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THEMATIC ISSUE

Assessment and evaluation of metal contents in sediment and water samples within an urban watershed: an analysis of anthropogenic impacts on sediment and water quality in Central Brazil

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Abstract The aim of this study was to assess the distribution of metals in sediments and surface water within the Lago Paranoá catchment in Central Brazil, and to evaluate metal enrichments due to anthropogenic activities. Concentrations of Al, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Sr, Ti and Zn were analyzed in sediment samples from sediment sources under different land uses, in alluvial sediment profiles, and in water samples. Principal component analysis was used to investigate the impact of different land use types on metal concentrations in source sediments. The anthropogenic impact of different land uses on metal concentrations in sediments was quantified by the calculation of enrichment factors, using the local geological background as reference. The data showed that different anthropogenic activities are related to specific metal enrichments in source and alluvial sediments. Particularly urban areas with high-density block development were characterized by higher enrichments of Cd, Cr, Pb, Sr and Zn compared to the local background values. Sediments from agricultural areas had higher concentrations of Cr, Cu and Ni compared to urban areas, which is caused by higher contents of clay and not due to human impact. The concentrations of Cd, Cr, Cu and Pb in surface water samples of the main rivers discharging into Lago Paranoá were very low. The values of Al, Fe, Mn, Sr and Zn differed between the sub-catchments and showed seasonal variation. Metal concentrations depended substantially on terrestrial inputs from anthropogenic and natural sources. The analysis of effluent water samples indicated that there is a temporary metal input into the lake from the two wastewater treatment plants, which might have caused metal enrichments in sediments and water. The regression analyses showed that there is a strong correlation between metal concentrations in alluvial sediments and corresponding water samples, as well as between metal accumulation in the alluvial sediments and shares of urban areas in the sub-catchment.

Keywords Metal enrichment · Sediments · Sediment sources · Water · Urban catchment · Brazil

Introduction

Many South American cities are experiencing a rapid population growth, frequently coupled with disorganized regional development. As such, many urban areas are characterized by a high degree of modification of their physical, chemical, and biological environment due to the construction of buildings and infrastructure (Taylor and Owens 2009). Compared to natural ecosystems the hydrological and sedimentological processes in urban basins are significantly different. Urban agglomerations are

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characterized by an alternation of areas with impervious land surfaces, like roads, roofs, or parking lots and unsealed areas with or without vegetation. Human-made structures and construction sites increase surface runoff, which in turn cause sediment mobilization from bare soil areas (de Carvalho et al. 2014). Due to reduced rates of infiltration and higher surface runoff the transport of sediments to watercourses is increasing (Poleto et al. 2009). Additionally, the abundance of contamination sources in urban areas results in geochemical modification of the sedimentary environments potentially causing high pollution concentrations and loadings in soils, sediments and water bodies (Duh et al. 2008; Horowitz and Stephens 2008; Laidlaw and Filipeli 2008; Wong et al. 2006), which in turn might have detrimental impact on human and ecosystem health. It was shown that most of the contamination load in rivers and lakes is associated with the sediment fraction (Horowitz 2008; Savenko 2006; Viers et al. 2009).

Metals, particular heavy metals, which represent potential contaminants to aquatic systems that are transported in dissolved or particulate form, have received considerable attention within urban catchments (Barcellos et al. 1991; Behrendt 1993; Foster and Charlesworth 1996; Karez et al. 1994; Salomons and Förstner 1984). Almost all of the studies have focused on concentrations and fates of dissolved contaminants, but less attention has been given to sediment-associated contaminants (Salomons and Förstner 1984). Nevertheless, focus on sediments and sediment related discharge in aqueous systems and the impact on the water quality was already addressed by Förstner and Müller (1974), Förstner and Wittmann (1981) and others (Bilotta and Brazier 2008; Owens 2008; Owens et al. 2005; Viers et al. 2009). Hence, the sediment quality has to be integrated in water resource management (Brils 2004; Förstner 2002).

In the past, the element content of urban sediments has been related to element accumulation in sediments on paved surfaces (Taylor 2007). Recent studies have shown that urban sediments and sources can be categorized in a broader manner to refer to any sediment present within urban environments (Franz et al. 2013a). Sources of sediments in river basins can be divided into (1) (semi-) natural sources, including mass movements (e.g. debris flows, landslides) and erosion of soils, and (2) sediments generated by anthropogenic activities, such as mining, construction, urban road network, and industrial point sources. In spite of water quality improvement many rivers and water reservoir still possess low sediment quality (Taylor and Owens 2009). Since residence time of sediments in rivers and reservoirs is much longer than that of water, sediment pollution can be considered as long-term problem in “urban” catchments (Taylor and Owens 2009; Walling et al. 2003). The necessity to consider sediments in water quality management at the watershed scale has been conclusively established and documented by the introduction of policy and legislation (Apitz and White 2003; Owens 2005, 2008). The European Water Framework Directive (WFD) and the Program of Measures (POM) are examples of the incorporation of sediment issues in river basin management within the European Union (Casper 2008). In South America by contrast, and particularly in Brazil, only few quality indices for water and sediments have been established so far (Brazil: CONAMA 1986, 2005; CAESB 2001, 2010). The implementation of environmental quality standards, which include water, sediment, biota, and their interaction at catchment scale is still lacking.

Within the urban conservative sediment cascade (Fig. 1), the processes, relationships and interactions between sediment sources, transport mechanisms, deposition, and post-depositional modification of sediment are complex and characterized by highly dynamic behavior (Taylor 2007). Urban areas have an important contribution to metal enrichments in sediments, particularly that of heavy metals (Molisani et al. 2007; Moreira 1996). In urban environments, metal dispersal and the release in the environment are part of daily human activities (Bailey et al. 2005; Fernandes et al. 1994; Irvine et al. 2009; Moreira

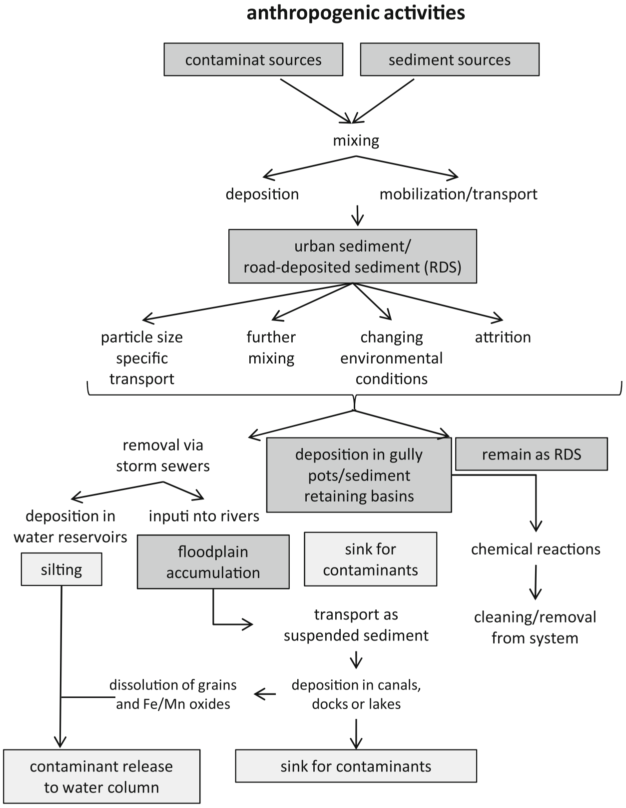

Fig. 1 The conservative urban sediment cascade [(Adapted from Taylor (2007)]

1996; Poleto et al. 2009; Poleto and Charlesworth 2010; Taylor and Owens 2009).

However, in Brazil most studies have focused on pollution by heavy metals due to mining activities, tanneries, industry parks or landfills (Barcellos et al. 1991; Jordão et al. 1997; Machado et al. 2002; Melamed et al. 1997; Villas Bôas 1997) or have provided information about heavy metal accumulation in costal and estuarine environments (Amado Filho et al. 2004; Barcellos et al. 1991; Bailey et al. 2005; Gomes et al. 2009; Karez et al. 1994; Lacerda and Molisani 2006). For the Distrito Federal there are several studies dealing with anthropogenic influence on the Lago Paranoá (Echeveria 2007; Fonseca 2001; Maia 2003; Maia et al. 2006; Menezes 2010; Moreira and Boaventura 2003), but less information is available about the relationship between metal enrichments in sediments and urban development within river basins (Franz et al. 2013a, b). To understand processes and interactions between anthropogenic sources of metals, metal transport and deposition of sediments, and the release of metals in streamwater, data of the metal concentrations in sediment sources, in alluvial sediments, and in water samples within the urban river basin are necessary. Information on metal pollution of sediments and water is crucial for integrated water resource management (IWRM), especially in urban catchments.

This study aims to determine the impact of anthropogenic activities, i.e. land use, on metal concentrations in source and alluvial sediments within a rapidly urbanizing catchment and to assess the influence of different land uses on the metal concentration in surface water of the river basin. The Lago Paranoá catchment in Central Brazil, in the center of the Distrito Federal of Brazil offers the unique opportunity to investigate the effects of human activities since 1960 in a region nearly without any previous interference.

