samples from the source areas and this involved compounding samples from representative areas.

All the containers and glassware involved in the collection procedure were washed with distilled water, kept in nitric acid solution of 14% (v/v) for 24 hours and then rinsed with deionized water before use.

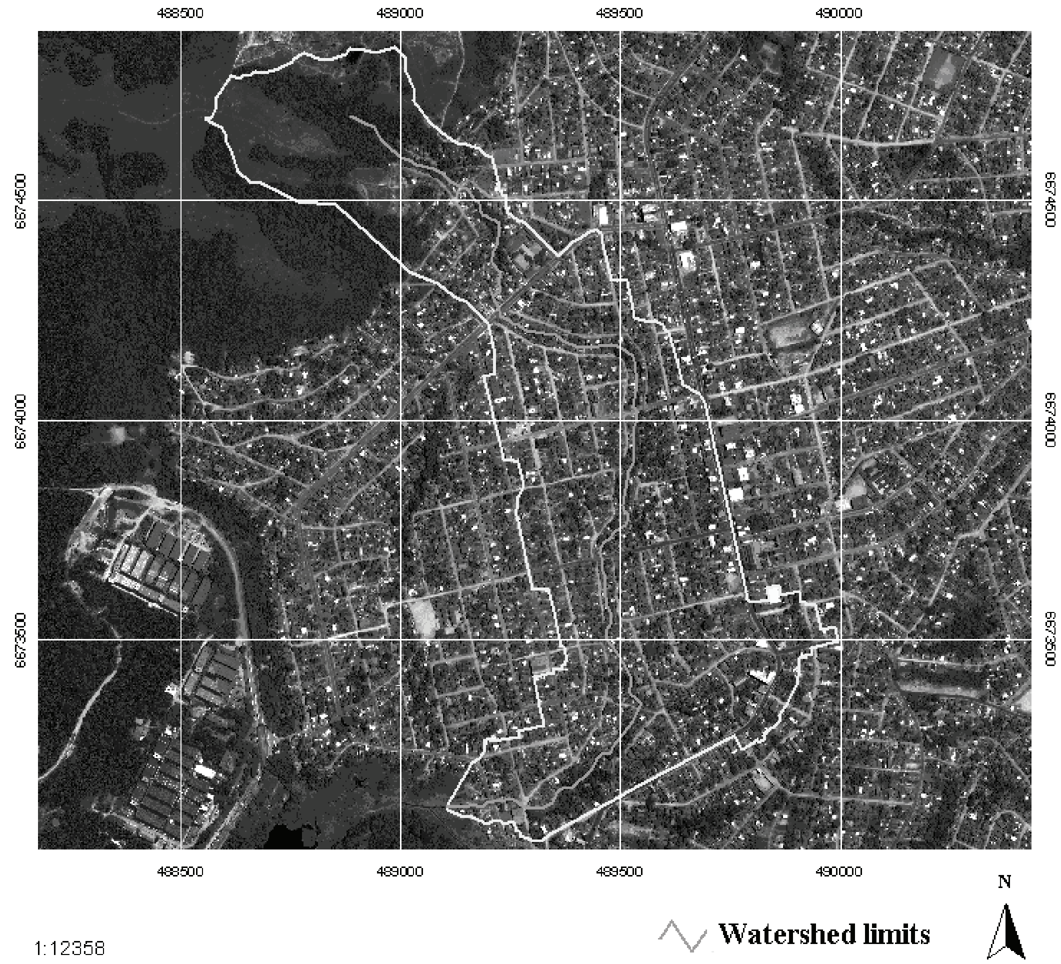

Fig. 2 Limits of the urban watershed (study area) and its stream. Based on Cardoso *et al.* (2006).

Characterization of suspended sediments and background samples

Mineralogical analysis was undertaken on both suspended sediments and background soil samples. The granulometry of the samples was determined by laser diffractometry using a Cilas 1180 analyser, after removal of organic matter with hydrogen peroxide (H_2O_2) and dispersal by ultrasound (Poleto *et al.*, 2006). Total organic carbon (TOC) of selected samples ($N = 84$) was determined using a TOC–V CSH analyser.

Twenty-five samples of fluvial suspended sediment were subject to acid digestion ($HCl - HF - HClO_4 - HNO_3$) to determine the total concentration of metals (Horowitz *et al.*, 2001). Care was taken to use very pure reagents (Merck®) and water (Milli-Q type) in this process. Results were compared to background soil samples after correction for particle-size differences.

