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Sodrzeieski, Pedro Alexandre; Andrade, Leonardo Capeleto de; Tiecher, Tales; Camargo, Flávio Anastácio de Oliveira
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Physico-chemical variability and heavy metal pollution of surface sediment in a non-channeled section of Dilúvio Stream (Southern Brazil) and the influence of channeled section in sediment pollution

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Pedro Alexandre Sodrzeski^{id}; Leonardo Capeleto de Andrade^{*id};
Tales Tiecher^{id}; Flávio Anastácio de Oliveira Camargo^{id}

Universidade Federal do Rio Grande do Sul (UFRGS), Porto Alegre, RS, Brasil
Departamento de Solos (DS). E-mail: pedroasod@gmail.com, eng.capeleto@gmail.com,
tales.tiecher@gmail.com, fcamargo@ufrgs.br

*Corresponding author

ABSTRACT

Dilúvio Stream flows through an area with a great population density in Porto Alegre, Southern Brazil. The anthropogenic influence in the surroundings impacted negatively the quality of the sediments of Dilúvio Stream and Lake Guaíba. This study evaluated the physico-chemical variability of surface sediments in a non-channeled section of Dilúvio Stream. Additionally, we compared the concentration of several heavy metals in this section with data from previous studies in the margins of Lake Guaíba near the outflow of Dilúvio Stream in order to evaluate the impact of urbanization on sediment pollution. The pH, bulk density, particle-size distribution, electrical conductivity, organic carbon, assimilable phosphorus, total nitrogen, mineralogical composition (X-ray diffractogram) and pseudo total concentration of several metals (Fe, Al, Ca, Mg, Na, K, Mn, Ba, Zn, V, As, Pb, Cu, Cr, Co, Ni, Cd, Mo, and Se) were evaluated. The results showed that the sediments in the non-channeled section of Dilúvio Stream are predominantly sandy, with heavy metal contents below the quality reference values. Quartz and feldspar predominated in all sites. The concentration of Zn, Pb, Cu, Cr, and Ni were lower than that observed in the margins of Lake Guaíba near the outflow of Dilúvio Stream, possibly due to pollution input throughout the channeled section. The Dilúvio Stream shows indications of an anthropogenic influence in the heavy metals concentration through the channeled area.

Keywords: metals, sediment contamination, urban pollution.

Variabilidade físico-química e poluição por metais pesados em trecho não canalizado do Arroio Dilúvio (RS) e a influência do trecho canalizado na poluição dos sedimentos

RESUMO

O Arroio Dilúvio percorre uma área com grande densidade populacional em Porto Alegre, sul do Brasil. A influência antrópica no entorno impacta negativamente na qualidade dos sedimentos do Arroio Dilúvio e do Lago Guaíba. O objetivo do trabalho foi avaliar a variabilidade físico-química em sedimentos superficiais do Arroio Dilúvio. Adicionalmente,



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comparou-se a concentração de vários metais na seção com estudos prévios das margens do Lago Guaíba, próximo à foz do Dilúvio, para avaliar o impacto da urbanização na poluição dos sedimentos por metais pesados. Avaliou-se pH, densidade aparente, granulometria, condutividade elétrica, carbono orgânico, fósforo assimilável, nitrogênio total, composição mineralógica (difratometria de raio X) e concentração pseudo total diversos metais (Fe, Al, Ca, Mg, Na, K, Mn, Ba, Zn, V, As, Pb, Cu, Cr, Co, Ni, Cd, Mo e Se). Os resultados demonstram que os sedimentos são predominantemente arenosos, com níveis de poluição por metais pesados abaixo dos valores de referência de qualidade. Quartzo e feldspato predominaram em todos os pontos. A concentração de Zn, Pb, Cu, Cr e Ni foram menores do que as observadas nas margens do Lago Guaíba próximos a foz do Dilúvio, possivelmente devido à presença de fontes de poluição na área canalizada. O Arroio Dilúvio mostra indicações de influência antrópica na concentração de metais pesados através da área canalizada.

Palavras-chave: contaminação de sedimentos, metais, poluição urbana.

1. INTRODUCTION

Anthropogenic activities are a major source of contaminants and heavy metal pollution (Zhang et al., 2016). Sediments can act as a reservoir of pollutants or interact directly with the environment, thus being an important indicator of the effects caused by pollution and human activities. Water bodies and sediments suffer impacts from many sources such as industrial activities, traffic, urban areas, agriculture, and can carry pollutants to other sites (Jartun et al., 2008; Sharley et al., 2016; Zhang et al., 2016).

Impermeable urban surfaces lead to serious problems such as an increase in runoff, flood risks, and lower water percolation, which results in drainage water directly into the rivers and lakes (Pignoret et al., 2016). Materials accumulated on impermeable surfaces are easily eroded during heavy rainfall and can be transported by suspension through the urban environment along with the pollutants which are at risk of being removed in the process (Jartun et al., 2008). Many sediments are formed in the roads, buildings areas, and are possibly linked to heavy metals and hydrocarbons, being easily transported by rainwater (Jartun et al., 2008; Pignoret et al., 2016).