Materials and methods

Study area

This study was conducted in the catchment of the Lago Paranoá reservoir, located in western Central Brazil. The catchment of the Lago Paranoá is situated in the city of Brasília (15°48′S and 47°50′W), the capital of Brazil. The region is part of the Cerrado biome (Brazilian savanna) of Central Brazil, at an altitude between 850 m and 1,300 m above sea level (Oliveira and Marquis 2002). The climate is characterized by dry winters (May to September) and rainy summer seasons (October–April), with a mean annual precipitation of 1,600–1,700 mm and a mean annual temperature of 20–21 °C (WMO 2010). A detailed description of the region is given in De Carvalho et al. (2006) and Gonçalves et al. (2009).

The topography is characterized by extensive plateaus and rolling landscape of the Planalto Central. The geological environment is dominated by metapelitic rocks, sandstone and quartzite of the Paranoá Group (Freitas-Silva and Campos 1998).

The Lago Paranoá reservoir is an artificial lake with a surface area of about 38 km^2, formed by the construction of the Paranoá Dam in 1960 (Monteiro and Dias 1980). The Lago Paranóa catchment has a size of 1,046 km^2. Its main tributaries are several small rivers, the Riacho Fundo Creek and Gama Creek in the south, and the Bananal and Torto Creek in the north. Urban land use, including residential, commercial, and infrastructural development, occupies approximately 34 % of the catchment area. Only about 8 % is used for agricultural production and 58 % of the land is in (semi-) natural state. Nevertheless, the land use and urbanization condition varies widely between the five sub-catchments (Fig. 2).

The sub-catchments to the south and southwest of the lake and the central part of Brasília are densely populated (484 inhabitants/km^2) and characterized by intensive construction activities and poorly organized land development with inadequate infrastructure (PGIRH 2006). The area to the north of the lake (Torto and Bananal sub-catchment) is characterized by a less disturbed environment. Large parts of these sub-catchments belong to Brasília's National Park Parque Nacional de Brasilía (Rocha 1994) (Fig. 2).

The Paranoá Lake has been divided into five sections, i.e. A (Riacho Fundo), B (Gama), C (Bananal), D (Torto), and E (Central Paranoá) (CAESB 1976). Two wastewater treatment plants are operating, one at the north part (ETE Norte) and one at the south part (ETE Sul) part of the lake (see Fig. 3 for location of sampling sites).

Sampling and laboratory analysis

Sediment samples

Sites of potential sediment sources were selected throughout the catchment after several field observations during storm events. After the identification of the sediment mobilization hot spots and transport processes operating within the study catchment, source sediment samples ($n = 98$) and alluvial sediment samples ($n = 24$) were collected during the rainy season of 2011. Sediment sources were divided into the land use categories of urban, agricultural, and (semi-) natural. The Riacho Fundo sub-catchment (branch A) is the sub-catchment with the highest disturbance and highest variability of land uses (Gioia et al. 2006; Franz et al. 2013a, b; Menezes 2010). Therefore, the urban, agricultural, and (semi-) natural sampling sites $n = 50$ were further subdivided in specific land use types to obtain the metal concentrations in the sediment according to different anthropogenic activities (Table 1).

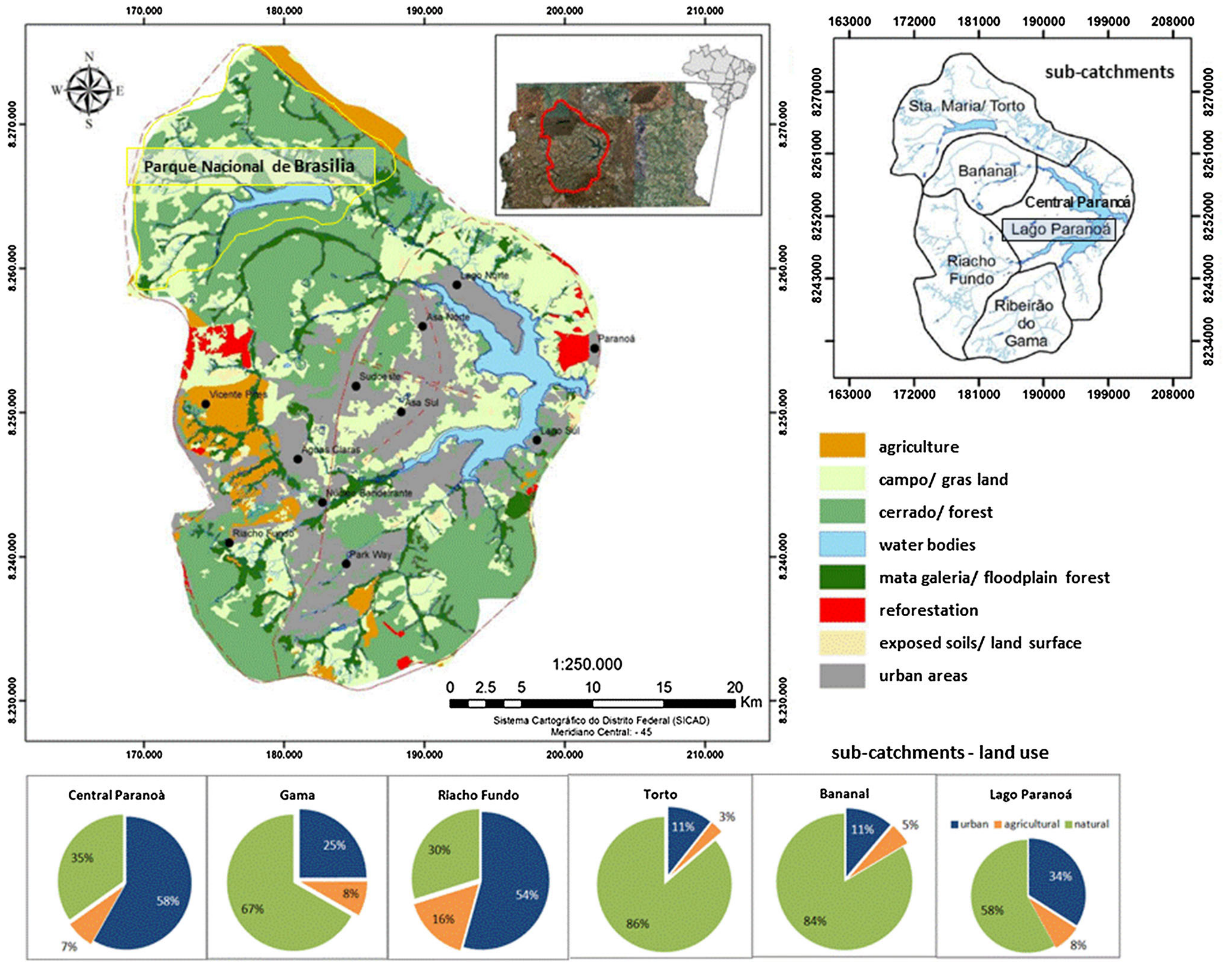

Fig. 2 Land use within the Lago Paranoá catchment and sub-catchments (Menezes 2010)

Samples retrieved from potential sediment sources were surface scrapes (0–5 cm) collected from areas identified as susceptible to mobilization of sediment by water erosion and its subsequent delivery in the river channel system and reservoirs. Subsurface samples were taken from gullies along a transect of about 10–15 m. Each source material sample comprised a composite of smaller scrapes (10) collected in the vicinity of the individual sampling sites (within an area of 100–400 m^2 for the land use categories and within a radius of 15 m for point sources of the land use sub-types) in order to increase the representativeness of the individual samples and of the over-arching sampling strategy.

To determine the metal concentrations in sediments which have been mobilized and transported towards the river channel system recently, profiles of alluvial sediments were sampled: four profiles up to a depth of 40 cm at each tributary to Lago Paranoá (sediment profiles in branches A, B, C, and D) and two profiles in the central part of the lake (branch E) (Table 1). Branch E shows only several small inflows (Fig. 3). The sites (rivers discharging to branch A–E) were identified as being regularly inundated during floods, and are therefore frequently subject to overbank deposition or to deposition in active silting zones at the Lago Paranoá.

All samples were collected using a non-metallic trowel, which was repeatedly cleaned to avoid inter-sample contamination. The rather homogenous metal concentrations of the bedrock and the small variation of top soils types across the catchment allowed for using mean values of metal concentrations as representative geological background values for the whole.

The sediment samples were dried at 40 °C until a constant dried mass was reached, then sieved (<2.0 mm), and ground using an agate mortar (with the exception of the texture analysis).

