ENVIRONMENTAL MONITORING OF HEAVY METALS IN AQUATIC MACROPHYTES BY ATOMIC ABSORPTION SPECTROMETRY ANALYSIS - AAS IN CASCAVEL RIVER BASIN, GUARAPUAVA, PR

Glauco nonose negrão[1]
Breno henrique marcondes de oliveira[2]
Mariane butik[3]

Abstract

High concentrations of heavy metals in urban watersheds can offer harmful effects to human health and have contributed to environmental contamination. The present work aims to evaluate the total concentration of Zn (Zinc), Mg (Magnesium), Lead (Pb), Cr (Chromium), Manganese (Mn) and Ni (Nickel) analyzed according to FAAS - Flame Atomic Absorption Spectrometry, in samples of the aquatic macrophyte Egeria densa present in the urban stretch of the Cascavel River watershed, Guarapuava, PR; and specific objectives to identify the potential sources of contamination by heavy metals and to obtain physical parameters of the water. The elements zinc, magnesium, manganese and lead showed higher potential emissions upstream, a fact associated with the proximity of the industrial zone of Guarapuava. It is likely that the increase in electrical conductivity values at the upstream points is related to the discharge of domestic effluents. The decrease of conductivity and total dissolved solids in the sample points occurs downstream, corresponding to the lower topography of the study area and the end of the urban stretch of the Cascavel River basin. Despite the concentrations of heavy metals being considered critical, the plant showed efficiency in bioaccumulation of these chemical elements, being an effective tool for research and environmental assessment, and aquatic macrophytes can be the basis for biomonitoring studies of urban environments impacted by heavy metals.

Keywords: Applied biogeography; Ecology; Environmental analysis; Analytical chemistry

Introduction

Among the various aspects of environmental pollution resulting from industrial, agricultural and urban activities; pollution by toxic metals is important due to its high resistance to degradation,

[1] Prof. Dr. Departamento de Geografia, Universidade Estadual do Centro-Oeste. gnegrao@unicentro.br ORCID: https://orcid.org/0000-0002-7733-4530

[2] Bachelor in Geography, Universidade Estadual do Centro-Oeste. brenohenrique@gmail.com ORCID: https://orcid.org/0000-0003-2301-6438

[3] Doutoranda em Química Universidade Estadual do Centro-Oeste. marianebutik@gmail.com ORCID: https://orcid.org/0000-0003-3367-408X

toxicity at low concentrations and potential for bioaccumulation in the aquatic system (ahmad et al, 2014). The release of methane through human activities to the environment has increased over the years (olowoyo et al, 2012), where its concentrations are gradually increased and consequently absorbed by organisms and/or sediment (arai et al, 2007).

Heavy metals are inorganic pollutants, pollutants and can alter the physical, chemical or biological characteristics of natural waters, air, soil, plants and food (karnitz júnior, 2007), and can be absorbed in river sediments or accumulated in benthic organisms, sometimes in toxic levels (arias et al, 2007), and contaminate the food chain by leaching to groundwater or by plant absorption and bioaccumulation (batista, freire, 2010), being associated with neurotoxicity, nephrotoxicity and hepatotoxicity in humans (divan junior, 2009).

In general, several plants have the ability to adapt and survive in contaminated environments (pio et al, 2013), being able to absorb and/or accumulate phytotoxic heavy metals present in contaminated soils, waters or atmosphere, manifesting varied symptoms, usually specific to each type of contamination. Aquatic plants have proven to be one of the most apt bioindicators in the aquatic ecosystem, being able to accumulate metals in all tissues and transfer them to the food chain, being this accumulation one of the topics of environmental interest nowadays, either because of the phytotoxicity of many of these metals or because of the potentially harmful effects on animal and human health (maiga et al, 2005). In addition, aquatic macrophytes can be used to assess the health of the water body, as remediators of ecosystems or even in constructed systems (wetlands), and can also be used to treat domestic and industrial effluents (sipaúba-tavares, 2012).

Among the various plant species that have proliferated in the urban stretch of the cascavel river basin, in the municipality of guarapuava, pr, stands out egeria densa, also known as "brazilian eloid", a submerged and rooted macrophyte of twelve submerged waters, with a limnetic and perennial environment (oliveira et al, 2005), a plant native to the southeastern coast of brazil (alfasane et al, 2010), which multiplies mainly by fragmentation of the canopy, being reproduction by seeds very rare (rodella et al, 2006), having a relatively high growth rate under ideal conditions.