Heavy metals are very common pollutants in urban areas, having global importance due to their risk to human and environment health, because of their persistence, bioavailability and toxicity (Pignoret et al., 2016; Sharley et al., 2016). Heavy metals in sediments are a common problem in urbanized areas marked by rapid population growth, industrial activities, and roads; having the tendency to increase diffuse sources of sediment pollution along with the increase of urban area in a drainage basin (Jartun et al., 2008; Sharley et al., 2016).

Erosion and siltation are also processes that may interfere with the sediment pollution and the impact along the channeled area. These processes take part with an imbalance between the water and sediment, occasioning problems in water and sediment quality and the diminution of the channel; alterations caused by human activities could influence these processes and alter their intensity (Yuan et al., 2018).

Dilúvio Stream is a small urban river located in Porto Alegre City, the capital of the State of Rio Grande do Sul in Brazil, with sources in the park Saint-Hilaire, in Viamão City (the neighboring city) and the outflow in Lake Guaíba, which is the main source of water supply for Porto Alegre City. Dilúvio's sub-basin, part of the Lake Guaíba drainage basin, is densely populated with about 446,000 inhabitants, suffering many effects from the disordered population growth and rapid industrialization in Porto Alegre, and lack of investments in basic sanitation (Mog et al., 2014). In addition, this region has large waterproofed areas and buildings in its surroundings, as well as the channeling and rectification of the stream with the

construction of Ipiranga Avenue (one of the busiest in the city) in a large section (almost 12 km) of its course.

The surrounding anthropic influence negatively impacts the sediment quality of Dilúvio Stream and Lake Guaíba. The environmental impacts occur mainly in the channeled part of the stream, with lower anthropic impact, where information of physico-chemical characteristics is lacking. Thus, the aim of this study was to evaluate the physico-chemical variability of surface sediments in a non-channeled section of Dilúvio Stream. Additionally, we compared the concentration of several metals in this section with data from previous studies carried out in the margins of Lake Guaíba near the outflow of Dilúvio Stream in order to evaluate the impact of urbanization on sediment pollution by heavy metals.

2. MATERIALS AND METHODS

2.1. Study area

Porto Alegre has a humid subtropical climate ("Cfa" in Köppen-Geiger classification). The annual climate means are 19°C for air temperature, 76% for air humidity and 1,324 mm of precipitation (Menegat et al., 2006). The sub-basin of Dilúvio Stream has 83.74 km², flowing through 17.6 km, with approximately 10.5 km channeled (Menegat et al., 2006; Mog et al., 2014), and sinuosity of 1.08, indicating the presence of a more-linear channel. Due to periodic floods that were displacing the citizens and curtailing development in the affected regions, it was decided between the mid-1930's and 1980's (Mog et al., 2014) that the stream would be transposed and channeled. However, even in 1913, some modification had taken place in the study's area, transposing it to the current place and filling the old bed flow (Ferlini, 1913).

Although it was transposed between 1912 and 1913, this non-channeled section located approximately 4 meters from the Dilúvio's source, is the closest to pristine characteristics. In this area, there is still the presence of ciliary forest and vegetation in the surroundings, almost as a forest reserve. Near the sources of Dilúvio Stream, there are modifications such as dams and irregular occupations, which cause pollution with the release of untreated sewage and wastes directly into the stream. Downstream of the channeled area there are a high number of buildings, waterproof areas, and high population density.

The study section is embraced by a riparian forest with almost 300 m on the right margin (Santana Hill) and 30 m on the left margin (Agricultural Science College - UFRGS) many roots and branches can be found across the river bed that may cause obstruction of the local water flux and form punctual deposition sites. This section has a riparian forest according to current Brazilian environmental legislation (Brasil, 2012). Thus, the study section is possibly only slightly impacted by its surroundings and retains many aspects of the natural conditions of Dilúvio Stream.

The section between the sources and the Agronomy neighborhood (Porto Alegre City) are marked by irregular occupations. The lack of sanitation and the sewage discharges directly into the water bodies cause the traces of pollution that can be noticed before even entering the channeled area (Mog et al., 2014).

2.2. Sediment sampling

Composite samples of surface sediment were collected (in May 2016) with a scoop-shaped sampler (crafted with PVC pipes) in the layer from 0-5 cm. Three subsamples were collected per site, being mixed to form the composite sample, and making laboratory triplicates of the sample for analysis. The samples were collected at an underwater depth of approximately 0.5-1.0 meters in the seven sites (Figure 1) of Dilúvio Stream in the portion located in the area of the Agronomy College of Universidade Federal do Rio Grande do Sul (UFRGS), Porto Alegre.