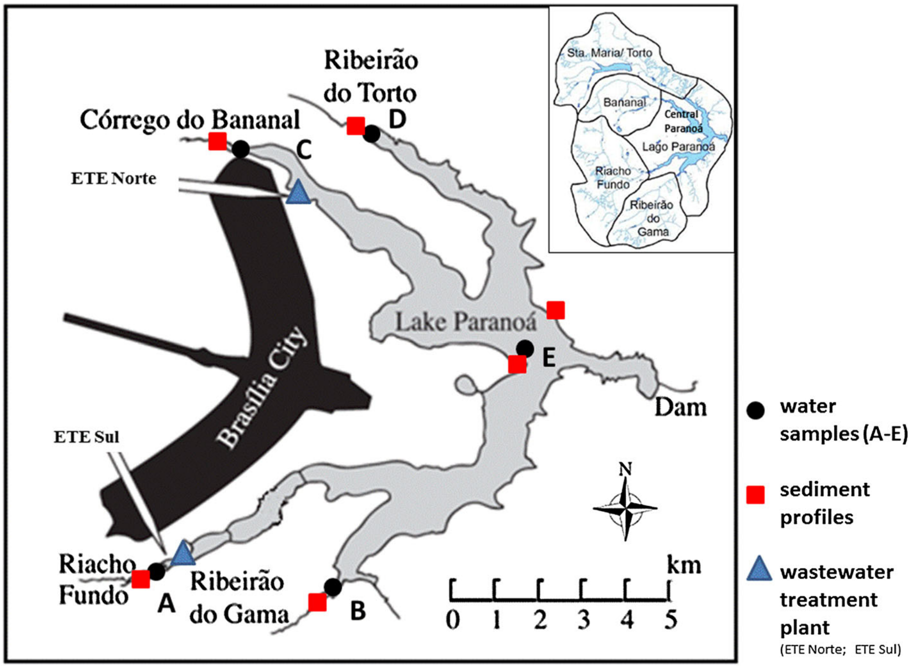

Fig. 3 Sampling sites of the water samples (branch A to E, wastewater treatment plants ETE Norte and ETE Sul) and alluvial sediment profiles (Menezes 2010; Padovesi-Fonseca et al. 2002)

The sample preparation process for the metal analysis (Al, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Sr, Ti, Zn) by atomic absorption spectrometry (Spectro Ciros CCD) includes dissolution by HNO_3 and microwave digestion (DIN ISO 14869-1 2003). This yields the total elemental load for the size class <2.0 mm, but does not discriminate the metals adsorbed to organic versus inorganic sediment particles (Impellitteri et al. 2002; Sun et al. 2001). Certified analytical grade reagents were used throughout the process. In addition, blanks were run through all experiments to detect any potential contamination.

Texture analysis was carried out according to the Köhn pipette method after the removal of the organic fraction and chemical (sodium pyrophosphate) and physical dispersion (ultrasonic treatment) (DIN 19683 1973). The pH values were measured electrometrically in soil–water suspension using “Bidest. water” and 0.01 M $CaCl_2$ (DIN ISO 10390 2005).

Water samples

Aqueous grab samples were collected from the river water to the branches of the main tributaries in the Lago Paranoá: Riacho Fundo (A, $n = 4$), Gama (B, $n = 4$), Bananal (C, $n = 4$), Torto (D, $n = 3$), and in the central part of the lake (Paranoá Jusante = Central Paranoá E, $n = 3$) were taken in different months. The sampling campaign was undertaken during the dry and rainy periods of 2011 and 2012 in collaboration with the Brazilian water supplier ‘Companhia de Saneamento Ambiental do Distrito Federal (CAESB). Additional 28 composite samples (time-proportional) were collected between 2010 and 2012 from the effluents of the two main wastewater treatment plants ETE Sul ($n = 12$) and ETE Norte ($n = 16$) during working weeks. The sites of the water samples are shown in Fig. 3.

Measurements of total metal concentrations were performed by means of inductively coupled plasma optical emission spectroscopy (ICP-OES) using a Vista-Pro CCD simultaneous ICP-OES spectrometer (Varian). The aqueous samples were filtered prior to analysis by using 0.45 µm membrane filters (cellulose acetate, 25 mm syringe filters) and acidified with HNO_3 (65 %, suprapur, Merck). Samples were diluted with MilliQ water (Millipore) according to the calibration range set for the different elements. Calibration was set from 5 to 2,000 µg/L, the standard deviation SD is ±2 % for each element.

Data analysis

Descriptive statistical analyses of the samples were performed as the first approach for the evaluation of the metal concentrations. Skewness and kurtosis were calculated with a Microsoft Excel software package (2007) to test for normal distribution. The relation between the metals was analyzed by using Pearson’s correlation coefficients and principal component analysis (PCA). The PCA allows the identification of the components responsible for the total variation of the data and the variable groups that explain these variations, which cannot be obtained by Pearson correlations. PCA with scaling focused on inter-species correlations were performed using the software package XLSTAT for WINDOWS 7 Excel (Microsoft). Varimax

Table 1 Sediment source categories and land use types (including the number of source sediment samples) and alluvial sediments collected within the whole Lago Paranoá catchment and the Riacho Fundo sub-catchment

Land use category	Lago Paranoá catchment ($n = 98$)		Land use sub-types	Riacho Fundo sub-catchment ($n = 50$)
Source sediments				
Urban	60	12	Construction sites	5
		13	Highway	3
			Paved road	3
			Unpaved road	3
		–	Ditches	3
		35	Residential area	5
			Detached/semi-detached houses	4
			High-density block development	4
			Rural residential area/nucleo rural	3
Agricultural	22	4	Farm track	3
		14	Crop land	4
		4	Pasture	3
Natural	16	11	Campo/cerrado	4
		–	Gully	3

Sub-catchment	Sediment profiles (0–40 cm depth) ($n = 6$)	Sediment samples ($n = 24$)
Alluvial sediments		
Riacho Fundo	1	4
Gama	1	4
Bananal	1	4
Torto	1	4
Central Paranoá	2	8

rotation was used to maximize variation explained by the components. A binary correlation matrix was computed for all land use categories to check for high correlations among metal concentrations indicative for the characterization of a specific land use category. The results of the PCA include the percent of variation explained, and reveal groupings of variables with respect to their different land use categories.

For each of the potential sediment source sets, the anthropogenic influence on metal concentrations was evaluated using the enrichment factor (EF) with the local mean geological concentrations as background (Blaser et al. 2000). The EFs of the metals Al, Cd, Cr, Cu, Fe, Ni, Mn, Pb, Sr, and Zn have been calculated according the following Eq. (1):

$$\mathrm{EF} = \frac{\frac{\frac{C(x)}{C(n)\text{sample}}}{Cx}}{Cn\ (\text{local background})} \times Z \qquad (1)$$

where Cx is the concentration of the x metal whose enrichment is to be calculated, and Cn is the concentration of the N normalizing element (Ti) assumed to be uniquely characteristic of the background (Burak et al. 2010; Franz et al. 2013a; Freitas-Silva and Campos 1998).

For this study, the ambient consists of samples from potential sediment sources and alluvial sediment profiles (depth 40 cm) in the silting zones of the Lago Paranoá. The local background values are taken from samples of the natural areas with Cerrado vegetation. A particle size correction factor Z was incorporated into the enrichment factor algorithm, particle size exerts a major influence upon element concentrations (Filipek and Owens 1979; Thorne and Nickless 1981; Horowitz and Elrick 1987).

The results of the total metal concentration in the alluvial sediments and water samples of each main river discharging to the branches (A, B, C, D) and of the Central Paranoá (E) were compared with the indices of water and sediment quality, defined by the CETESB (Companhia de technologia de sanemento ambiental—Company of Environmental Sanitary Technology from the Office of Environment of Sao Paulo State, Brazil). CETESB is a Brazilian State Agency that proposed the first tabulation of guidance values for metals to identify maximum acceptable values of contamination in Brazilian soils, sediments and water (CETESB 2001, 2005). Beside the reference values, CETESB (2005) also proposed prevention and intervention values. Concentration values above the prevention values suggest a potential risk to human health, which already exists, if the metal concentrations are above the intervention values.

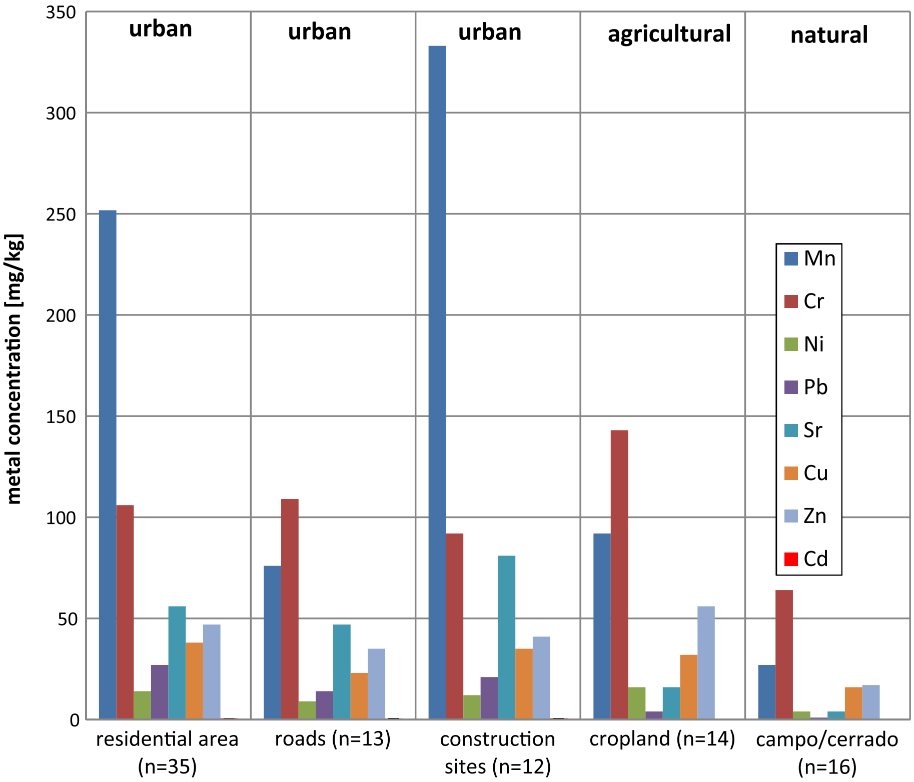

Fig. 4 Mean values for metal concentrations in source sediments within the Lago Paranoá catchment

Regression analyses were used to compare the metal concentration in the alluvial sediments and in the water samples of each sub-catchment and to examine the correlation between metal concentration in sediments and area of urban land use.