The trace elements selected for study were cobalt (Co), arsenic (As) and zinc (Zn) and the sequential extraction procedure was based on the protocol developed by Tessier *et al.* (1979) and allows speciation into five phases (exchangeable, $CaCO_3$, Fe oxides, organics and residual or crystalline) (Fig. 3).

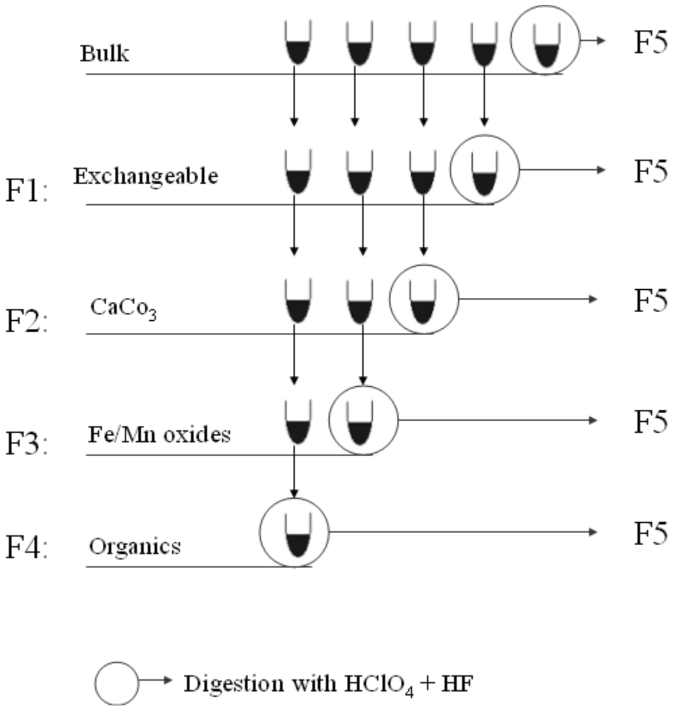

Fig. 3 Schema of the sequential extraction process. Adapted from Poleto & Teixeira (2006).

In this procedure, samples previously dried and frozen were homogenized in an agate mortar, and 0.5 g weighed out for each phase of the sequential extraction. In all the phases of the extractions, the samples were analysed in duplicate using blank samples, and all reagents were freshly prepared.

Half of the analyses were carried out in Brazil at the Federal University of Rio Grande do Sul (UFRGS) and half in the Laboratories of the US Geological Survey in Atlanta, USA, in order to allow quality control.

RESULTS AND DISCUSSION

Assessment of potential environmental risks from sediments

In order to assess the possible ecological impact of sediment-associated metals, the Co, Zn and As concentrations in suspended and background sediment samples were compared (Figs 4, 6 and 7).

The cobalt concentrations presented in suspended sediment samples had an average value of 24.16 μg g^{-1} and a standard deviation of 8.91, and for the most part exceeded background levels. Only three samples had concentrations below this limit, and this suggests suspended sediment increases the level of this contaminant. The spatial distribution of Co concentrations is shown in Fig. 5.

The major areas of high Co concentrations were on the paved streets and in the downstream portion of the catchment, the latter reflecting transport of metals from the streets to the stream in storm conditions.

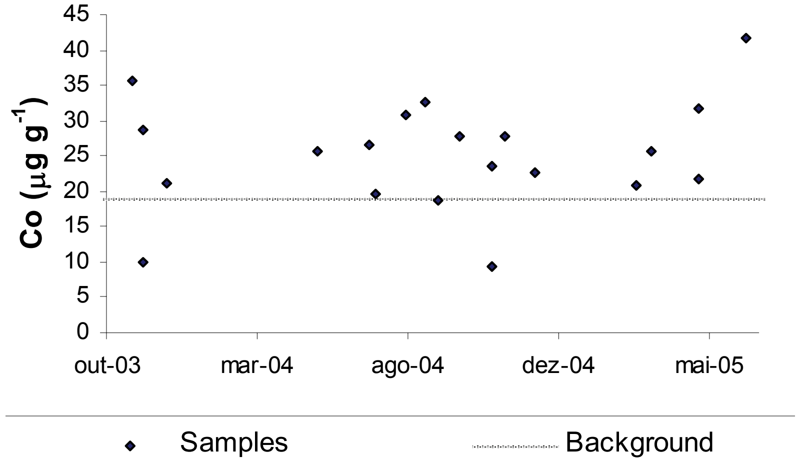

Fig. 4 Frequency of Co concentrations in urban suspended sediments, compared with background values (dashed horizontal line).