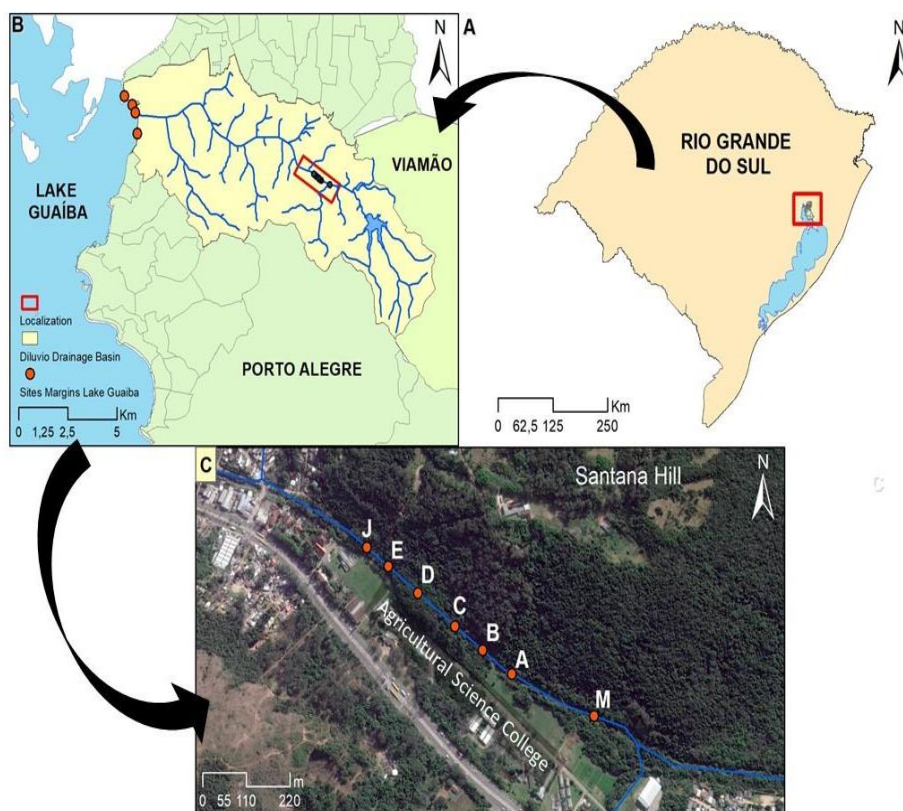


Figure 1. Location of the sites in a non-channelized section of the Dilúvio Stream.

2.3. Sample preparation

The samples were immediately taken to the laboratory, oven dried (50°C) and sieved (2 mm) according to CONAMA Resolution No. 454 (Conama, 2012) which provides the methodology and reference values for sediment studies in Brazil. Samples in natural condition were maintained under refrigeration as counterproofs.

2.4. Physico-chemical analysis

The following analyses were evaluated: pH in CaCl₂ (ratio 1:2.5; v/v), bulk density (Ds) and particle size (pipette; 70 g per repetition); electrical conductivity (EC; sediment/deionized water in proportion 1:5); total organic carbon (TOC; Walkley-Black; 3.5 g per repetition), assimilable phosphorus (P; Melich-1; 3.0 mL of sediment per repetition); Total Kjeldahl Nitrogen (TKN; 0.5 g per repetition); and pseudo-total elements, by acid digestion using 1 gram per sample according to EPA-3050B (USEPA, 1996) - Iron (Fe), Aluminum (Al), Calcium (Ca), Magnesium (Mg), Sodium (Na), Potassium (K), Manganese (Mn), Barium (Ba), Zinc (Zn), Vanadium (V), Arsenic (As), Lead (Pb), Cooper (Cu), Chrome(Cr), Cobalt (Co), Nickel (Ni), Cadmium (Cd), Molybdenum (Mo), and Selenium (Se).

All analyzes were performed in triplicates. The concentration of elements in the extracts (EPA-3050B analysis) was analyzed by Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES; *PerkinElmer® Optima™ 8300*) using internal standards for control and verification of procedures (with a recovery between 81 and 105% to Zn, Pb, Cu, Cr and Ni and Limits of Detection (LD) of: Zn - 2.0; Pb - 2.0; Cu - 0.6; Cr - 0.4; Ni - 0.4; Cd - 0.2 ug/g.). The X-ray diffractograms (XRD) were made into powder (*Bruker® D2-phaser*), with CuK α radiation [$\lambda = 1.54 \text{ \AA}$], pitch = 0.020° and amplitude from 4 to 70° 2 θ . Halite (H) was used as an internal marker at 0.282 nm to characterize the samples. Identification of minerals was performed according to Brindley and Brown (1980).

2.5. Statistical analysis

The results were submitted to analysis of variance (ANOVA) and, when significant, means were compared by the Tukey test, at a 95% confidence level ($p < 0.05$). All graphs and statistical analyzes were performed using the software *Statistica*® v13.

Moreover, the comparison of metal concentrations between the evaluated section of the Dilúvio Stream (AD) and two “before” (Ga) and two “after” (Gd) sites closest to the outflow (De Andrade et al., 2018) was performed by comparing the data with box-plot and submitting to statistical analysis of Kruskal-Wallis at 5% significance in completely randomized analyses with different numbers of repetitions.

2.6. Standardization

Standardization by Al was performed by dividing the concentrations of metal by the Al concentration in each sample, then analyzing the coefficient of variation of the sites. The Al was chosen because it is one of the most common metals in the earth's crust and easily found in high concentrations in soils and sediments. This standardization compensates the different particle sizes, due to the major metal concentrations in small particle sizes.