Results and discussion

Metal concentrations and EFs in potential source sediments

The metal concentrations in sediments of potential sources with respect to specific land uses (urban, agricultural, and (semi-) natural) are different from each other (Fig. 4).

In general metal concentrations in urban and agricultural source sediments are higher than those from (semi-) natural sites. Sediments from urban areas have higher concentrations of Cr, Cu, Mn, Ni, Pb, Sr and Zn. The concentrations of Cd are low (<200 µg/kg).

Urban sediments are likely to contain higher concentrations of metals due to runoff from urban surfaces, such as from metallic surfaces (Cr, Ni, Pb) or weathered paint of buildings (Cr) (Granier et al. 1990). However, the concentration of elements vary between the urban sites with different anthropogenic activities (land use subtypes). The highest values for Sr (81 mg/kg) and Mn (333 mg/kg) are found in sediments from construction sites. Building materials, like steel and alloys are assumed to be the primary sources of these elements (Granier et al. 1990).

The highest concentrations of Pb (27 mg/kg) are measured in sediments from residential areas, which exceeds the natural background value by about 27 times. Potential anthropogenic Pb sources are household goods and automobiles, including alloys, batteries, cable coatings and pigments (Taylor and Owens 2009). In addition, sediments from residential areas and construction sites are characterized by higher mean concentrations of Cu (35; 38 mg/kg) and Ni (14; 12 mg/kg) compared to the natural background (Cu: 14 mg/kg; Ni: 5 mg/kg). Cu–Ni alloys are commonly used for mechanical and electrical equipment, medical equipment, zippers, jewelry items, and as material for strings instruments (Copper Development Association 1982).

In sediments from agricultural areas the concentration of Cr (143 mg/kg), Cu (32 mg/kg) and Zn (56 mg/kg) are higher than in urban sediments. However, sediments from agricultural areas are characterized by higher contents of clay (59–63 %) and silt (11–27 %) than sediments from urban (clay: 12–40 %; silt: 10–32 %) and natural sites (clay: 32–48 %; silt: 24–27 %). Clay and silt rich soils are likely to contain higher amounts of these metals, which are preferential adsorpted by the fine fraction. Therefore, the higher metal concentrations are rather caused by textural variability than by human impact.

Table 2 Enrichment factors of metals (EFs: mean values) in source sediments within the Lago Paranoá catchment

Enrichment factors	Al	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Sr	Zn
Residential area	2.8	8.5	1.7	2.4	2.7	9.3	3.5	27.0	14.0	2.8
Roads	2.1	7.5	1.7	1.4	2.2	2.8	2.3	14.0	11.8	2.1
Construction sites	2.6	9.5	1.4	2.2	2.5	12.3	3.0	21.0	20.3	2.4
Agricultural areas	4.5	4.5	2.2	2.0	3.6	3.4	4.0	4.0	4.0	3.3

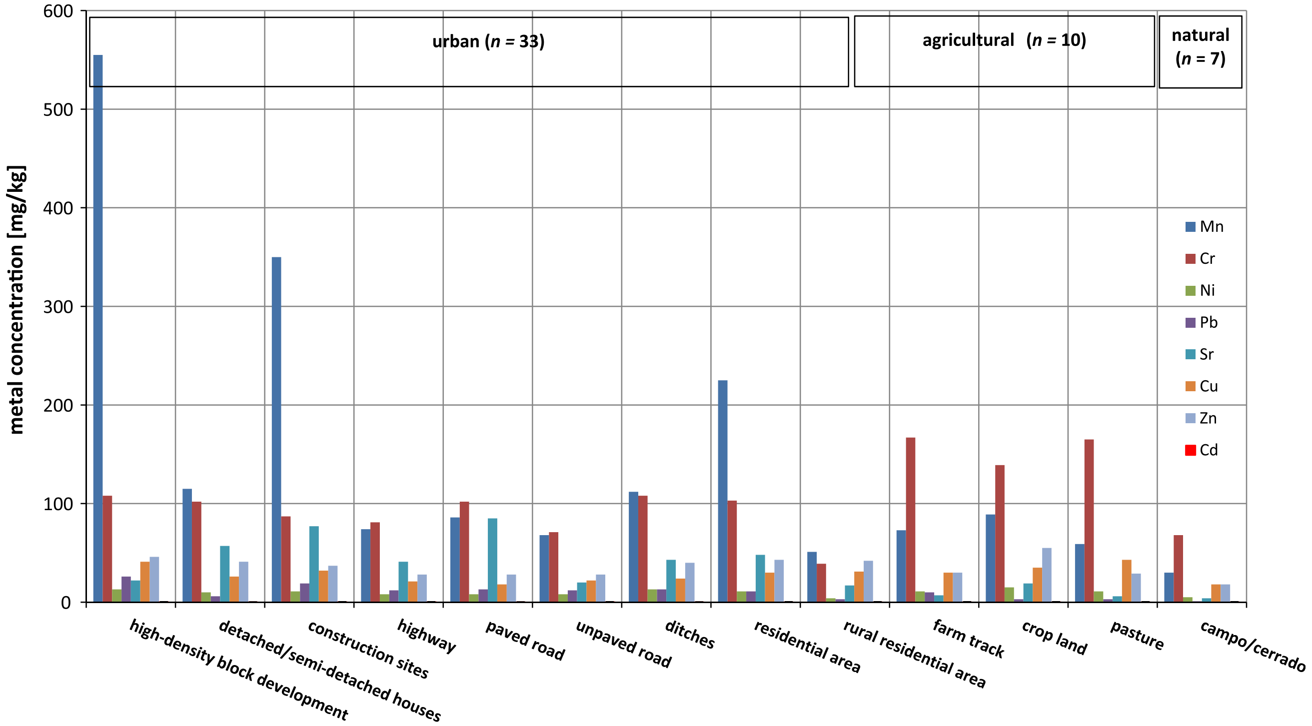

Fig. 5 Mean values for metal concentrations in source sediments within the Riacho Fundo sub-catchment

Despite the almost homogenous geological background within the basin distinct differences are also observed for Al (urban: 67,223–177,320 mg/kg; agriculture: 153,150–164,603 mg/kg, (semi-) natural: 27,835–34,491 mg/kg) and Fe (urban: 54,789–79,116 mg/kg; agriculture: 68,664–93,283 mg/kg, (semi-) natural: 16,858–24,575 mg/kg).

In addition, the metal concentration values obtained from the analysis of potential source sediments are used for the calculation of enrichment factors (EFs) to demonstrate the differences in metal concentrations in sediments between urban, agricultural and natural areas (Table 2).

Metals with EF values higher than 1.0 (Cd, Cr, Cu. Mn, Ni, Pb, Sr, Zn) and higher than 2.2 (Al and Fe) can be considered as not originating from the local geological background.

The EF values of Pb (EF = 27.0), Sr (EF = 20.3), Mn (EF = 12.3) and Cd (EF = 9.5) are highest in urban sediments, particularly in sediments from residential areas and construction sites. Among the urban sediment source types, road sediments have the lowest EFs for all metals, except for Cr. In contrast to the EF of urban sediments, agricultural sediments are characterized by high EF values of Al (EF = 4.5), Cr (EF = 2.2), Cu (EF = 2.4) Fe (EF = 3.6), Ni (EF = 4.0) and Zn (EF = 3.3). Even using the particle size correction factor, the enrichment of these metals in agricultural sediments are influenced by the dominating clay fraction and by pedogenetic enrichments due to the transformation of mineral phases and the stronger sorption of the transition elements (Ni^{2+}, Cu^{2+}, Zn^{2+}) by Fe- and Mn-oxides.

The analyses of the metal concentrations of 13 different land use sub-types within the Riacho Fundo sub-catchment show a similar pattern of metal concentrations in source sediments as obtained for land use categories [urban, agricultural and (semi-) natural] within the Lago Paranoá catchment (Fig. 5).