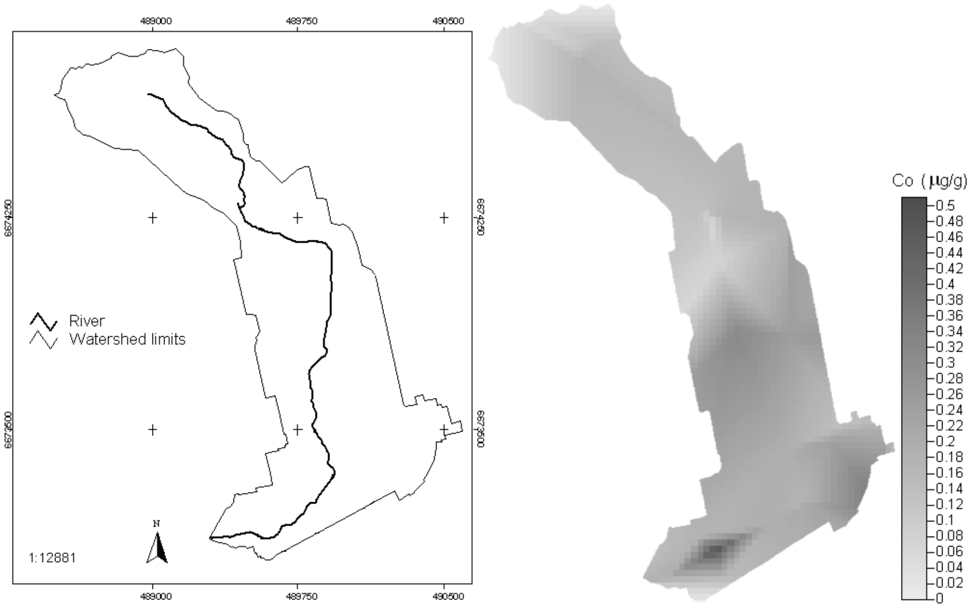

Fig. 5 Distribution of the Co concentrations in the urban area.

The results for Zn show that all of the suspended sediment samples had concentrations above the reference (background) value (Fig. 6). The average concentration for the suspended sediment samples was 326.16 µg g^{-1}, with a standard deviation of 108.64, which is similar to that found in a study of urbanized areas in Hawaii (De Carlo *et al.*, 2004). The results from the present study suggest the local sediment has been highly enriched with Zn.

The average concentration of As in suspended sediment samples was 66.34 µg g^{-1}, with a standard deviation of 21.79. Individual concentrations were in some cases more than twice the background values, and only 20% of the samples were below this reference level (Fig. 7).

The spatial distribution of As in the urban area is shown in Fig. 8, and it can be observed that the major concentrations are in some paved streets, which experience

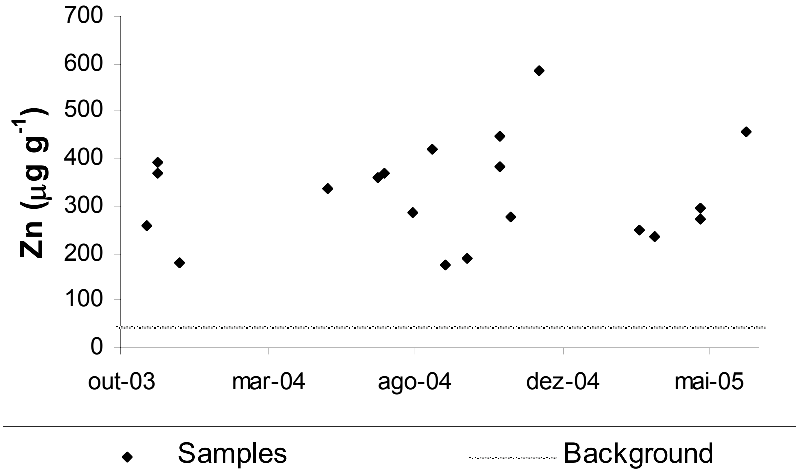

Fig. 6 Frequency of Zn concentrations in urban suspended sediments, compared with background values (dashed horizontal line).