3. RESULTS AND DISCUSSION

3.1. Variation of physico-chemical properties of sediments in short distances in the non channeled section of Dilúvio Stream

The surface sediments of the non-channeled section Dilúvio Stream showed high variation in some metals (from 31% to 199%). However, after Al standardization, the physico-chemical variability greatly decreases from 7 to 31% between the evaluated sites (Table 1). The particle size was predominantly (>50%) composed of coarse sand (0 to 2 ϕ) with substantial proportions of gravel, except at site D where the lowest values for this variable were observed and the large accumulation of finer fractions (Table 1).

Smaller particles have a higher tendency to resuspension and move to longer distances in the stream (Sangster et al., 2015). Site D is probably a deposition site, because it is located after a curve, favoring the deposition of finer particles.

However, the high clay and silt variation coefficients disappear when these two granulometric fractions are summed up (Table 1) and low levels of these compounds may have influenced the high coefficient of variation, occurring in a similar fashion as the fine sand. In contrast, the gravel content presents more pronounced variations in its pattern, despite having a coefficient of variation below the other variables.

For pseudo total metals, there was no difference between the evaluated sites. However, Mn and Ba tended to present larger values upstream and V downstream. Most of the pseudo total metals present high (>50%) coefficients of variation (relative to all sites) and some cases like Mn (151%) and Ba (199%), which differ from the other metals (Table 1).

The coefficient of variation (<30%) decreased when compared by Al standardization. Thus, particle size variations and/or total organic carbon (TOC) increased the levels at some sites. These physico-chemical changes affect the variability of the metal contents when not analyzed by a standardization of Al. Therefore, it could be inferred that there is low variability in the physical-chemistry of Dilúvio Stream sediments at short distances in the non-channeled section.

Table 1. Particle size (%), bulk density (Ds), electrical conductivity (EC), pH (CaCl₂), and Total Organic Carbon (TOC) and pseudo total levels of calcium, magnesium, manganese, sodium, vanadium, barium, and cobalt in the sediments of Dilúvio Stream in the study's area.

Site		M	A	B	C	D	E	J	CV%	m ± s.e.	CV%/Al
Gravel	%	31 ^{bc*}	42.8 ^a	43.9 ^a	23.3 ^c	7.8 ^d	32.9 ^b	36.4 ^{ab}	39	31.2 ± 2.7	-
Coarse sand	%	655 ^{bc}	54.1 ^d	55.0 ^d	73.2 ^b	85.9 ^a	65.8 ^{bc}	62.0 ^{cd}	16	65.9 ± 2.3	-
Fine sand	%	2.8 ^{bc}	2.6 ^{bcd}	0.5 ^e	3.1 ^b	5.2 ^a	0.9 ^{de}	1.2 ^{cde}	69	2.3 ± 0.4	-
Silt	%	0.1 ^c	0.2 ^c	0.4 ^{ab}	0.2 ^{bc}	0.7 ^a	0.2 ^{bc}	0.2 ^{bc}	71	0.3 ± 0.0	-
Clay	%	0.5 ^a	0.4 ^{ab}	0.1 ^{cd}	0.3 ^{bcd}	0.3 ^{abc}	0.1 ^d	0.2 ^{bcd}	54	0.3 ± 0.0	-
Clay + Silt	%	0.6 ^b	0.5 ^b	0.6 ^b	0.5 ^b	1.0 ^a	0.4 ^b	0.4 ^b	40.0	0.6 ± 0.1	-
Ds	g cm ⁻³	1.52 ^{bc}	1.53 ^b	1.51 ^c	1.56 ^a	1.56 ^a	1.53 ^b	1.56 ^a	1	1.5 ± 0.0	-
EC	μS cm ⁻¹	62.2 ^{ab}	63.7 ^{ab}	63.5 ^{ab}	64.3 ^{ab}	67.0 ^a	57.8 ^b	59.4 ^b	6	63 ± 0.8	-
pH	(CaCl ₂)	6.6 ^a	6.6 ^a	6.5 ^{ab}	6.4 ^c	6.3 ^c	6.6 ^a	6.4 ^{bc}	2	6.5 ± 0.0	-
TOC	g kg ⁻¹	1.1 ^a	0.8 ^b	0.9 ^b	0.8 ^b	1.0 ^{ab}	0.1 ^c	0.1 ^c	62	0.7 ± 0.1	-
Ca	mg kg ⁻¹	248 ^a	278 ^a	242 ^a	266 ^a	293 ^a	329 ^a	286 ^a	44	278.0 ± 9.0	11
Mg	mg kg ⁻¹	188 ^a	214 ^a	213 ^a	260 ^a	322 ^a	249 ^a	325 ^a	31	253.0 ± 15.4	18
Mn	mg kg ⁻¹	181 ^a	154 ^{ab}	108 ^{bc}	116 ^{bc}	96 ^c	125 ^{abc}	144 ^{abc}	151	132.0 ± 7.2	24
Na	mg kg ⁻¹	54 ^a	65 ^a	69 ^a	80 ^a	69 ^a	80 ^a	73 ^a	64	70.0 ± 3.0	16
V	mg kg ⁻¹	7 ^b	6 ^b	7 ^b	10 ^{ab}	9 ^{ab}	12 ^a	8 ^b	32	8.3 ± 0.5	26
Ba	mg kg ⁻¹	13 ^{ab}	17 ^a	12 ^{ab}	11 ^{ab}	13 ^{ab}	10 ^b	11 ^{ab}	199	12.5 ± 0.7	20
Co	mg kg ⁻¹	2 ^a	2 ^a	2 ^a	2 ^a	2 ^a	2 ^a	2 ^a	40	1.7 ± 0.1	11
Al	mg kg ⁻¹	1846 ^a	1856 ^a	1607 ^a	1795 ^a	2204 ^a	1823 ^a	1831 ^a	16	1852.0 ± 1.0	-
Coordinates		-30.07227, -51.1351	-30.07173, -51.13673	-30.07122, -51.13743	-30.07075, -51.13812	-30.06996, -51.13897	-30.06963, -51.13973	-30.0694, -51.1405	-	-	-
Distance from site M	meters	0	170	257	340	463	546	625	-	-	-