Table 3 Enrichment factors of metals (EFs: mean values) in source sediments within the Riacho Fundo sub- catchment

Enrichment factors	Al	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Sr	Zn
High-density block development	3.1	8.5	2.6	2.3	3.3	18.5	2.6	26.0	5.5	2.6
Detached/semi-detached houses	6.4	7.5	1.5	1.4	4.7	3.8	2.0	6.0	14.3	2.3
Construction sites	2.6	9.0	1.3	1.8	3.4	11.7	2.2	19.0	19.3	2.1
Highways	2.4	8.5	1.2	1.2	3.6	2.5	1.6	12.0	10.3	1.6
Paved roads	3.1	7.5	1.5	1.0	3.2	2.9	1.6	13.0	21.3	1.6
Unpaved roads	2.1	8.0	1.0	1.2	3.8	2.3	1.6	12.0	5.0	1.6
Ditches	1.6	7.5	1.6	1.3	3.0	3.7	2.6	13.0	10.8	2.2
Residential areas	5.6	7.0	1.5	1.7	4.4	7.5	2.2	11.0	12.0	2.3
Rural residential areas “nucleo rural”	1.2	6.0	0.6	1.7	1.4	1.7	0.8	3.0	4.3	2.3
Farm tracks	5.5	5.5	2.5	1.7	5.3	2.4	2.2	10.0	1.8	1.7
Cropland	5.9	5.0	2.0	1.9	4.1	3.0	3.0	3.0	4.8	3.1
Pasture	5.6	4.5	2.4	2.4	5.5	2.0	2.2	3.0	1.5	1.6

The division of the three land use categories into 13 sub-types indicates differences in element concentrations among urban areas with different anthropogenic activities. Sediments in high-density block development areas, such as the residential area “*Aguas Claras*” (Fig. 2), with paved roads and intensive construction activity, are characterized by enrichments in Cr (108 mg/kg), Cu (41 mg/kg), Mn (555 mg/kg), Ni (13 mg/kg), Pb (26 mg/kg), Sr (86 mg/kg) and Zn (47 mg/kg). In contrast, sediments from residential areas with detached or semi-detached housings, e.g. “*Vincente Pieres*” (Fig. 2), show significant lower mean concentrations of Cu (26 mg/kg), Mn (115 mg/kg), Pb (6 mg/kg) and Sr (58 mg/kg). But the differences in the mean concentration of Zn (42 mg/kg) are relatively low, compared to residential areas with high density block development. Although the geological background is almost homogenous within the Riacho Fundo sub-catchment, the mean concentration of Al and Fe shows extreme differences between residential areas with high-density block development (Al: 87,343 mg/kg and Fe: 35,819 mg/kg) and detached or semi-detached housing areas (Al: 177,204 mg/kg and Fe: 79,116 mg/kg). The high difference in Al and Fe concentrations reflects that less surface sealing and unpaved roads are largely responsible for the sediment generation from highly weathered soil layers, which contain high concentration of Al and Fe as stable residues in acidic well-aerated soils (Marques et al. 2003).

Agricultural sediments are characterized by a different geochemistry and texture, compared to the sediments from urban as well as from natural sites. High enrichments were found for Cu (36 mg/kg), Cr (157 mg/kg), Ni (12 mg/kg) and Zn (54 mg/kg) based on the local geological background values.

The concentrations of Cd are <300 µg/kg, whereas sediments from urban are characterized by higher Cd contents (180–290 µg/kg) than sediments from (semi-) natural sites (<50 µg/kg = below detection).

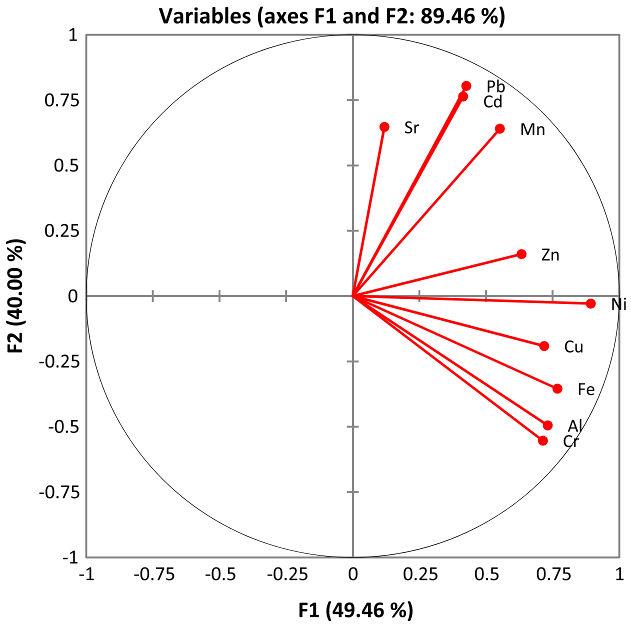

Fig. 6 Factor loadings and the correlation from principal component analysis of metals

Among the 12 urban and agricultural land use sub-types within the Riacho Fundo sub-catchment, urban sediments from high density block development show the highest EF values for most of the analyzed metals, particularly for Cd (EF = 8.5), Cr (EF = 2.6), Cu (EF = 2.3), Mn (EF = 18.5), Ni (EF = 2.6), Pb (EF = 26.0) and Zn (EF = 2.6). In contrast, EF values for these metals are lower in sediments from urban areas with detached/semi-detached houses: Cd (EF = 7.5), Cr (EF = 1.5), Cu (EF = 1.4), Mn (EF = 3.8), Ni (EF = 2.0), Pb (EF = 6.0) and Zn (EF = 2.3) (Table 3).

The most distinct differences in metal enrichments exist for Pb and Mn between these two urban land use types.

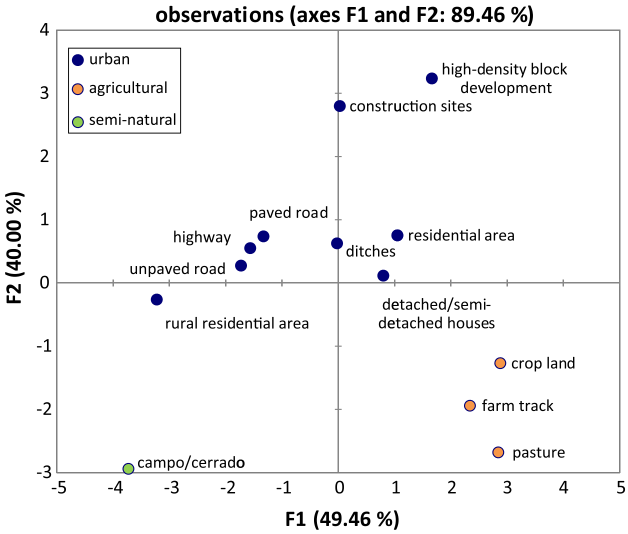

Fig. 7 Biplot of factor 1 (F1) and factor 2 (F2) and factor loading with respect to the land use types

Within urban areas, construction sites are characterized by high EFs of Cd (EF = 9.0), Pb (EF = 19.0), Sr (EF = 19.3). Urban road network shows also considerable EFs (>1) for all metals, whereas the highest EF value for Sr (EF = 21.3) was obtained for unpaved roads. The lowest EFs were calculated for rural residential areas ("nucleo rural"—single farms in campo/cerrado areas), which represent areas with minor anthropogenic influence.

Principal component analyses (PCA) of metal concentrations in source sediments

Significant positive correlations were found in source sediments for Pb–Mn, Zn–Ni, Cr–Ni, and Sr–Cd. In the PCA two factors with eigenvalue higher than 2.0 were extracted. This model explained 89.46 % of the total variance in the data (Fig. 6).

The metals Pb–Cd and Al–Cr are significantly positive correlated, while no correlations were found among Sr–Cu, Pb–Al and Cr–Cd. The F1 (49.46 % of the total variance) had strong positive loadings on Pb, Cd, and Sr, and moderately positive loadings on Mn and Zn, which represented anthropogenic sources (urban sediments). F2 (40.00 % of the total variance) had strong negative loadings on Cr, Al, and Fe, and lower negative loadings on Cu and Ni, likely representing other natural conditions or human impacts (agricultural sediments). The transfer of these results into the biplot of the land use categories indicates that Sr Pb, Cd and Mn are characteristic for urban land use and individual sub-types. Agricultural sediment sources can be identified by the concentration pattern of Ni, Cu, Fe, Al and Cr (Fig. 7).

Supporting the previous comparison of total metal concentrations using the natural sites as reference, the PCA shows that residential areas with high density block development (urban sites) and paved roads have significantly higher correlations with Pb, Mn and Cd (81 %; $p < 0.05$), than potential sediment sources under agricultural land use. Urban sites dominated by residential housing and unsealed surfaces, such as unpaved roads and unsealed spacing between single houses, have strong correlations with Sr (74 %; $p < 0.05$). In contrast, the elements Cr, Ni, Cu, and Zn (84 %; $p < 0.05$) are characteristic for sediments from areas with agricultural land use, indicating preferential adsorption of these metals at the clay and silt fraction.

Metal concentrations and EFs in alluvial sediments

Geochemical studies by Moreira (2002) and Gioia et al. (2006) showed that metal concentrations in sediments of the Torto branch (branch D) reflect almost the natural background concentrations for the elements Cr, Cu, Cd, Pb and Zn in the lake sediments. Based on these results in our studies the sediment quality in the Torto branch is used as background level for the sediment quality within the Lago Paranoá basin.

The analysis of the alluvial sediment profiles of each main tributary (sub-catchments), which are discharging into branches and silting zones A to E (Fig. 3) and the calculation of enrichment factors (EF) show that the metal concentrations in the alluvial sediments of each sub-catchments are different and that there are variations within each of the 40 cm profiles (Fig. 8). Based on an average sedimentation rate of about 2.5 cm/year within the Lago Paranoá catchment (Franz et al. 2012), the 40 cm of sediment deposits are representative at least for the sedimentation of the last 10 years.

In general, the alluvial sediments are characterized by lower mean concentrations of metals, compared to the mean concentrations in potential urban source sediments (Fig. 4). An exception is Zn, which was found in higher concentrations in the alluvial sediments of the Central Paranoá (64 mg/kg) and of the Bananal (55 mg/kg).

For the evaluation of the metal concentrations in the alluvial sediments and of the anthropogenic impact within each sub-catchment, enrichment factors were calculated, using the local geological background values (Table 4).

