Anuário do Instituto de Geociências
Universidade Federal do Rio de Janeiro
https://revistas.ufrj.br/index.php/aigeo/

ISSN 0101-9759
e-ISSN 1982-3908

Contamination of Urban Watersheds: the Case of Arroio Moinho, Porto Alegre, Rio Grande do Sul, Brazil

Contaminação de Bacias Hidrográficas Urbanas: o Caso do Arroio Moinho, Porto Alegre, Rio Grande do Sul, Brasil

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Abstract

This article aims to analyze the contamination of water and bottom sediment at Arroio Moinho (Mill Stream), in Porto Alegre (Rio Grande do Sul, Brazil). From two sample collections, a series of diagnostic measurements were carried out, such as: a) physical-chemical and biological analysis of the water; b) water quality index (WQI); c) metal contamination, granulometric and mineralogical analyses of the bottom sediment; d) total organic carbon (TOC); e) categorization into water quality classes; f) contamination factor (CF) and geoaccumulation index (Igeo) geoindicators; g) analysis of *per capita income* and population density. The analytical results of the water at the two sample locations exceeded the limits established by Class 4 (restricted use). The WQI revealed the worst level (very bad in 2012 and bad in 2018) at all sampling points. The bottom sediment analysis showed that the spring has a low fine-grained fraction content (<3%) and TOC levels between 8 and 17%. However, the sediments revealed high levels of metals such as Zn and Cu and low to moderate Pb levels. These results allowed the stream to be classified as Class 3 in terms of soil quality, requiring identification of the source of the pollution and ongoing inspection to monitor contamination.

Keywords: Water resource contamination and pollution; Water and soil quality; Dilúvio Stream

Resumo

O presente artigo tem como objetivo analisar a contaminação da água e do sedimento de fundo do Arroio Moinho, em Porto Alegre (RS). A partir de duas coletas de amostras, realizou-se uma série de diagnósticos, como: a) análises físico-químicas e biológicas da água; b) índice da qualidade da água (IQA); c) análises químicas de metais, granulométrica e mineralógica dos sedimentos de fundo; d) carbono orgânico total (COT); e) enquadramento em classes de qualidade; f) geoindicadores (FC e Igeo); g) análise da renda *per capita* e densidade populacional. Os resultados analíticos da água em dois pontos amostrados extrapolaram os limites estabelecidos pela Classe 4 (uso restrito). O IQA revelou o pior nível de qualidade (muito ruim em 2012 e ruim em 2018) em todos os pontos. Já os resultados analíticos do sedimento de fundo demonstraram que o manancial apresenta baixo teor de grãos finos (<3%) e teores de COT entre 8 e 17%. No entanto, os sedimentos apresentaram altos teores de metais como Zn e Cu e baixo a moderado de Pb. Esses resultados permitiram enquadrar o manancial na Classe 3 de qualidade do solo, onde se estabelece a necessidade de identificar a fonte poluidora e o consecutivo controle de emissão para monitorar a contaminação.

Palavras-chave: Contaminação de recursos hídricos; Qualidade da água e de solo; Arroio Dilúvio

1 Introduction

Disorderly urban growth is causing concomitant environmental degradation in ecological systems (Knoll, Lübken, U. & Schott 2017; Perini & Sabbion 2017; Postel & Richter 2003; Rodrigues 2015; Smol 2008). This is an important topic since the United Nations (2019a, 2019b) and the Population Reference Bureau (2020) estimate that the world's urban population, by 2050, would increase by 60%, growing from 4.2 billion (4.2 x 10^9) in 2019, to 6.6 billion (6.6 x 10^9) inhabitants concentrated in cities. Thus, the current rate of 55% of the total population concentrated in cities would become 68% of the possible total of 9.77 billion (9.77 x 10^9) in 2050. Of the roughly 210 million inhabitants in Brazil, 86% live in cities (United Nations 2019b). It is estimated that in 30 years, the country's total population would grow 11%, reaching 232.9 million inhabitants. This population projection associated with the current economic model that transforms forests, mineral resource, ecosystems in commodities points to an evident ecological collapse (Population Reference Bureau 2020; United Nations 2019a).

In this context, contamination of urban water resources becomes increasingly critical, since one of the leading causes of contamination of urban springs is the release of untreated water into waterways after domestic and industrial use (Postel & Richter 2003; Tundisi & Tundisi 2011). Gomes (2013) illustrates how water is currently seen as simply an economic resource and thereby reduces the relationship between humanity and water to a market problem, no longer a geosystemic issue. It is necessary to analyze rivers as complex ecosystems that do not align strictly to human actions. The various benefits of river ecosystems include water supply, water quality, flood control, erosion control, and fluvial aquatic life (Wohl 2017).

In Brazil, urban river pollution and the high incidence of waterborne diseases are common problems, according to the National Water Agency (Agência Nacional de Águas 2019). Management of organic matter discharged into water sources is a challenge for water quality managers in the country. This challenge is directly related to sanitation levels. The National Sanitation Secretariat of the Ministry of Regional Development (Ministério do Desenvolvimento Regional da Secretaria Nacional de Saneamento 2019) revealed that only 46.3% of the total volume of sewage generated in Brazil was treated in 2018. In urban areas, the average rate of sewage collection is 60.9%, with an average of 45.4% in the country's southern region. Brazil still releases 53.7% of sewage untreated into streams, which corresponds to 4.98 billion cubic meters per year or the equivalent of more than 5,000 Olympic pools of sewage per day.

In light of this, the interventions proposed by water managers are commonly restricted to the underground canalization of streams located in urban centers and the consolidated metropolitan area (Mauch & Zeller 2008; Perini & Sabbion 2017). This action creates a loss of awareness of the stream as a fundamental feature of the landscape inherent to the quality of urban life. This type of intervention separates an essential natural element - the stream and the ecological services it provides - from the local population and culture (Massard-Guilbaud 2017). In shantytowns on the outskirts of the cities, the streams still maintain their natural course and therefore retain a particular ecological relationship with the stream banks and ecosystemic benefits. Nonetheless, even in these locations, the streams often take on contaminating loads, generally organic.

The study area is located in Porto Alegre, capital of the state of Rio Grande do Sul (Figure 1A). This municipality is located on the shores of Lake Guaíba, (volume 1.5 km³, surface area 496 km², according to Departamento Municipal de Água e Esgotos 2020), which supplies the water for the city and also is the destination of industrial and sanitary sewage for the entire metropolitan area of around 4.3 million people. Therefore, the water supply quality depends on the water of the streams and rivers' quality that flow into the lake. These require an integrated analysis of the entire water system. Among the different streams in Porto Alegre that contribute to the capacity of the Guaíba the Arroio Moinho stands out despite of its small volume because it runs through a region of urban-rural interface, in an urban periphery shantytown where single-family homes predominate. This work aims to test the hypothesis that, in these circumstances, the contamination in the spring is exclusively organic, or there might be strong metal contamination and what that would reveal.