*Statistical difference is referred by exponential letters. Averages followed by the same letter do not differ statistically from each other. Tukey Test was applied at the 5% probability level. Phi (φ): Krumbein particle size scale. Gravel: -1 to -2 φ; coarse sand: 0 to 2 φ; fine sand: 3 to 4 φ; silt: 5 to 8 φ; clay: φ > 9. Densities, EC, pH, and TOC in the fraction <2 mm. CV% - coefficient of variation. m ± se - mean ± standard error m±se - mean ± standard error; /Al - metal standardized by Aluminum; As, Cd, Mo, and Se were not detected.

The bulk density of the sediment had an spread ranging from 1.51 to 1.56 g cm⁻¹ (Table 1) with higher values in the downstream sites (C, D, and J) and smaller in the upstream (site B). There was a high correlation of bulk density with gravel content ($r = -0.72$). The electrical conductivity (EC) of the surface sediment ranged from 58 to 67 $\mu\text{S cm}^{-1}$ (Table 1), showing a high correlation with TOC ($r = 0.81$; $p < 0.05$) and clay plus silt ($r = 0.82$; $p < 0.05$). The pH had low variation, ranging between 6.3 and 6.6 (Table 1). None of these variables had a correlation with the accumulated distance.

The TOC showed a variation around 10 times with the highest values found in the upstream points (M, A, B, C, and D) and the lowest values in sites E and J. The TOC had a high correlation with the accumulated distance ($r = -0.81$; $p < 0.05$), evidencing a decrease in the contents along the watercourse, and with clay ($r = 0.76$; $p < 0.05$), so, places with higher clay content tend to have higher TOC due to an adsorption effect between clay and organic matter. Overall, the pseudo total metal (Table 1) concentration was low. Some metals were present at non-detectable levels (*e.g.* As, Cd, Mo, and Se). However, significant values of V, Cr, and Fe were found at site E. A high correlation with the accumulated distance was found for Mg ($r = 0.84$; $p < 0.05$), Na ($r = 0.76$; $p < 0.05$), and Ni ($r = 0.91$; $p < 0.05$), although there was no difference between the evaluated sites.

X-ray diffraction (Figure 2) indicated similar mineralogical compositions among all evaluated sites. There were very low mineral intensity reflections from the micas group in the vicinity of 1.0 nm and kaolinite (Kt) in most of the samples. The primary minerals quartz (Qz) and feldspar (Ft) predominated in all samples analyzed.