In general, the highest EFs are present in the alluvial sediments from the Central Paranoá. Pb, Cd and Sr are highly enriched by 17.4, 7.2 and 5.6, indicating a strong influence of urban land use on the accumulation of these metals in sediments. Moderate enrichments have been observed for Fe (3.6), Mn (3.1), Zn (3.0), Cu (2.8), Cr (1.3) and Ni (1.6). Since the concentrations of Mn and Fe are

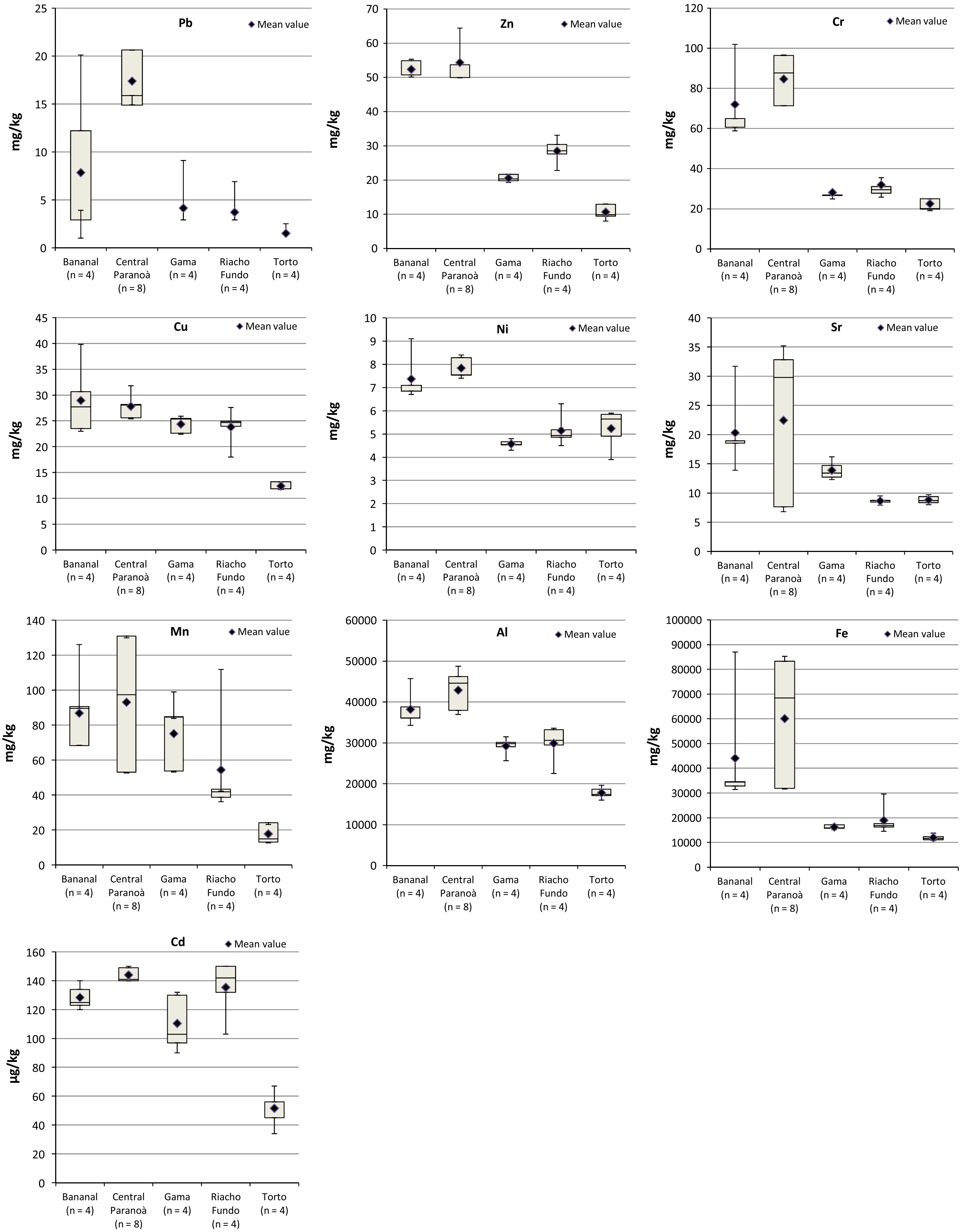

Fig. 8 Metal concentration in alluvial sediments of each discharge to branch A–E/sub-catchments (mean concentration and ranges 25- and 75-percentile)

Table 4 Enrichment factors of metals (EFs: mean values) in alluvial sediments of each sub-catchment

Enrichment factors	Al	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Sr	Zn
Bananal	1.4	6.4	1.1	2.9	2.6	2.9	1.5	7.8	5.6	2.9
Central Paranoà	1.3	7.2	1.3	2.8	3.6	3.1	1.6	17.4	5.6	3.0
Gama	1.1	5.5	0.4	2.4	1.0	2.5	0.9	4.1	3.5	1.1
Riacho Fundo	1.1	6.8	0.5	2.4	1.1	1.8	1.0	3.7	2.2	1.6
Torto	0.6	2.6	0.3	1.2	0.7	0.6	1.0	1.4	2.2	0.6

increasing with depth in the profiles, the enrichment of these metals might be influenced by pedogenetic translocation and therefore not only resulting from anthropogenic sources.

In contrast, the sediments of the Bananal show also higher EFs for Pb (7.8), Sr (5.1), Cd (6.4), Cu (2.9), Zn (2.9) and Ni (1.5), but having low human activity along the tributaries within the Bananal sub-catchment (11 % of the total area with urban land use) (Fig. 2). Therefore, the recent/current intensive construction activities, primarily transportation network development, within this sub-catchment and other sources of metals in sediments, e.g. point sources, have to be considered within the Bananal sub-catchment. Even the EF values in the alluvial sediments of the Riacho Fundo and Gama are lower than in the alluvial sediments of the Central Paranoá and Bananal, Cu and Pb are highly enriched, showing EFs twice as high than those of the Torto sediments. The low EFs in the alluvial sediments of the Torto sub-catchment are resulting from the large proportion of the National Park (86 % of the areas are natural area) within this sub-catchment. However, the EF values of Cd (2.6), Cu (1.2), Pb (1.4) and Sr (2.2) are >1, which might be attributed to anthropogenic sources within the Torto sub-catchment. Therefore, even the urban influence is still low within the Torto sub-catchment, it has already an important contribution to metal enrichments in sediments.

The results suggest that the EFs are related to the land use proportioning of each sub-catchment (see Fig. 2). Therefore, the stronger the human impacts due to urbanization, the higher are the metal concentrations and EFs in the sediments.

Metal concentrations in surface water samples

The metal concentrations of the rivers discharging into the Lago Paranoá lake (influent to branches A–D from the sub-catchments) are shown in Fig. 9. The concentrations of Cd, Cr, Cu, and Pb are low, no seasonal variability has been observed. The concentrations are close to the detection limit of the analytical method used (Cd: <2 µg/L; Cr: <5 µg/L, Cu: <10 µg/L; and Pb: <20 µg/L). Concentrations of Al, Fe, Mn, Sr and Zn of the water samples at the influent into the branches are higher and are different during the rainy and dry season. Although only a limited number of samples have been analyzed (mid rainy season: December 2011, January 2011), second half of the rainy season (March 2012), and end of the dry season (September 2012) it is most reasonable that the variations in the concentration might result from the spatial and temporal variability of surface runoff within the different sub-catchments during rain events (da Anunciação et al. 2014). In the rainy season the concentrations of Al and Fe are highest. The concentrations are decreasing during the rainy season (December–January). At the end of the rainy season (March) the concentration range is almost the same as during the dry season (September). This trend is most obvious for the four main rivers Riacho Fundo, Gama, Bananal and Torto. The effect is less distinct in the water samples from the Central Paranoá which has less discharger from surface waters out of the sub-catchment. The seasonal variations are not so pronounced for Mn (range of the rainy season: 2–70 µg/L; range of the dry season: 3–26 µg/L) and Sr (range of the rainy season: <5–74 µg/L; range of the dry season: 5–54 µg/L), as the concentrations are much lower compared to Fe (range of the rainy season: 33–2,085 µg/L; range of the dry season: 270–604 µg/L) and Al (range of the rainy season: 38–2,272 µg/L; range of the dry season: 73–165 µg/L).

The highest concentrations of Al, Fe, Mn and Sr are analyzed in water samples discharging into the Riacho Fundo branch whereas the concentrations for samples from Banal, Torto and Gama are lower. This holds for the rainy and dry season. Comparing the concentrations of samples from Torto and Gama the concentrations of the Bananal water samples are only higher in the rainy season. In the dry season (September) the differences in the concentrations are less distinct. The lowest concentrations are shown in samples from the Central Paranoá.

In contrast to the increased concentrations of Al, Fe, Mn and Sr in the rainy season, the concentration of Zn in the water samples were higher during dry season. The highest concentrations of Zn have been analyzed in samples of the Torto influent in September (about 127 µg/L), whereas the lowest concentration is given in the water samples of the Central Paranoá (about 5 µg/L and less). The Zn concentration of the water samples from the Bananal, Riacho Fundo and Gama are slightly lower than those of the Torto.