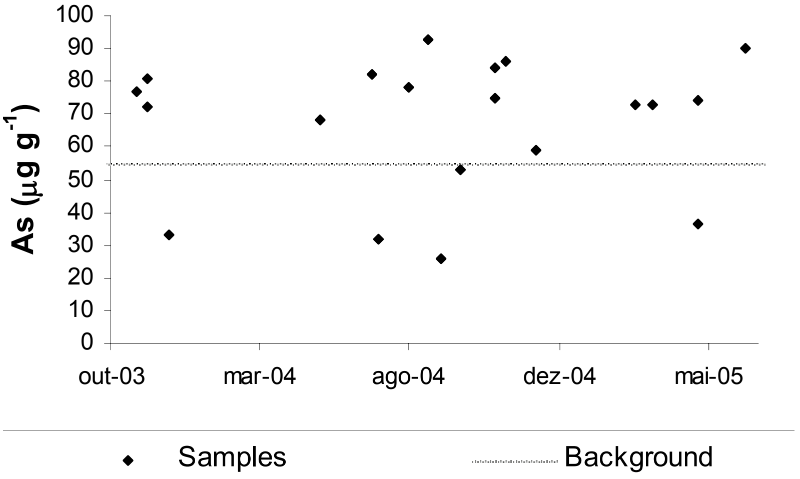

Fig. 7 Frequency of As concentrations in urban suspended sediments, compared with background values (dashed horizontal line).

more car movements, and near to the watershed outlet in an area of sediment deposition.

The concentrations of these elements vary temporally during storm events, because of inputs of road runoff containing elevated concentrations of elements associated with vehicular traffic and other anthropogenic activities.

Geochemical partitioning of metals (sequential extraction)

The analysis of the total concentrations is not sufficient to fully evaluate risks of metal contamination in the environment, and information on fractionation of metals is required. Data on the chemical fractions of Co, As and Zn in the fluvial suspended sediments of the study watershed are presented in Fig. 9 and Table 2. The chemical fractioning for the Co, As and Zn in fluvial suspended sediments for the urban

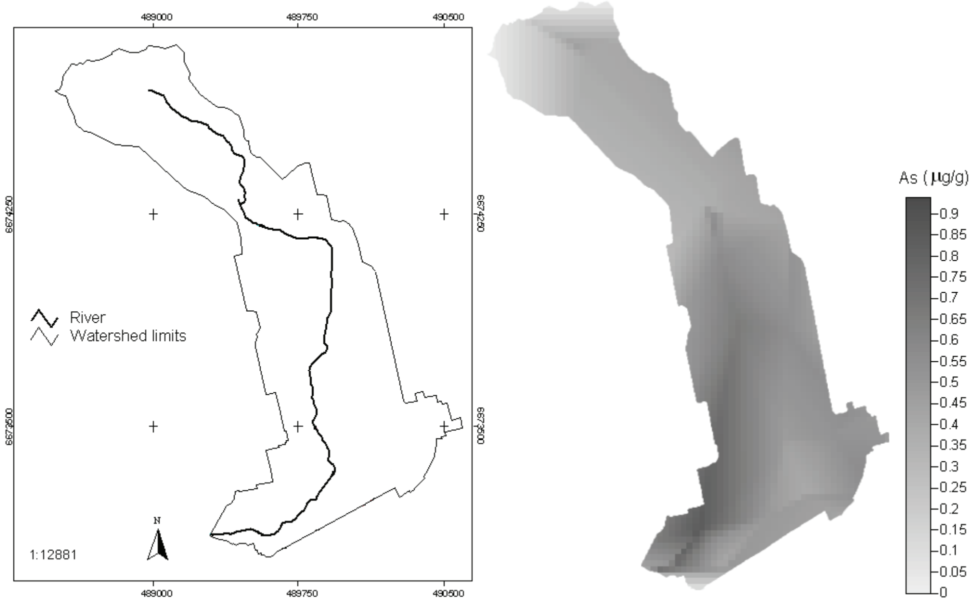

Fig. 8 Distribution of As concentrations in the urban area.