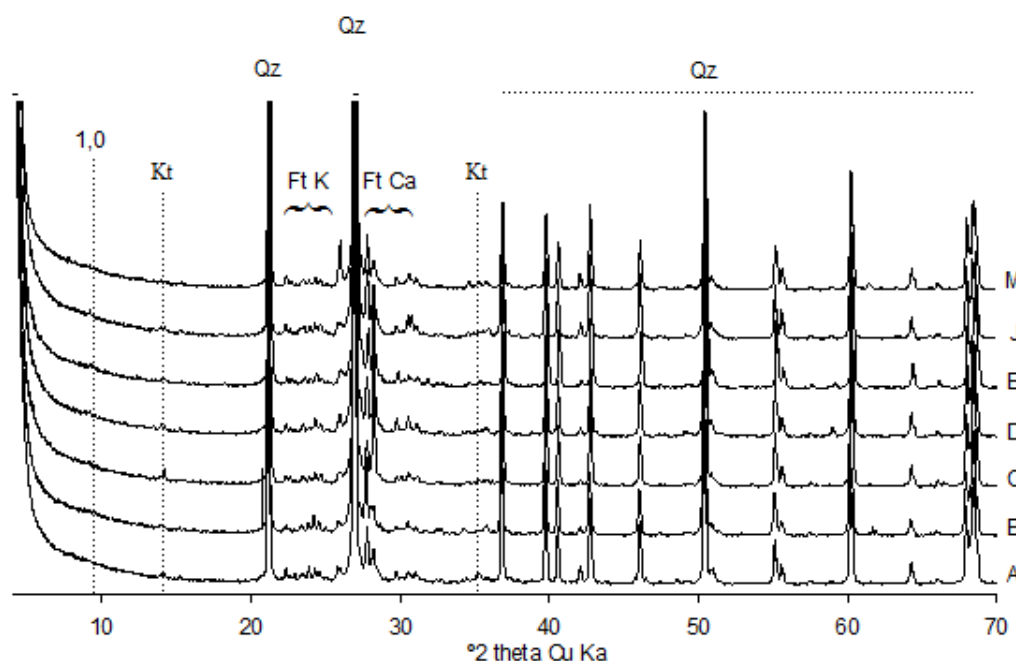


Figure 2. X-ray diffractograms (XRD) of fine sediments in the Dilúvio Stream in the study's area. Minerals 2:1, clay vermiculite and/or smectite (1.58 nm); (0.10 nm); potassium feldspar (Ft K) and calcium (Ft Ca) (0.404-0.402 nm and 0.321-0.299); quartz (Qz) (0.334 nm) and kaolinite (Kt).

3.2. Influence of the channeled section of Dilúvio Stream on sediment metal concentration

Comparing the section of Dilúvio Stream in the study's area (AD) with the sites in the margins of Lake Guaíba, there was difference between the site upstream of the Dilúvio's outflow (Ga) in all analyzed metals, except for K. Al and K had lower levels in the section upstream of the outflow (Ga) and Cr had lower values in the non-channeled section (Figure 3). Sites upstream (Ga) and downstream (Gd) shows that the non-channeled section has levels of

metals similar to Ga and both were higher than Gd. Thus, the main pollution source of this environment is located in the channeled section of Dilúvio Stream, along with the Ipiranga Avenue. However, the values of the pseudo total metals when compared to the quality reference values of CONAMA Resolution N°. 454 (Conama, 2012), indicate that the metal concentrations were below the reference values for Level I. Fine sediment can complex metals affecting their availability (Yu et al., 2012), but CONAMA Resolution N°. 454 (Conama, 2012) does not consider particle size as a factor for determination of guidelines values, meaning that even if the concentrations are lower than the guiding value, that does not mean that there is no pollution in the sediment.

Ipiranga Avenue has an intense traffic of vehicles, as well as a strong presence of buildings and waterproofed areas in its surroundings. These issues increase the deposition and contamination rates of road dust that flow to surface water bodies by runoff carrying metals such as Zn, Pb, Cu, Cr, and Ni (Sharley et al., 2016; Zhang et al., 2016). Nevertheless, Cr is also associated with atmospheric deposition near industrial areas (Sharley et al., 2016), with an historical use in leather and footwear industries in the Lake Guaíba drainage basin (De Andrade et al., 2018).

In a study evaluating the sediment sources in Dilúvio's drainage basin stream, Poletto et al. (2009) found that 46% of the suspended sediment comes on average from paved roads, 23% from unpaved roads, and 31% from the stream channel itself (channel bank). Since the majority of the sediments come from roads (paved or unpaved), it is possible to infer that the lower modification of the surroundings of the section of Dilúvio Stream in the non-channeled area could influence the minor levels of metals and TOC presented in the canal when compared to other locals like Ga and Gd.

All the levels of pseudo total metals standardized by Al showed statistical differences among AD, Ga and Gd sites (except K). The site AD (non-channeled section of Dilúvio Stream) had lower levels ($p < 0.05$) when compared to sites Ga and Gd (in Lake Guaíba margins). Ga and Gd differed only for Cr ($p < 0.05$) and Ni ($p < 0.1$), with the highest values found in Ga. The environmental changes and anthropogenic influence on the surroundings of the channeled section may not appear clearly in the surface sediment standardized with Al for several reasons, such as its high sand content; the metal's enrichment by the increasing of clay plus silt and carbon; and the possibility of pollution being accumulated elsewhere downstream from Lake Guaíba. Pollution by the channeled section did not have a visible influence on heavy metal values in the sediments of Gd compared to Ga when standardized by Al (Figure 4). The difference in the proportion of fine sediments between the points may be one of the causes of the variation in concentrations between the three areas.