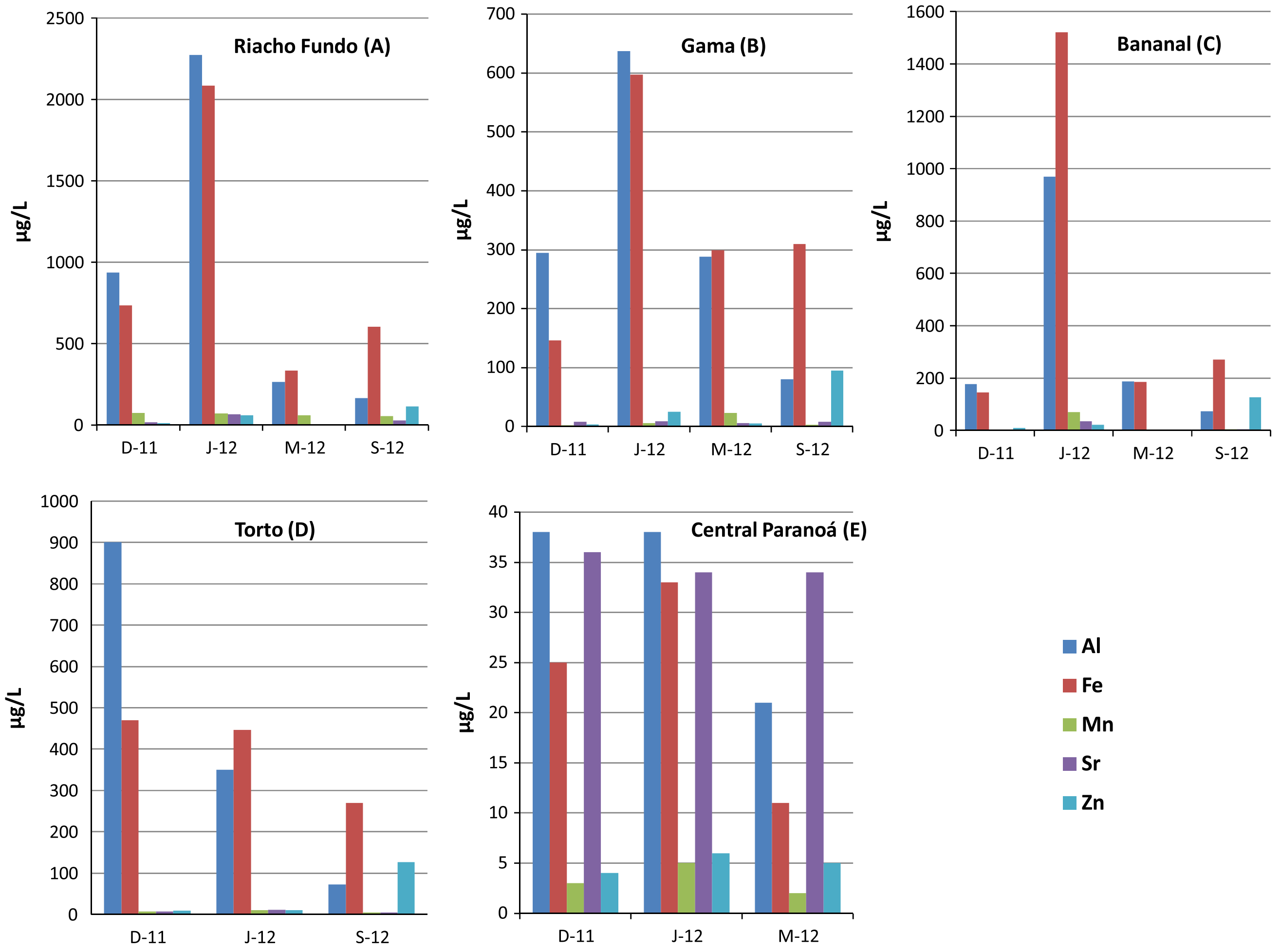

Fig. 9 Concentration of Al, Fe, Mn, Sr and Zn in water samples of each branch (sub-catchment) and the variation within the rainy season 2011/2012 (December 2011–March 2012)

The metal concentrations at Central Paranoá differ significantly from those of the other sub-catchments. Concentrations of Al and Fe are very low (Al: range of 20–50 µg/L; Fe: range of 10–35 µg/L), while at the other branches (A–D) the concentrations of Al and Fe are more than ten times higher. For Mn and Sr the concentrations are in the range of 2–5 and 34–36 µg/L.

The spatial and temporal variations in the concentrations of metals in the surface water might be dependent on several factors: (1) the input due to anthropogenic activities, which is related to the land use proportion within the sub-catchments, point sources (e.g. wastewater treatment plants, leakages of boot fuel), (2) the variation of precipitation between the sub-catchments, which involves locally concentrated (convective) storm events and storm-water overflows (e.g. runoff) from different land use types, (3) the relationship between the water volume that contributes to the lake and the size of the branch, and (4) the flows and dilution processes within the lake (Gioia et al. 2006; Kochhann et al. 2013).

The seasonal variation, especially the higher Al and Fe concentrations in the rainy season, suggests terrestrial (anthropogenic and natural) inputs via the rivers (Balkis et al. 2010). Heavy rain events, increased runoff and flows contribute to higher suspended solids (turbidity), which increase the input of these metals in the Lago Paranoá. Metal concentrations due to terrestrial inputs depend strongly on the impact of urban areas within each sub-catchment (for comparisons see Figs. 2, 3, 4, 5, 6, 7, 8, 9).

The distinct differences in the metal concentrations in water samples between the discharge of the four main rivers (A–D, particularly of the Riacho Fundo) and the Central Paranoá (E) might be also a result of different inflow morphologies. Moreira (2002) explained that this fact might be attributed to the relationship between the water volume that contributes to the lake and the size of the branches. Out of the four branches, the Riacho Fundo branch is more shallow and narrow, and therefore a higher particle transport can be emphasized. The Riacho Fundo branch has the smallest resistance to the entrance of water

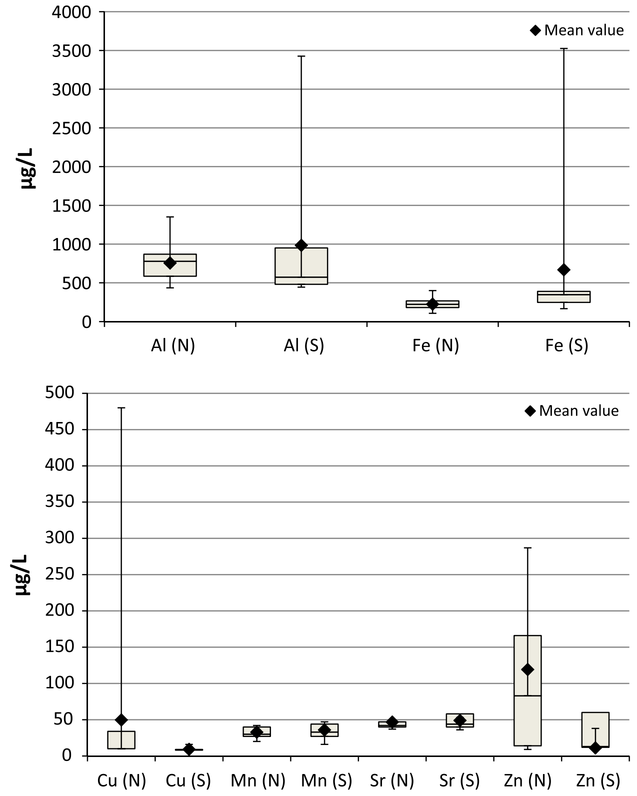

Fig. 10 Metal concentrations in effluent water samples of the two wastewater treatment plants ETE Norte (N) and ETE Sul (S) (mean values and ranges 25- and 75-percentile)

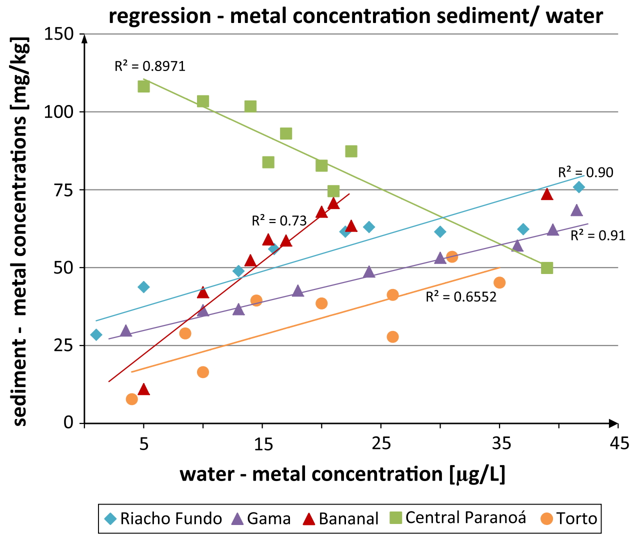

Fig. 11 Regression analysis for the correlation between metal concentrations (Cd, Cr, Cu, Mn, Ni, Pb, Sr, Zn) in alluvial sediments and water samples (discharge to branches A–E) of each sub-catchment

and the highest discharge from the main tributary into the lake, and therefore, the highest terrestrial input of metals in the water. In contrast, the Central Paranoá is characterized by discharges due to several small tributaries (inflows). Consequently, the terrestrial inputs (anthropogenic and natural) might be less important in this part of the lake, resulting in lower concentrations of Al, Fe and Mn in the water. Furthermore, the sampling site of Central Paranoá (sampling site Paranoá Jusante) is located in the central part of the lake, and therefore the site is more influenced by flows of the other branches. Dilution effects, sediment saltation and solution of different metal salts within this part of the lake are likely to have a higher impact on the metal concentrations in the samples than in those of the other discharges (sub-catchments). Beside these parameters, the differences in metal concentrations in the water samples between the five sampling sites (discharges into the lake; A–D) might be also be influenced from point sources (e.g. wastewater treatment plants, leakages of boot fuel) (Gioia et al. 2006).