1.1 Study Area

The municipality of Porto Alegre is formed by 27 subwatersheds that comprise the Guaíba Hydrographic Region, one of the three hydrographic regions (Figure 1B) in Rio Grande do Sul. Of the subwatersheds that integrate the municipality, the most populous is Arroio Dilúvio (Figure 1C), with 446 thousand inhabitants in an area of 83.74 km², and length of 13.14 km. It is considered by Menegat & Kirchheim (2006) to be the most crucial watershed in the city. The waters of the micro-watersheds of the arroios (streams) Cascata, Mato Grosso, Águas Mortas, and the object of this research, the Arroio Moinho (Figure 1D), flow into it.

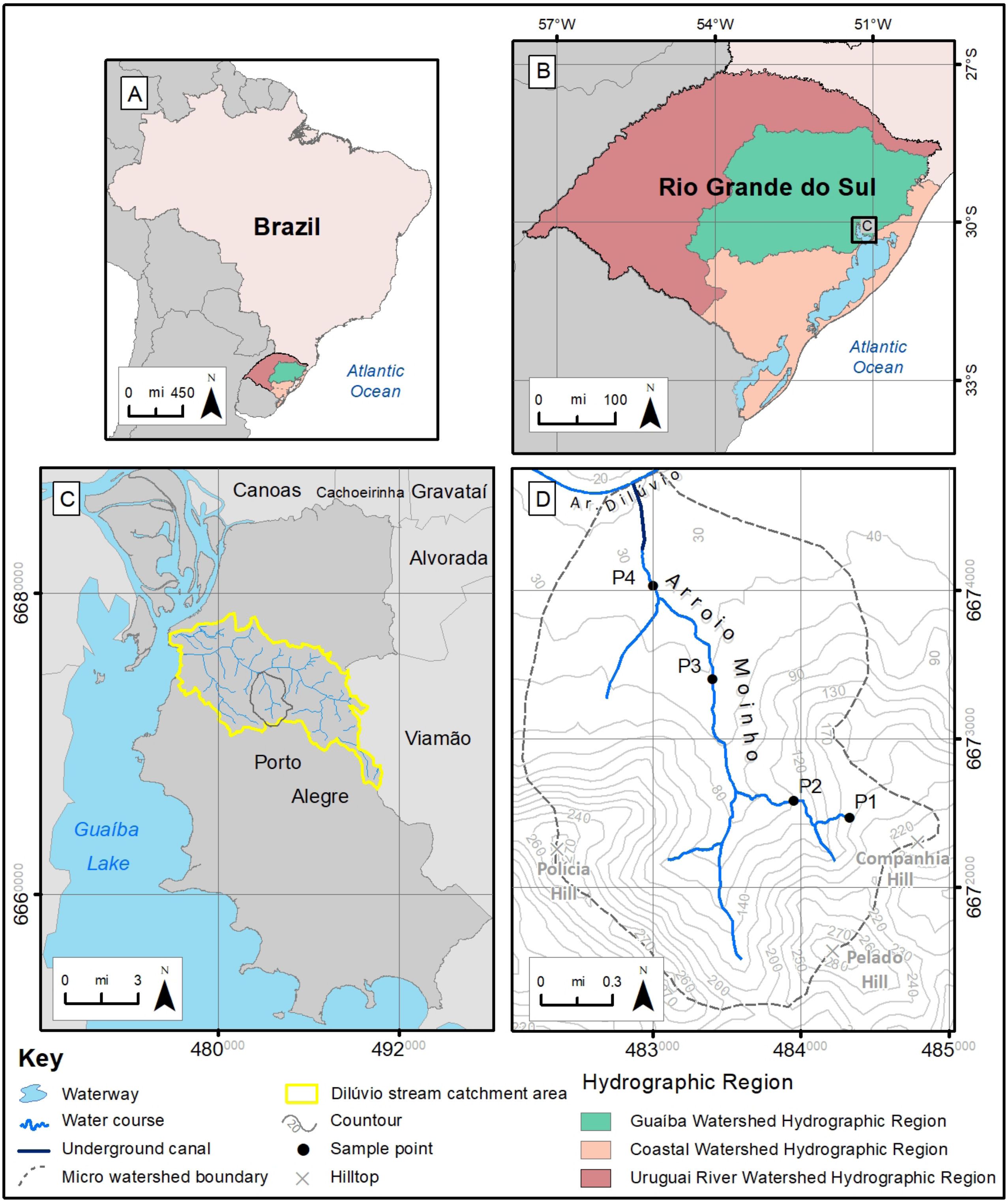

Figure 1 A. Map of the state of Rio Grande do Sul in the south of Brazil; B. Map of hydrographic regions of the state and location of the city of Porto Alegre; C. Map of the Arroio Dilúvio subwatershed, belonging to the Guaíba Hydrographic Basin, yellow outline identifies the Arroio Moinho microwatershed (modified by Hasenack, Weber & Marcuzzo 2008); D. Map of the Arroio Moinho microwatershed and locations of the sampling points P1 to P4

The springs for Arroio Moinho are located on the slopes of the Polícia, Pelado, and Companhia hills (Figure 1) in the central portion of the Porto Alegre Ridge, the municipality's main elevation, 22 km long. The Arroio Moinho micro-watershed encompasses areas of the Coronel Aparício Borges, São José, Partenon, and Vila João Pessoa neighborhoods and has a population of 58,561 inhabitants (Instituto Brasileiro de Geografia e Estatística 2011). The total area of the micro-watershed is 6.54 km² and the main channel is 3.58 km long, with the last 450 m channeled through an underground tunnel. In this segment, Duarte (2002) analyzed flow measurements to be between 0.4485 and 0.00525 m^3s^{-1}.

The micro-watershed is considered a sub-basin with a reduced area, though there is no consensus in the bibliography (Cecílio & Reis 2006) as to the maximum size. According to Faustino (1996), a micro-watershed is one whose drainage area is less than 100 km² and runs directly into the main course of a sub-watershed.

The Arroio Moinho runs through three geological units from its sources to its mouth (Figure 2). The highest portion of the micro-watershed is made up of Santana Granite. The lower portions, however, where the middle segment of the stream runs, are made up of Três Figueiras Granodiorite. Finally, the mouth runs through old Holocene alluvial deposits (Menegat et al. 2006, Tomazzeli & Villwock 2000).

The city of Porto Alegre has a humid subtropical climate characterized by meteorological variability throughout the year. The municipality is in a climatic transition zone between tropical maritime air masses and cold maritime air masses. The arrival of cold air masses in the city causes sudden drops in temperature. Maximum temperatures occur in January, with an average of 24.9°C. The minimum temperatures occur in June and July, with an average of 15.2°C. The average annual rainfall is 1,324 mm and falls principally from June to September (125 mm to 135 mm) (Livi 2006).