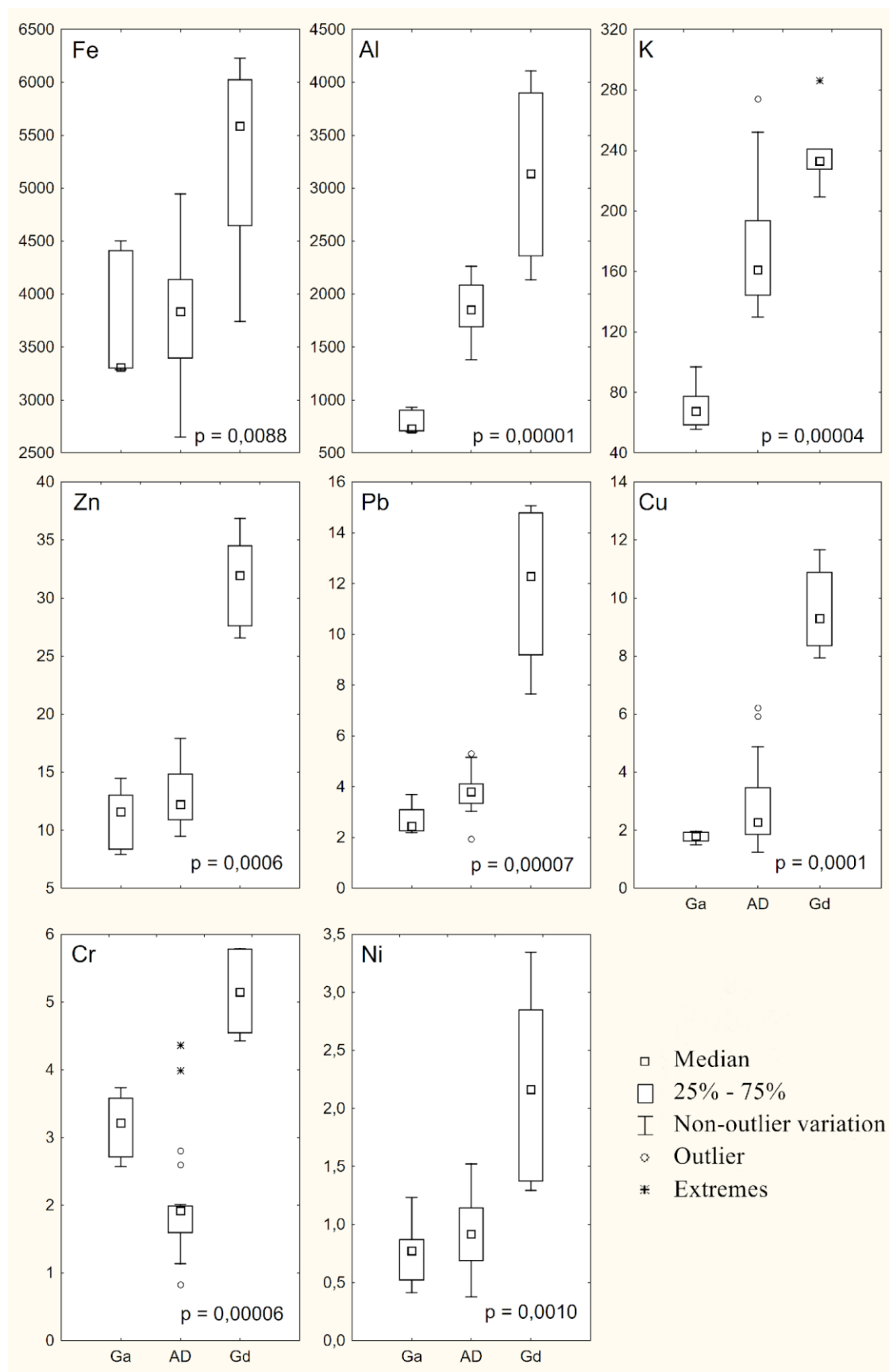


Figure 3. Pseudo Total element values (mg kg⁻¹) in sediments of Dilúvio Stream in the study's area (AD) and sites in Lake Guaíba margins Upstream (Ga) and Downstream (Gd) of the Dilúvio's outflow. Kruskal-Wallis test at 5% probability.