According to the discussion above, it is most obvious that the metal concentration in the surface water samples of Riacho Fundo, Gama, Bananal and Torto are highly influenced by the soil derived metal input during the rainy season. For the site Central Paranoá the influence of point sources, inflow morphology and dilution effects might be more important.

The comparison of the metal concentrations with the quality standard values of the CONAMA n° 20 (Brazil—Conselho Nacional do Meio Ambiente 1986, 2005) showed that Cd, Cr, Mn, Ni and Pb satisfy the standards even for drinking water supply. Although the concentrations of Al and Fe are higher than the quality maximum values (200 µg/L) in the four inflow sites, the concentrations are decreasing to values below the parametric values at site Central Paranoá (below 50 µg/L).

Metal concentrations in the effluent from the wastewater treatment plants

Effluent water from the wastewater treatment plants (ETE Norte, ETE Sul) was sampled during the dry and at the beginning of the rainy season (July 2011, August 2011, September 2011, November 2011 and September 2012). The data show that mean metal concentrations are temporary higher in the effluents than in the water samples of the influents discharging into the different branches (Abbt-Braun et al. 2012; Börnick et al. 2013). The concentrations of Cd, Cr, Ni and Pb are low or close to the detection limit of the analytical method applied. Al, Cu, Fe, Mn, Sr and Zn show higher concentrations. Figure 10 shows the mean metal concentrations and the variability in the effluent water samples from ETE Norte and ETE Sul.

The mean values are lower for samples from ETE Norte, both for Al and for Fe (ETE Sul: 983 µg/L Al, 669 µg/L

Fe; ETE Norte: 755 µg/L Al, 225 µg/L Fe). Compared to the Al and Fe the concentrations of Cu, Mn, Sr and Zn are much lower. There are no differences in the two effluent samples for the mean concentration of Cu, Mn and Sr. For Zn the mean concentration in the effluent water of ETE Norte is ten times higher (119 µg/L Zn) than in the effluent of ETE Sul.

Regression analyses

A regression analysis of the metal concentrations (Cd, Cr, Cu, Ni, Pb, Sr and Zn) in the alluvial sediments and in the water samples of each sub-catchment was performed (Fig. 11).

The regression analysis shows that the metal concentrations in the sediments are negative correlated with the concentrations in the water ($R^2 = 0.90$) for the Central Paranoá sub-catchment. In contrast, for all other sub-catchments the regression model indicated a positive correlation between metal concentrations in the sediment and water. Therefore, the terrestrial input of metals (anthropogenic and natural) into the lake is more important in the sub-catchments, having one main tributary discharging to the branches (A–D) than in the Central Paranoá (E). The most significant positive correlation between the metal concentrations in alluvial sediments and in the water was verified for the Gama (branch B) ($R^2 = 0.91$) and Riacho Fundo (branch A) ($R^2 = 0.90$) sub-catchment, whereas the correlation were less positive for the Bananal ($R^2 = 0.73$) and Torto ($R^2 = 0.66$) sub-catchment.

As shown above for the Central Paranoá sub-catchment the intensive urban land use has a direct impact on metal enrichments (Cd, Cr, Cu, Ni, Pb, Sr and Zn) in the sediments. Although this is not reflected in the metal content of the aqueous phase.

For the Riacho Fundo and Gama sub-catchment it is obvious that particularly during the rainy period the terrestrial input of metals (anthropogenic and natural derived) affects both the sediment and the water body. This is less pronounced for the Bananal and Torto sub-catchment.

Finally, the positive correlation ($R^2 = 0.63$) between metal concentrations in the alluvial sediment and the area of urban land use suggests, that urban activities have an contribution to metal accumulation in sediments within the Lago Paranoá catchment (Fig. 12a). Particularly within the Riacho Fundo ($R^2 = 0.89$) and Central Paranoá ($R^2 = 0.88$) sub-catchments the correlation seems to be related to the intensive urban land use, which is characterized by high density block development with paved roads and constructions sites (Fig. 12b).

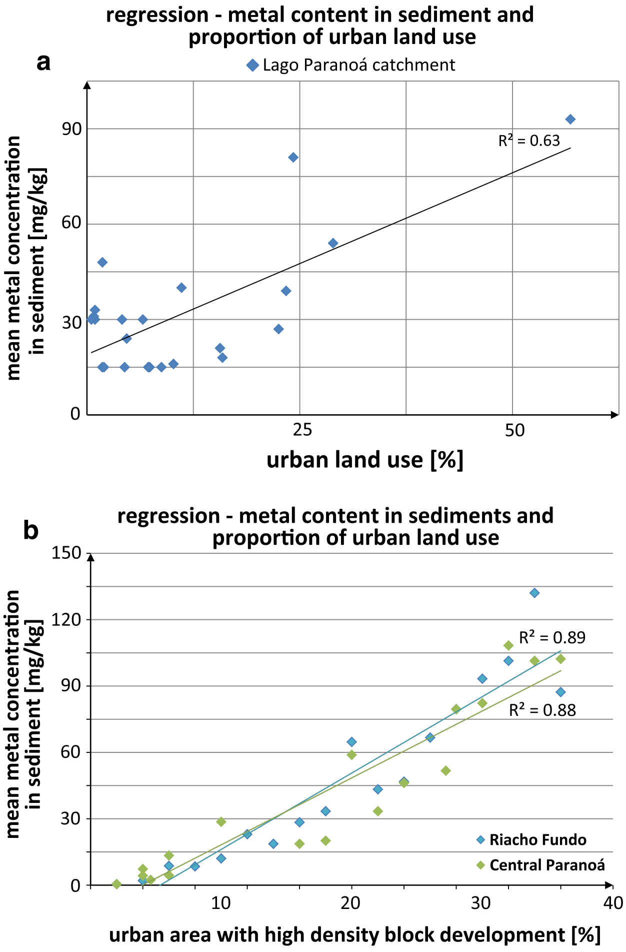

Fig. 12 **a** Regression analysis for the relationship between metal concentration (Cd, Cr, Cu, Ni, Pb, Sr, Zn) in sediments and the proportion of urban areas for the whole Lago Paranoá catchment. **b** Regression analysis for the relationship between metal concentration (Cd, Cr, Cu, Ni, Pb, Sr, Zn) in sediments and the proportion of urban areas with high-density block development for the Central Paranoá and Riacho Fundo sub-catchment

Conclusions

The purpose of this study was to investigate the metal concentrations in potential source sediments, alluvial sediments, and surface waters, and to determine the specific effects of different land uses on metal concentrations in sediments and water within the Lago Paranoá catchment.

The concentration of metals varied among source sediments and alluvial sediments, as well as among the five sub-catchments of the Lago Paranoá basin. Metal enrichments in sediments depend on both the extent of urban land use and the textural characteristic of the sediments in the respective river basin. Sediments from urban areas and alluvial sediments of the Riacho Fundo and Central Paranoá sub-catchment show enrichments in Pb, Sr, Mn, Cr, Ni and Zn due to human impact. Metal concentrations in surface water of the main tributaries to the Lago Paranoá are generally low, but show seasonal variability. Terrestrial inputs of metals occur during the rainy season and depend largely on the influence of urban land use. In addition, heavy metals, like Cu, Cd, Cr, and Zn are discharged from point sources like the effluents of the wastewater treatment plants.

In conclusion, the study has given following findings:

- There is no evidence for metal pollution of surface water within the Lago Paranoá catchment. Nevertheless, further monitoring is needed for the maintenance of high raw water quality within the Lago Paranoá catchment in the future.
- There is a strong relationship between metal enrichments in sediments and urban areas. The metal concentrations in alluvial sediments of the Riacho Fundo and Central Paranoá sub-catchment showed that urban areas, especially high density block development and construction activities, are a major source of sediments within the basin. The agglomeration Brasília is still growing. Thus, it is likely that the future urban development and constructions will cause an increasing metal enrichment in sediments within the Lago Paranoá catchment. Thus, the implementation of an appropriate land use and sediment management plan will be a major element in the protection of water resources.
- There is evidence that metal enrichments in alluvial sediments might be a possible risk for water pollution in the near future due to the remobilization of metals. Since silting is a serious problem for the Lago Paranoá, especially at the Riacho Fundo branch, this legacy of metal pollution is one of the largest problems facing urban catchments. The residence time of sediment in rivers and reservoirs is much longer than that of water, thus the substantial reduction of sediment input into the river system and reservoirs areas is of high priority.

Hence, there is a need for further measurements to validate the current data and trend*s*, to prove the given hypothesis, and to understand the complex processes and interactions within the sediment and water cascade of urban river basins. Particularly the establishment of a sediment monitoring network with high temporal resolution will be an essential element to understand the effects of urbanization and soil management on sediment generation and to provide detailed information on metal pollution of sediments and water. This scientific basis is crucial for IWRM and in scope of a sediment management plan, especially in urban catchments.

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