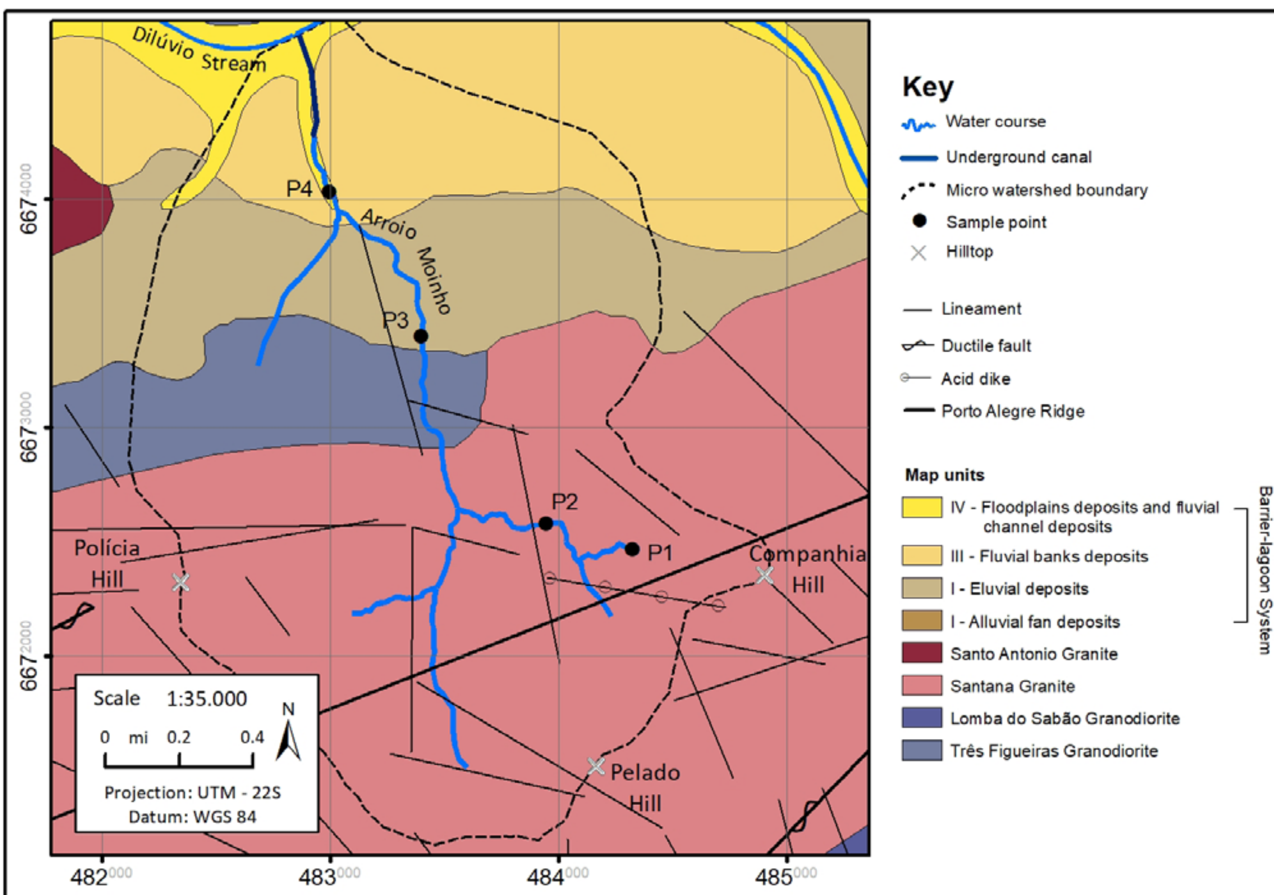

Figure 2 Geological map of the Arroio Moinho region (adapted from Menegat et al. 2006).

2 Materials and methods

2.1 Parameters Analyzed

Considering the legal environmental guidelines for water resources (Conselho Nacional do Meio Ambiente 2005), physic-chemical and biological parameters of water that characterize the influence of anthropogenic sources in aquatic environments (Libânio 2016) were chosen. These parameters are dissolved oxygen, biochemical oxygen demand, total nitrogen, total phosphorus, and total phenol, fecal coliforms *Escherichia coli*, total solids, temperature, potential of hydrogen (pH), turbidity, total arsenic, total aluminum, and total lead. The objective of classifying water bodies in classes according to principal use is to systematically manage water resources and quality (Brazil 1997). Water quality monitoring allows for priorities for water pollution control to be set (Agência Nacional de Águas 2019).

In addition to the classification of stream waters, the Water Quality Index (WQI) of Brown et al. (1970), adapted by a river basin management committee for rivers in the State of Rio Grande do Sul (Comitê de Presevarção, Gerenciamento e Pesquisa da Bacia do Rio dos Sinos 1990) and considered by the National Water Agency (Agência Nacional de Águas) as the main indicator of the condition of water bodies in the country, was determined. The index incorporates nine parameters considered important in assessing water quality. Water quality variation curves were established for each parameter (Agência Nacional de Águas 2005, 2012, 2019). Equation (1) was used to establish the WQI:

$$WQI = \sum_{i=1}^{n} q_i^{Wi} \quad (1)$$

Where: n = number of parameters that enter the calculation; q_i= relative quality of the i-th parameter obtained in the "average quality variation curve" as a function of the concentration of the parameter; w_{ii} = is the relative weight of the i-th parameter assigned according to its importance in the calculation; and i = parameter order number.

A weight is assigned to each parameter in the equation. Five WQI intervals were thus determined (Fundação Estadual de Proteção Ambiental do Rio Grande do Sul 2020), with the first two quartiles, WQI intervals between 0 and 50, representing very bad water quality and bad water quality. The next three intervals, WQI between 51 and 100, represent good water quality to excellent water quality. National Water Agency (Agência Nacional de Águas 2005), does not consider the influence of the different forms of nitrogen and phosphorus adopted by different states to prevent meaningful comparison among the WQI results. In this study, total nitrogen and total phosphorus were used in the calculation.

These analyses were carried out at the Analytical Center of the Feevale University (RS), duly accredited by the state environmental agency, the State Foundation for Environmental Protection (Fundação Estadual de Proteção Ambiental do Rio Grande do Sul, FEPAM). The standard analytical methodologies of the *Standard Methods for the Examination of Water and Wastewate*r (American Public Health Association et al. 2012, 2017) were used for this study.

Concerning the Arroio Moinho bottom sediment, the metals frequently introduced into urban springs as by-products of human activities were analyzed, these being: Cd, Cu, Cr, Ni, Pb and Zn (Berg & Steinnes 2005). The laboratory responsible for the analyses was *GREEN LAB* (RS), which is accredited by State Foundation for Environmental Protection, an environmental policy body in Rio Grande do Sul. The concentrations of these metals were obtained through acid digestion (Environmental Protection Agency 1996), an analytical methodology established by the Environmental Protection Agency of the United States, internationally accepted as required by law (Conselho Nacional do Meio Ambiente 2009). Total organic carbon content (TOC) was determined by the gravimetric method. The results were compared with the environmental law guidelines (Conselho Nacional do Meio Ambiente 2009, Fundação Estadual de Proteção Ambiental do Rio Grande do Sul 2014) to determine the soil quality classes. The results were also compared with the average, minimum and maximum concentrations found in the region's underlying lithology. From the analyses, geoindicators frequently used in studies of contamination assessment in urban environments were calculated to reveal and distinguish anthropogenic contamination in sediments. These geoindicators are the Contamination Factor (CF) and the Geoaccumulation Index (Igeo). CF is defined as the relationship between the measured concentration in the bottom sediment (Cs) compared to its natural base level concentration (Cref) (Förstner & Wittmann 1989). According to Equation (2):

$$CF = Cs/Cref \quad (2)$$

Igeo is the ratio of the concentration of each element (Cs) measured in the sediments with a reference concentration (Cref) corresponding to the background value. This procedure eliminates possible errors due to natural fluctuations in metal concentrations or minor anthropogenic influences (Müller 1979). It is interesting to note that the Igeo has a safety margin (1.5 x Cref), so small fluctuations in the metal concentration at the collection points do not erroneously result in the site being classified as contaminated, as seen in Equation (3):

$$Igeo = log\ (Cs/1.5Cref) \tag{3}$$

Müller (1979) grouped Igeo results into seven intervals, where the duplication of the *Cs/1.5Cref ratio* designates the upper limit of each class. The classes (Igeo class) of the sediment quality represent increasing levels of pollution from zero (0), for virtually unpolluted sediments, to six (6) for very heavily polluted sediments (Table 1). The Igeo 6 class represents an increase of at least 96 times the background concentration multiplied by 1.5.