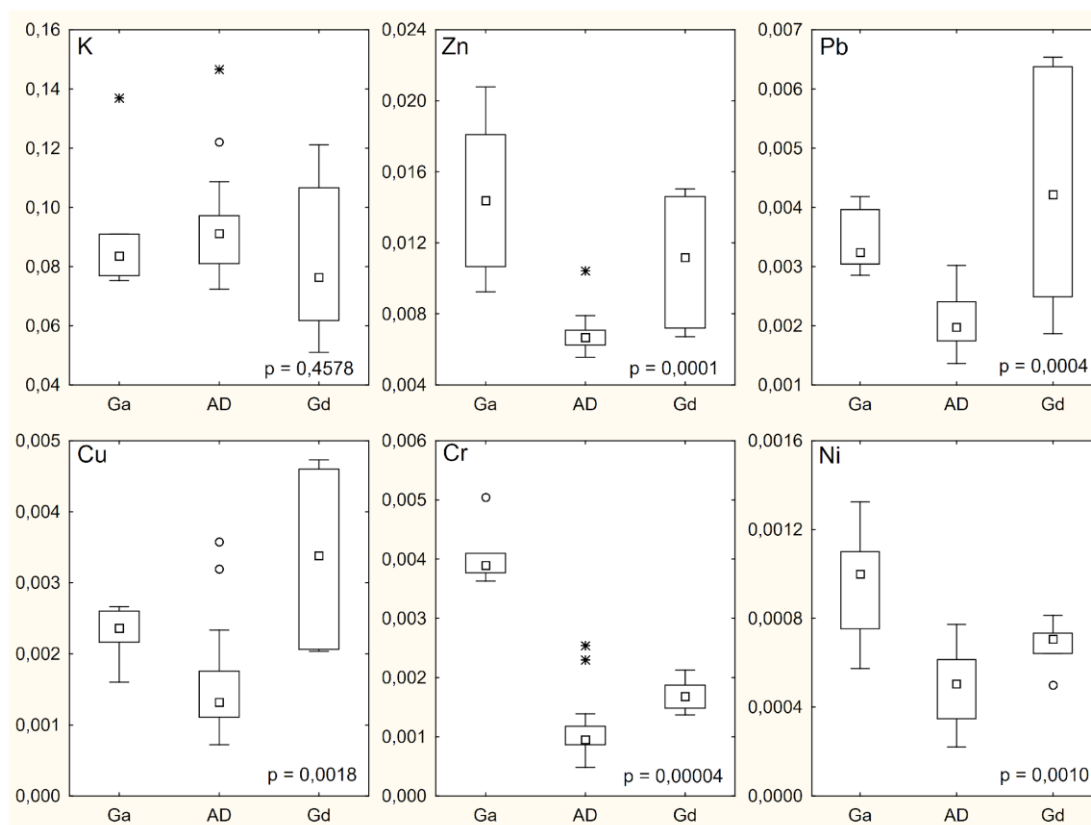


Figure 4. Pseudo Total element values (mg kg⁻¹) standardized by Al in sediments of the Dilúvio Stream in the study's area (AD) and the in the sites Upstream (Ga) and Downstream (Gd) of the Dilúvio's outflow. Kruskal-Wallis test at 5% probability.

Soares et al. (2004) also found higher concentrations of Fe, Al, K, Zn, Pb, Cu, Cr, Ni, Ca, Mg, Mn and Na in Salso Stream (a stream from Porto Alegre City) when compared to Dilúvio Stream. The Geoaccumulation Index, based on average values and geochemical data of basement rocks of the local drainage basin, showed that the sediments presented low contamination (Cr, Cu, Ni, Pb, Zn), although one of the indicators showed considerably high pollution with Cu, Ni and Zn (Soares et al., 2004). The higher metal levels showed in the study are probably due to the higher levels of TOC found in the bed sediment (8.10-9.98%), despite the similar sources (marginal vegetation, phytoplankton, and anthropogenic sources such as domestic effluents) and similar particle-size distribution (Upstream sites) in comparison with Dilúvio Stream. Because the metal concentrations in the AD showed lower values than in the Salso Stream, it could be expected, at least, an equal to lower anthropic influence in the section of the study of Dilúvio Stream, presenting that this section could be possibly used as a good parameter for pollution comparison with other sections of Dilúvio Stream.

Anthropogenic sources such as waste, urban sediments, traffic and domestic and industrial effluents can contribute to higher concentrations of heavy metals (Pinto et al., 2009). Nearby vegetation and phytoplankton can generate higher concentrations of organic matter that by natural reactions could maintain a higher level of heavy metals complexed in bed sediments or solubilized in water (Soares et al., 2004; Pinto et al., 2009).

Metal enrichment by fine sediment could be a factor affecting the concentration of heavy metals in the sites of Dilúvio Stream and Lake Guaíba. However, part of these sediments may come from the suspended sediment of Dilúvio Stream, having heavy metals adsorbed or not, and accumulating downstream. Azevedo et al. (2016) attribute some of the imbalance of sediment deposition in the tidal inlet of São Luís, Maranhão, Brazil to alterations, such as the

construction of roads and the development of the nearby urban area in the river basins. The urban development in Dilúvio's drainage basin may have been misbalanced due to these alterations, as some evidence is found through the channeled area, like the accumulation of sediment and the reduction of the channel that occurs in the periodic dredging of the sediment.

Channelization results in gradual degradation impacting the biotic and abiotic components of the system, which may lead to a high and fluctuating concentration of contaminants and nutrients (Pandey et al., 2018). A previous study in Lake Guaíba (De Andrade et al., 2018) shows that the main source of punctual sediment pollution in the margins of the Lake Guaíba comes from urban streams, such as Dilúvio. Therefore, in the channeled area there is possibly an important input of pollution from anthropogenic sources in the surroundings.

The area suffers from many different and diffuse types of pollution, as it has many sources with highly varied composition, such as the traffic, building and road deterioration, untreated domestic sewage, pluvial sewage, siltation and heavy metal enrichment by fine sediment. Further studies are needed to better understand the variations and the specific sources of heavy metals in Dilúvio's drainage basin.

4. CONCLUSIONS

The concentration of metals in the surface sediment of the non-channeled section of the Dilúvio Stream presented a high coefficient of variation, but this variation decreased when standardization by Al was applied. The concentration of heavy metals in the non-channeled section of Dilúvio Stream was similar to the site in the margins of Lake Guaíba before the outflow of Dilúvio Stream and smaller than both points in the margins of Lake Guaíba when compared with the Al standardization. The Dilúvio Stream channeled area possibly suffers anthropogenic influence through diffuse pollution sources and the imbalance of sediment deposition, especially in the outflow, that may be causing metal enrichment by fine sediments.

The improvement of the environmental conditions in the Dilúvio Stream should be targeted by local government policies in order to mitigate the pollution of Dilúvio Stream and Lake Guaíba, improving the quality of life, environment and local population. To achieve this goal, the government should apply a management plan to the whole basin and focus not only on the stream itself.

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