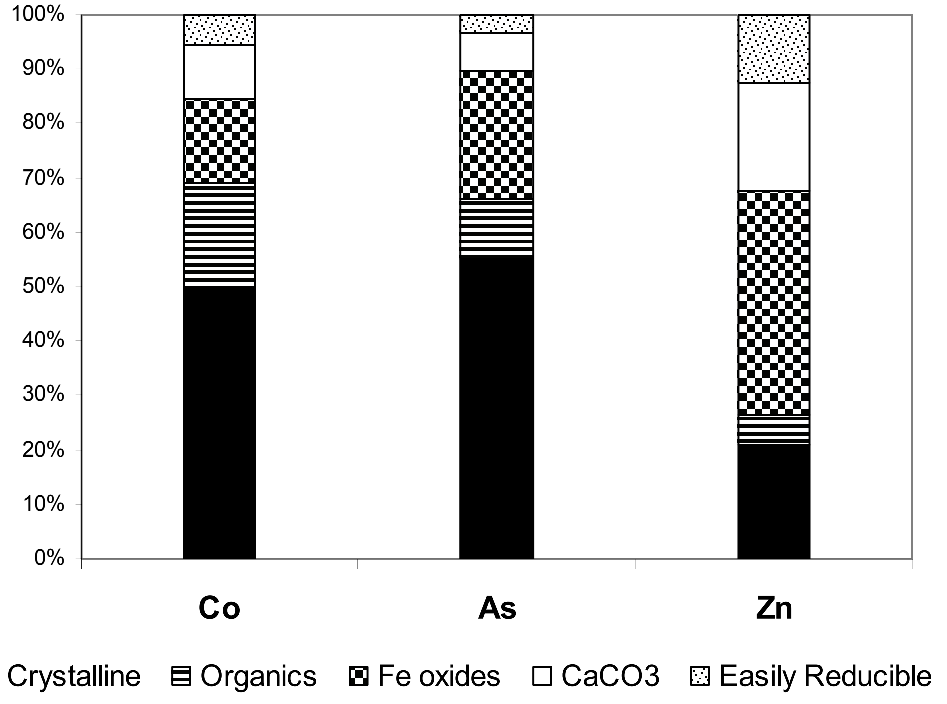

Fig. 9 Chemical partitioning of selected trace elements associated with suspended sediment.

watershed under study are presented in Fig. 9. Table 2 presents the average distribution of the concentrations of the three elements in the five phases.

Cobalt and As are found predominantly in the residual phase, 50% and 55.1%, respectively, while Zn has its bigger concentration in the oxide fraction (41.3%). The oxides also represent an important fraction for the As (23.6%). The metals in the oxide

Table 2 Results of sequential extraction for metals (%) in urban sediments samples. (see Fig. 3 for key to phases).

	Extraction phases: F1	F2	F3	F4	F5	Total (µg g^{-1})
Co	5.4	10.1	15.4	19.1	50.0	24
As	3.4	7.0	23.6	10.9	55.1	66
Zn	12.4	19.9	41.3	5.4	21.0	326

Table 3 Metal distribution in the samples of urban sediments indicating total and labile metal concentrations (exchangeable + carbonate).

	Total concentrations (µg g^{-1})	Labile metal concentrations (F1 + F2) (µg g^{-1})
Co	24	7
As	66	7
Zn	326	105

fraction are relatively mobile in aquatic environments, since they are dependent on alterations in the values of redox (Eh). Changes in redox conditions are favoured in the study catchment by the high levels of organic matter (average TOC in the suspended sediment samples is 6.38%).

The percentage of As and Zn in the organic fraction is smaller than 10%, but for Co, it is more important and approaches 20%. These results agree with various published studies. In the study area, the attachment of the trace elements to the organic material presented is thought to reflect the effects of an illegal sewer.

Metals contained in phases 1 and 2 (exchangeable and carbonates) can be easily released when pH is lowered and are more mobile than those associated with other fractions (Banerjee, 2003). Table 3 shows that a high proportion of Zn, more than 30%, is held in labile fractions, but this proportion is lower for Co and As. Nevertheless, concentrations of all three metals are relatively high and pose a potential threat to the environment.

CONCLUSIONS

Anthropogenic enrichment, in the order of two to three times greater than background levels, was evident for the three elements studied (Co, As and Zn) in samples of fluvial suspended sediments in the study watershed, which although urbanized did not contain industrial activity. In general, highest concentrations were found in streets, but metals were transported to the river channel during storms. Zn was the most closely associated with labile fractions and was susceptible to release with changes in pH levels. In addition, this element also appeared predominantly attached to oxides and was at risk of release with redox changes. Further studies are required to identify measures that can remediate risks of metal contamination in the study catchment.

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