Table 1 Geoaccumulation index (Igeo) of metals analyzed in the Rhine River sediments, Germany, and their respective classes (Müller 1979).

Pollution Intensity	Igeo	Igeo Class
Very highly polluted	> 5	6
Highly to very highly polluted	4 - 5	5
Highly polluted	3 - 4	4
Moderately to highly polluted	2 - 3	3
Moderately polluted	1 - 2	2
Unpolluted to moderately polluted	0 - 1	1
Unpolluted	< 0	0

In this project, water was collected on June 12, 2012, and August 14, 2018. Sediment collection was performed only on August 14, 2018. Both sample collections were in winter, and it should be noted that the rainfall before the June 12, 2012 date had been lower than that before the second collection date of August 14, 2018. According to the database of the National Institute of Meteorology (Instituto Nacional Metereologia 2020), the total accumulated precipitation in the week of the first collection (between June 5 and 12, 2012) was 0.6 mm, noting that 0.4 mm was due to the precipitation on June 11, the day before the sample was collected. On the collection day, June 12, 2012, the climatological data were: the absence of precipitation, a minimum temperature of 11.2°C, and a maximum temperature of 25.6°C. The total accumulated precipitation in the week before the second collection (between August 7 and August 14, 2018) was 15 mm. However, on August 13, the day before the collection, there was no precipitation. On the collection day, August 14, 2018, the meteorological data were: precipitation 0.1 mm; minimum temperature, 10.4°C; and maximum temperature, 24.8°C.

The sampling points (Table 2) were determined based on Strahler's stream order criteria based on geomorphology (Strahler 1967), so there was at least one sampling located on each hierarchical level of the stream. P1 was in a first-order channel, P2 in a second-order channel (Figure 3), P3 and P4 in a third-order channel (Figure 4), the highest level of this stream, as shown in Table 2.

The superficial sediment layer sampling, collected using a stainless steel shovel, was carried out on the banks (P3 and P4) and in the center of the cross-section (P1 and P2) of the channel. The average weight of each sample was 500 grams. The samples were placed in flasks adequately prepared according to the laboratory protocol. According to Föstner & Wittmann (1989), the leading geochemical carriers of both natural and anthropogenic origins are found in the fine-grained fraction of the sediment. The fine-grained fraction of the sediment must, therefore, be separated for chemical analysis. The procedure consisted of wet sieving in PVC sieves to separate the fine-grained fraction, dried in an oven at approximately 40°C, and then homogenized by crushing the particles (Guerra 2000).

Table 2 Location of sampling points (positioning of the points, according to Strahler 1967).

Point	Figure	UTM Coordinates	Altitude (m)	River Segment Hierarchy	Region
P1	3A, B	0484326 mE 6672463 mS	165	1st order	Source or higher
P2	3C, D	0483950 mE 6672572 mS	102	2nd order	Intermediate to higher
P3	4A, B	0483422 mE 6673398 mS	43	3rd order	Intermediate to lower
P4	4C, D	0482998 mE 6674030 mS	30	3rd order	Lower

Figure 3 A. Gray water at the water collection site at Point 1 (P1), in the region near the springs, south view of the canal (2012); B. Material accumulated in the streambed and along the banks, dark gray colored water at P1, north view of the channel (2018); C. Location of Point 2 (P2), in the upper segment of the stream; south view of the canal (2012); D. Waste accumulated in the channel, dark gray colored water at P2, south view of the channel (2018). Arrows indicate the sample collection locations.

The capacity of a spring to retain metals is related to its bottom sediment's fine-grained fraction content. For this purpose, in Arroio Moinho, the granulometric analysis was performed on the samples using the wet sieving method (Suguio 1973). Part of the fine-grained fraction (F_F<0.062 mm, Wentworth granulometric scale) obtained through sieving, drying in an oven, and mechanical disaggregation, was analyzed by X-ray diffraction, by the procedures described by Alves (1987).

Besides the environmental determinations (pollution of the water by organic material and inorganic contamination of the sediment), an analysis of the socioeconomic context of the population residing in the micro-watershed was carried out. The objective was to understand the social context of the population living in that region. For this analysis, the micro-watershed was divided into geomorphological regions as follows: (a) lower course, being the area ranging from 0 m to 39 m in elevation; (b) mid-course, from 40 to 99 m; and (c) upper course, between 100 and 298 m. In addition, socioeconomic data of the residents and the nominal income classes were analyzed. These income classes are: no income; up to 1 monthly minimum salary (MS); between 1 and 3 monthly minimum salaries; and above 3 monthly minimum salaries. For calculation purposes, Brazilian Institute of Geography and Statistics (Instituto Brasileiro de Geografia e Estatística 2011) used the 2010 minimum monthly salary in Brazil of R$510 (US$290) as reference. Data for the 84 census tracts throughout the different geomorphological regions of the micro-watershed were used to find the results. There were 19 tracts in the lower course, 40 in the mid-course, and 25 in the upper course.

Figure 4 A. Accumulation of solid waste in the streambed and along the banks of the channel at Point 3 (P3), in the middle segment of the stream, north view of the channel (2012); B. Gray waters and accumulation of residues at P3, south view of the channel (2018); C. Solid waste accumulated on the banks of the channel, gray waters at the location of Point 4 (P4), close to the mouth, south view of the channel (2012); D. Gray waters and accumulation of residues on the banks of the channel at P4, north view of the channel (2018). Arrows indicate the sample collection locations.

2.2 Water and Soil Quality Classification Framework

The National Environment Council (CONAMA), in using the powers given to it by the National Environment Policy (Brazil 1981) to "establish norms, criteria, and standards related to the control and to the maintenance of the quality of the environment to guide the reasonable use of environmental resources, especially water resources," published the resolutions that classify bodies of water (Conselho Nacional do Meio Ambiente 2005) and soil (Conselho Nacional do Meio Ambiente 2009) in the nation.

Resolution 357 (Conselho Nacional do Meio Ambiente 2005) establishes possible uses of water according to quality classification, defined as a set of conditions and standards of quality necessary to meet current or future uses. The standard represents the required values for a specific water quality parameter. Thus, each substance has its limits (minimum and maximum) for each classification. Better quality water may be used for less stringent uses, so long as the water quality itself is not impaired. Freshwaters are classified into five classes: a particular class, and classes 1 to 4. In the particular class, the water body's natural conditions must be maintained, and no limits are assigned. The standards for freshwater quality classes 1 to 4 of the substances analyzed in this study are shown in Table 3.

Concerning the evaluation of bottom sediment quality in aquatic systems, norms, and reference values based on resolutions defined for soil studies were used. National Environment Council has established standards for the control and maintenance of soil quality (Conselho Nacional do Meio Ambiente 2009). In this legislation, council recognizes the serious public health risk presented by contaminated areas, and the need to prevent contamination

Table 3 Standards of freshwater quality of the substances analyzed in this research (modified from Conselho Nacional do Meio Ambiente 2005).

Parameter	Unit	Class 1	Class 2	Class 3	Class 4
DO	$mg.O_2.L^{-1}$	≥6	≥5	≥4	≥2
$BOD_{5.20}$	$mg.O_2.L^{-1}$	≤3	≤5	≤10	≤10
FC *E. coli*	MPN	≤200	≤1,000	2,500	2,500
Total Phosphorus[1]	$mg.L^{-1}$	≤0.10	≤0.10	≤0.15	≤0.15
Total Nitrogen[2]	$mg.L^{-1}$	3.70	3.70	13.30	13.30
Turbidity	NTU	≤40	≤40	≤100	100
Total Phenol	$mg.L^{-1}$	0.003	0.003	0.01	1.0
Total dissolved aluminum	$m.L^{-1}$	0.100	0.100	0.200	0.200
Total Arsenic	$mg.L^{-1}$	0.010	0.010	0.033	0.033
Total Lead	$mg.L^{-1}$	0.010	0.010	0.033	0.033
pH	–	6 to 9			
TDS	$mg.L^{-1}$	500			

DO: dissolved oxygen; $BOD_{5.20}$: biochemical oxygen demand required to oxidize organic matter over five days, at an incubation temperature of 20°C; FC E. coli: fecal coliforms Escherichia coli; MPN: most probable number in 100 ml; (1) lotic and distributary channel environments of intermediate environments; (2) for pH≤7.5; NTU: nephelometric turbidity units; pH: potential of hydrogen.

of the soil and subsequent surface water and groundwater contamination and the importance of maintaining soil function. Thus, the following guiding values were defined to determine soil quality: quality reference value (background-QRV, to be defined by the environmental agencies of the states according to regional geology); prevention value (PV) (similar to the Dutch "target values"); and intervention value (IV).

State Foundation for Environmental Protection defined the QRVs taking into account the state's geological provinces (Fundação Estadual de Proteção Ambiental do Rio Grande do Sul 2014). The results were grouped as follows: 1) Mesozoic volcanic rocks from the Paraná Basin that make up the Southern Plateau; 2) igneous and metamorphic rocks of the Dom Feliciano Belt and the Rio de La Plata Craton exposed in the Rio Grande do Sul Shield; 3) Peripheral Depression pelitic sedimentary rocks; 4) sandstone sedimentary rocks of the Plateau of the Rio Grande do Sul Shield and the Peripheral Depression; and 5) Cenozoic deposits from the Coastal Province.

Because the Arroio Moinho is located predominantly in granitic-gneissic units of the Rio Grande do Sul Shield (see item Study Area), the soil QRV standard corresponding to FEPAM's group 2 were used (Table 4). For the sake of comparison, this project compared the results obtained in the research with the average concentrations analyzed in Santana Granite, the predominant lithology in the study area that comprises Arroio Moinho (Oliveira, Koester & Soliani Jr. 2001) (see Figure 2, Table 4).

Table 4 Quality reference values (QRV), prevention values (PV), and intervention values (IV) established by Brazilian legislation and average concentration (Avg) found in the predominant lithology in the region for the parameters analyzed in the research. Units: mg kg^{-1} (from: Conselho Nacional do Meio Ambiente 2009, Fundação Estadual de Proteção Ambiental do Rio Grande do Sul 2014, Oliveira, Koester & Soliani Jr. 2001).

Metals	FEPAM	CONAMA		Santana Granite
	QRV	PV	IVR	Avg
Cd	0.40	1.30	8	0.04
Cr	40	75	300	44.6
Cu	9	60	400	na
Ni	12	30	100	2.4
Pb	18	72	300	22.0
Zn	31	300	1.000	47.2

QRV: **quality** reference value for the crystalline rock soils of the Rio Grande do Sul Shield; Avg: average concentrations; IVR: intervention value for residential use; na: not analyzed.

The PV is the limit of the concentration of a substance in the soil that protects soil functions. It is determined based on phytotoxicity tests or by toxicological risk assessment. The IV is the concentration of a substance in the soil above which there are potential risks, direct or indirect, to human health. National Environment Council considered standardized exposure scenarios for different land uses and occupations, thereby assessing human health risk. Table 4 shows the IV for residential land use, IVR.

Four quality classes were defined according to the guidelines, with Class 1 corresponding to the lowest contaminant load and Class 4 to the maximum, which require interventions to restore the environment. Soils with contaminant concentrations less than or equal to QRVs comprise Class 1. Those with concentrations of at least one chemical substance higher than QRV and less than or equal to PV correspond to Class 2. Soils with concentrations of at least one chemical substance higher than the PV and less than or equal to the intervention value, IV, are Class 3. The soils that have concentrations of at least one chemical substance higher than the IV are Class 4.

Soil classification allows for the establishment of contamination prevention and control procedures so that Class 1 does not require actions. Class 2 may require an investigation of the potential source of contamination and an assessment of the substance's natural occurrence. In this case, it is necessary to evaluate the implementation of preventive control actions. Class 3 requires the identification of the potential source of contamination, the control of contamination sources and the monitoring of soil and groundwater quality. Class 4, on the other hand, requires specific actions to manage contaminated areas to eliminate the danger or minimize the risk to human health and the environment.

3 Results

3.1 Water Analysis and Water Quality Classification

The results show that the water at the four points sampled in both 2012 and 2018 exceeded the standards determined in Class 3 (Table 5), a class that allows water to be destined for human consumption once it has undergone advanced treatment and that would also be safe for uses involving potential human body contact. The results also exceeded the limits of Class 4, water that can only be used for landscaping and navigation.

Table 5 Results of the physico-chemical and biological analyses of the sampled points (P1 to P4, Table 2) at Arroio Moinho in 2012 and 2018 (modified from Conselho Nacional do Meio Ambiente 2005).

Parameter	Class 3	P1		P2		P3		P4	
		2012	2018	2012	2018	2012	2018	2012	2018
DO ($mg.O_2.L^{-1}$)	≥4	1.18	8.04	0	7.07	0	5.37	1.08	3.74
$BOD_{5,20}$ ($mg.O_2.L^{-1}$)	≤10	400	25	100	75	150	30	100	45
FC *E. coli* (MPN)	≤2500	>$2.4x10^6$	$2.2x10^5$	$1.4x10^3$	$2.0x10^6$	$9.1x10^5$	$5.8x10^5$	>$2.4x10^6$	$4.4x10^5$
TC (MPN)	$2.4x10^6$	>$2.4x10^6$	$6.9x10^5$	>$2.4x10^3$	$2.4x10^6$	>$2.4x10^6$	$1.6x10^6$	>$2.4x10^6$	$1.0x10^6$
Total Phosphorus[1] ($mg.L^{-1}$)	≤0.15	4.87	1.632	1.7	1.642	2.17	1.315	2.38	1.778
Total Nitrogen[2] ($mg.L^{-1}$)	13.30	39.33	19.18	16.77	17.18	21.53	14.11	27.23	17.88
Turbidity(NTU)	≤100	30.3	11.3	25.5	22.367	18.5	10.167	33.3	10.733
Total Phenols ($mg.L^{-1}$)	0.01	0.003	<0.04	0.003	<0.04	0.006	<0.04	*	<0.04
Total Aluminum ($mg.L^{-1}$)	0.200	0.398	*	0.221	*	0.198	*	0.214	*
Total Arsenic ($mg.L^{-1}$)	0.033	*	$5x10^{-4}$	*	$4x10^{-4}$	*	$4x10^{-4}$	*	$5x10^{-4}$
Total Lead ($mg.L^{-1}$)	0.033	*	*	0.012	*	*	*	*	*
pH	6-9	7.07	7.4	7.12	7.45	6.97	7.37	7.11	7.4
TDS ($mg.L^{-1}$)	500	472	347	374	346.5	322	324	432	429.5
T (°C)	15	15.3	15	15.2	15.5	15.9	17	15.6	17.5

DO: dissolved oxygen; $BOD_{5.20}$: biochemical oxygen demand required to oxidize organic matter over five days, at an incubation temperature of 20°C; FC *E. coli:* fecal coliforms *Escherichia coli;* TC: total coliforms; MPN: most probable number in 100 ml; NTU: nephelometric turbidity units; (1) lotic and distributary channel environments of intermediate environments; (2) for pH ≤ 7.5; (*) parameter not detected; na: parameter not analyzed; pH: potential of hydrogen; and TDS: total dissolved solids; T: water temperature in °C.

3.2 Water quality index (WQI)

The results (Table 6) of the first sampling ranged from 13.6 (at P3) to 18.7 (at P2). That puts the WQI at all sample points in the worst category, very bad. The temperature was estimated using data from Instituto Nacional de Metereologia (2020), since there was no field measurement in this case.

Table 6 Water Quality Index (WQI) of the sampled points (P1 to P4) at Arroio Moinho in 2012 and 2018.

Point	WQI 2012	Quality Level	WQI 2018	Quality Level
P1	14.0	very bad	30.9	bad
P2	18.7		25.4	
P3	13.6		27.9	
P4	15.4		21.3	

In 2018, the range of results was between 21.3 (at P4) and 30.9 (at P3). They showed improvement over the 2012 results, they were at a bad level.

The improved results of the second sampling can be attributed to the dilution effect caused by the accumulated precipitation of 15 mm (Instituto Nacional de Metereologia 2020) in the week before the collection. In comparison, in 2012, the accumulated rainfall in the week before sampling was 0.6 mm (Instituto Nacional de Metereologia 2020).

3.3 Bottom Sediment Analysis

3.3.1. Chemical Analysis of the Bottom Sediment and Classification Framework

Among the bottom sediment samples, all samples revealed at least one metal with a concentration higher than the QRV and lower than the IV, consequently falling into Class 3 (Table 7). It is then necessary to identify the source of contamination, whether natural or anthropogenic since the classification as Class 3 requires monitoring the sources of contamination sources and the soil quality.

Copper and Zinc showed the highest concentrations, with all samples exceeding the prevention value, indicating harmful changes to the soil and groundwater quality. The Zn values at all points P1 to P4, ranging from 308 to 428 mg kg^{-1}, far exceeded the maximum value found in Santana Granite (47.2 mg kg^{-1}). These results for Zn were up to 13 times higher than the background value of 31 mg.kg^{-1}. At P1 to P4, the concentrations for Cu exceeded the PV by up to 35%, with values ranging from 63.4 mg.kg^{-1} at P1 to 81.2 mg.kg^{-1} at P4. The concentrations exceeded the quality reference value for this element by 7 to 9 times.

Table 7 Results of chemical analysis of metals in the Arroio Moinho bottom sediment and guidelines and concentrations measured in Santana Granite. Concentrations between QRV and PV are indicated in yellow. Concentrations between PV and IVR are indicated in orange. Units: mg.kg^{-1} (modified from: Conselho Nacional do Meio Ambiente 2009, Fundação Estadual de Proteção Ambiental do Rio Grande do Sul 2014, Oliveira, Koester & Soliani Jr. 2001).

Metals	Santana Granite			2018				FEPAM	CONAMA	
	Min	Max	Avg	P1	P2	P3	P4	QRV	PV	IVR
Total Cadmium	0.04	0.45	0.043	<0.06	<0.06	<0.06	<0.06	0.40	1.3	8
Total Lead	20	24	22.00	48.9	15.6	41.5	89.6	18	72	300
Total Copper	*	*	*	75.5	63.4	79.5	81.2	9	60	400
Total Chrome	35	65	44.60	14.1	14.8	12.9	14.1	40	75	300
Total Nickel	2	4	2.40	12.5	14.8	10.9	11.9	12	30	100
Total Zinc	42	55	47.20	428	350	308	416	31	300	1,000
TOC (%)	*	*	*	13.9	16.6	8.63	17.2	nl	nl	nl

Min: minimum; Max: maximum; Avg: average; QRV: quality reference value for soils located in crystalline rocks of the Rio Grande do Sul Shield; PV: prevention value; IVR: intervention value for residential land use; TOC: total organic carbon; (*) element not analyzed; nl: no legislation concerning this parameter.

Regarding the Cd and Cr concentrations, the analysis revealed values lower than what defines the natural quality of the soil (QRV) of each element at all sampling points. For Cr, the concentrations found were from 12.9 $mg.kg^{-1}$ at P3 to 14.8 $mg.kg^{-1}$ at P2, while Cd was not detected at any sampling point. The Ni concentrations measured were close to the QRV of 12 $mg.kg^{-1}$, ranging from 10.9 $mg\ kg^{-1}$ at P3 to 14.8 $mg.kg^{-1}$ at P2. The Pb concentration at P2 was below the QRV, but at P1 and P3, the values exceeded the QRV of 18 $mg.kg^{-1}$, being 49 $mg.kg^{-1}$ and 41 $mg.kg^{-1}$, respectively. These values are approximately twice as high as the maximum concentration of 22 $mg.kg^{-1}$ found in Santana Granite. At P4, the Pb concentration was 89.6 $mg.kg^{-1}$, exceeding the PV of 72 $mg.kg^{-1}$ and roughly five times the QRV.

3.3.2. Granulometric, Mineralogical and Total Organic Carbon Content (TOC) Analyses

The results of the granulometric analysis are shown in Table 8. All samples show the fine-grained fraction lesser than 3%. The total organic carbon is higher in the P1, P2 and P4 that the P3. This result is related with the channel gradient variation. At points P1 and P2, the stream channel is located on a small geomorphological plateau in the spring region, favoring organic matter accumulation. Similarly, at point P4, the channel is established in the fluvial plain of the mouth region, also favoring the accumulation in the point and channels bars. Differently, at point P3, the channel is located in a steeper area in the intermediate region, favoring the water flow and hindering the formation of lateral and channel deposits.

The X-ray diffraction analysis indicates that all points have a similar mineralogical composition: feldspar, quartz, and kaolinite. These minerals are the same as those described by Oliveira, Koester & Soliani Jr. (2001), similar to the mineralogical composition of Santana Granite, the predominant lithology in the region. In the FF fraction <2 µm, kaolinite was found to be the dominant clay in all samples.

3.4 Geoindicators

3.4.1. Contamination Factor (CF)

The metals calculated contamination factor is shown in Table 9, as well as the concentrations of the reference concentration (Cref). The metals Cu and Pb (for P1, P3, and P4), Ni (P1 and P2), and Zn (all points) present CF values between 1 and 13, showing enrichment of these elements at the points studied. The elements Cr and Pb (at P2) showed values lower than one, indicating the elimination of these elements from the stream. Ni showed a ratio near one at the sampling points, except at P2, where the CF was 1.23.

3.4.2. Geoaccumulation Index (Igeo)

The geoaccumulation indices at the points analyzed are shown in Table 10, and the geoaccumulation index results allowed the conclusion that there was practically no Cr or Ni contamination (Igeo class 0) at the sampled points (P1 to P4) nor by Pb (at P2). Pb concentrations, however, (at P1 and P3) were of low to moderate intensity (Igeo class 1) and of the highest intensity at P4 (Igeo class 2, moderate). The intensity of contamination by Cu at the four points, and by Zn, at P2 and P3, were moderate to strong (Igeo class 3). The highest contamination recorded was by Zn, Igeo class 4 (strong) at P1 and P4.

Table 8 Particle size analysis and total organic carbon content (TOC) of the bottom sediment from the points sampled at Arroio Moinho, expressed as a percentage (%).

Point	Granulometry							TOC
	Pb, Gr	Sand					Si + Cl	
	FF > 2 mm	VCSa	CSa	MSa	FSa	VFSa	FF < 0.625 µm	
P1	38.86	22.88	16.79	13.60	4.50	1.04	2.34	13.9
P2	49.39	23.08	14.03	7.91	3.23	0.83	1.52	16.6
P3	50.51	22.43	15.18	7.94	2.12	0.61	1.21	8.63
P4	63.90	20.98	8.96	4.29	1.13	0.18	0.52	17.2

Pb: pebble; Gr: granule; Sand: VcSa: very coarse; CSa: coarse; MSa: medium; FSa: fine; VFSa: very fine; Si: silt; Cl: clay; TOC: total organic carbon.

Table 9 Contamination factor (CF) of the metals analyzed in the bottom sediments at points P1 to P4 in Arroio Moinho, highlighting Cu and Zn with the highest concentrations recorded.

Metal	Cref	2018			
		CF1	CF2	CF3	CF4
Cd	0.4	nd	nd	nd	nd
Pb	18	2.72	0.87	2.31	4.98
Cu	9	8.39	7.04	8.83	9.02
Cr	40	0.35	0, 37	0.32	0.35
Ni	12	1.04	1.23	0.91	0.99
Zn	31	13.81	11.29	9.94	13.42

Cref: reference concentration in $mg.kg^{-1}$; nd: not detected.

3.5 Monthly Income *per capita* and Population Density

According to census tracts analysis originating in the 2010 Demographic Census (Instituto Brasileiro de Geografia e Estatística 2011), the Arroio Moinho micro-watershed has a population of about 58,561 inhabitants, which represents about 4% of the population of Porto Alegre. The results are presented in Table 11.

The *per capita* income of the residents decreases significantly with increasing elevation. Approximately half the population (49.1%) of the entire micro-watershed region receives up to 1 MS (R$ 510), and 38% earn between 1 and 3 MS (R$ 510 to R$ 1530). At the extremes of the monthly income distribution, approximately 3% of residents have no income, and 10% receive more than 3 MS (over R$ 1,530). Despite the population density upstream being lower than further downstream, the population in this area is overloading the stream capacity, as evident in the research results.

In the micro-watershed's lower course region, between 0 and 39-meter elevations, approximately 30% of the population earns up to 1 MS. About 45% receive between 1 and 3 MS and 23% receive above 3 MS. While the resident population in the middle elevations, between 40 and 99 meters, approximately 46% of the population receives up to 1 MS, and 42% earn between 1 and 3 MS. In the upper course of the watershed, at the top of the hills, where the altitude is 100 to 298 meters, about 65% of the population earns up to 1 MS per capita. About 4% have no monthly income, and 28% receive between 1 and 3 MS. At lower and middle elevations, the percentage of residents without income is similar (2.4%), but that percentage increases going upstream, with 3.5% of the population at the highest elevations having no income. It should be noted that newcomers to urban shantytowns in Brazil often must seek unoccupied land further up the hill to find a place to settle.

Table 10 Geoaccumulation indices (Igeo) of the metals Cd, Pb, Cu, Cr, Ni, Zn reported at the sampled points (P1 to P4) in Arroio Moinho. In red, the metals with the highest recorded concentrations. In light orange, low to moderate intensity concentrations.

Metals	Cref	Igeo				Igeo Class			
		P1	P2	P3	P4	P1	P2	P3	P4
Cd	0.4	nd	nd	nd	nd	nd	nd	nd	nd
Pb	18	0.86	-0.79	0.62	1.73	1	0	1	2
Cu	9	2.48	2.23	2.56	2.59	3	3	3	3
Cr	40	-2.09	-2.02	-2.22	-2.09	0	0	0	0
Ni	12	-0.53	- 0.28	-0.72	-0.60	0	0	0	0
Zn	31	3.20	2.91	2.73	3.16	4	3	3	4

Cref: reference concentration adopted for soils located in crystalline rocks of the Rio Grande do Sul Shield in $mg.kg^{-1}$ (Fundação Estadual de Proteção Ambiental do Rio Grande do Sul 2014); nd: parameter not detected.

Table 11. Nominal monthly income per capita of permanent private households. (Research data according to Instituto Brasileiro de Geografia e Estatística 2011).

Geomorphological Region Level	Elevation (m)	Pop. Dens. ($pers.km^{-2}$)	No Income		Up to 1 MS		1 to 3 MS		Above 3 MS	
			Abs	%	Abs	%	Abs	%	Abs	%
Lower watercourse	0-39	8,005	94	2.45	1,101	28.72	1,750	45.66	888	23.17
Mid watercourse	40-99	12,610	203	2.42	3,855	45.92	3,526	42.00	811	9.66
Upper watercourse	100-298	6,858	222	3.55	4,117	65.87	1,744	27.90	167	2.67
	Total	8,954	519	2.81	9,073	49.10	7,020	37.99	1,866	10.10

Dens. pop.: population density; pers km^{-2}: persons per square kilometer; Abs: absolute number of people; MS: reference minimum monthly salary (in 2010) R$ 510 (US$ 290).

The average population density of the micro-watershed is 8,954 people per square kilometer. The highest density is observed in the middle elevations at 12,610 $pers.km^{-2}$. In the upper portion, the density is the lowest, 6,858 $pers.km^{-2}$. Moreover, in the lower course, the value is intermediate, being 8,005 $pers.km^{-2}$.

4 Discussion

The region near the spring of the Arroio Moinho, despite having the lowest population density in the micro-watershed (6,858 $pers.km^{-2}$), demonstrates very poor water quality (WQI) in both 2012 and 2018. The water at point (P1) falls under CONAMA WQI Class 4, so it is restricted to landscaping use only. Although located at the headwaters of the hills, these waters could not be directed to the human water supply after advanced treatment, as is permitted for waters classified as Class 3 (Conselho Nacional do Meio Ambiente 2005). Concerning the bottom sediments, this point (P1) presented little to moderate contamination by Pb (Igeo class 1), moderate to strong Cu contamination (Igeo class 3), and strong contamination by Zn (Igeo class 4). The concentrations of these metals exceeded the prevention values of class 3 for soils (Conselho Nacional do Meio Ambiente 2009), above which the environmental agency warns about the possibility of damaging impacts on the ecosystem. It is necessary to consider that the fine-grained fraction content is 2%, which is considered low, and the total organic carbon content is 13%. This indicates that contamination by metals is associated with organic matter that has a high cation exchange capacity and, at this point, is high (Zn: Igeo class 4, CF 13; Cu: Igeo class 3, CF 8). The research data showed that this region's population had the worst micro-watershed's monthly income *per capita* (Instituto Brasileiro de Geografia e Estatística 2011). In 2010, 65% of the high hill population had a monthly income of up to R$510 (equivalent to 1 minimum monthly salary in 2010, US$290) *per capita* and 27% received between R$510 and R$1,530 (1 MS and 3 MS in 2010, US$290 to US$870) per capita (Instituto Brasileiro de Geografia e Estatística 2011).

The mid-elevation region (P2 and P3) had the highest population density in the micro-watershed (12,610 $pers. km^{-2}$). People had a better monthly income per capita than the aforementioned high hill residents. About 45% of the population received up to 1 minimum monthly salary, and 42% earn between 1 and 3 MS per capita in 2010 (Instituto Brasileiro de Geografia e Estatística 2011). The results of the water analyses at P2 and P3 were better than P1; however, the water quality level (WQI) remained very poor. These results correspond to the Class 4 water quality limits (Conselho Nacional do Meio Ambiente 2005). As with the water at P1, water use at these points (P2 and P3) is limited for landscaping. Regarding the pollution of bottom sediments by metals, the results revealed low to moderate contamination by Pb at P3 (Igeo class 1, CF 2), and moderate to strong contamination by Cu and Zn (Igeo class 3, CF between 7 and 11) at both points. Thus, points P2 and P3 located in the middle portion of the watershed were also consistent with the class 3 soil quality limits (Conselho Nacional do Meio Ambiente 2009), as at P1. In this region, the bottom sediments' granulometric distribution revealed fine-grained fraction content of approximately 1% at both points (P2 and P3), while the TOC was 16% (P2) and 8% (P3).

Finally, the results of the samples' analysis from the point located in the lower region of the watershed (P4) followed the same pattern as the other points. Here, the population density of 8,005 $pers.km^{-2}$, and they exhibited the highest micro-watershed's monthly income per capita, where 28% of the population received up to 1 MS and 45% between 1 and 3 MS in 2010 (Instituto Brasileiro de Geografia e Estatística 2011). The waters at the sample point in this region (P4) revealed the worst quality index (WQI) - very bad in 2012 and bad in 2018. In terms of water quality, the results corresponded to CONAMA Class 4 (Conselho Nacional do Meio Ambiente2005). The fine-grained fraction of the bottom sediment at P4 was half a percentage point (0.5%), while the TOC was 17%. Chemical analysis of metals showed that the stream bed, at P4, was polluted by Cu (moderate intensity, Igeo class 3; CF 9), as at the previous points. However, the intensity of pollution by Zn was increased (strong intensity, Igeo class 4; CF 13) - similar to P1, at the headwater region - and by Pb (moderate intensity, Igeo class 2; CF 4.9), also found at P1 and P3 (low to moderate intensity, Igeo class 1; CF 2). As at the other points, the results of the analysis of metals in the bottom sediment categorizes P4 as Class 3 soil according to National Environment Council guidelines (Conselho Nacional do Meio Ambiente 2009).

5 Conclusion

The high organic load released by the local population into the Arroio Moinho is causing high levels of contamination in the study area, as demonstrated by the results of this investigation. The domestic sewage load is overwhelming the natural capacity of the stream to purify and renew itself. As a result, the water samples taken from the stream in both the 2012 and the 2018 samples exceeded the limits of the lowest quality water, Class 4. Furthermore, in addition to the domestic effluents, solid waste such as household waste, furniture, and construction debris is dumped along the banks and streambed along the entire watercourse, transforming this essential element of the landscape into a disease transmission pathway. Due to the quantity of solid waste present in the streambed and along the banks, the stream cannot even fulfill its function as a landscape feature, the only use allowed by its Class 4 designation.

Considering that the region has predominately single-family homes, occupied by a low-income population, one would not expect very high levels of zinc and copper in this waterway. Such increases do not correspond to the regional lithology, as shown in studies by Oliveira, Koester & Soliani Jr. (2001) on the rocks of the region. On the one hand, these metals may be related to solid waste deposits along the entire channel and streambed. This residue may contain materials such as batteries, sources of Pb and Zn (Zn-carbon, Zn-chloride, Zn-air and Pb-acid systems) (Silva 2010). According to the International Association of Lead (International Association of Lead 2015), 80% of the Pb's world production was destined for the manufacture of lead-acid batteries that year. Galvanized materials and construction waste (roofing tiles, gutters, white pigment) (Sandstead 2015) may contribute to the Zn concentration. Domestic sewage should be considered an essential source of Zn emission in urban waterways since zinc is used in fungicides, topical antibiotics, and lubricants (Ellingsen, Møller & Aaseth 2015). The possibility that the increased Cu levels be related to corrosion of copper-containing waste materials such as metal alloys, electronic parts, wood preservatives and fungicides and pigments for paint should be considered. On the other hand, high levels of metals may be linked to past illegal dumping sites, where the springs are located (Guimarães2004).

The research reveals that the current solid and sanitary waste management carried out by the local population and managers in the region is causing concerning levels of contamination in the Arroio Moinho aquatic system and poses a danger to the public health of the population that lives along its banks. Managers recognize the problem and the difficulty in planning measures to change the situation (Agência Nacional de Águas 2019). However, this inaction merely promotes environmental and social degradation as well as deterioration of the health of the local population and all the residents of Porto Alegre, since the water quality of the streams of the Porto Alegre Ridge ends up impacting Lake Guaiba.

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Received: 03 August 2020

Accepted: 31 March 2021

How to cite:

Rodrigues, B.B., Mizusaki, A.M.P., Menegat, R., Figueiredo, A.R., Galligan, T.A. & Portella, M.B.P. 2021, 'Contamination of Urban Watersheds: the Case of Arroio Moinho, Porto Alegre, Rio Grande do Sul, Brazil', *Anuário do Instituto de Geociências,* vol. *44*: 36744. https://doi.org/10.11137/1982-3908_2021_44_36744