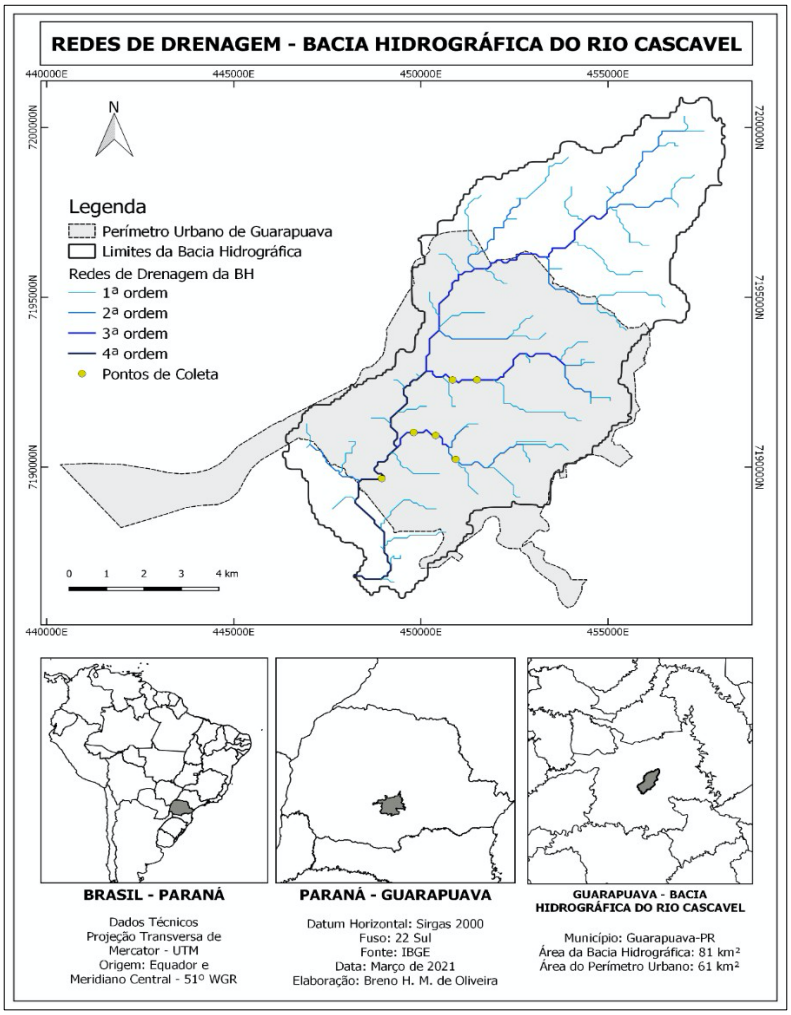
In this work we consider the hypothesis that the entry of heavy metals resulting from urban pollution in the urban stretch of the hydrographic basin of the cascavel river, municipality of guarapuava, pr, may compromise the different environmental uses of this hydrographic basin in the medium and long term, since this hydrographic basin drains almost all the drainage of this city (peres et al., 2008). Thus, it is considered that the analysis of the occurrence of heavy metals in dense egeria along the urban basin of the cascavel river, which presents different forms and intensities of degradation and degradation, with sources of pollution from residences located nearby, agricultural activities, industries, irregular waste disposal and urban sludge, could be an effective measure of environmental monitoring.

The general objective of this article is to evaluate the spatial variability and total concentration of zn (zinc), mg (magnesium), chumbo (pb), cr (chromium), manganese (mn) and ni (nickel) in the aquatic plant egeria densa, in the urban stretch of the cascavel river basin, with the specific objectives of identifying the potential sources of heavy metal contamination in the study area and obtaining physical parameters of the water. The total concentration of heavy metals in organic matter was analyzed according to faas "flame atomic absorption spectrometry", one of the most widely used techniques in the determination of elements in low concentrations, which are present in a variety of

samples, whether liquid, solid, suspended or even gaseous, and can be associated with flow analysis systems and allow speciation studies (amorim et al, 2008).

The collection of the determined tracts, identification, cataloguing, sample preparation and preliminary results took into consideration the seasons of the year and specific laboratory processes in the hydrology laboratory - labhidro, of the geography department and the trace analysis and instrumentation laboratory - chemistry department, both located at the midwest state university - unicentro, cedeteg campus, guarapuava, pr.

Thus, it is considered the possibility of establishing an environmental monitoring program of heavy metals, for the analysis of the occurrence of these metals in aquatic macrophytes in the urban environment, aiming at the protection of human health, determination of spatial and temporal trends of pollution processes and their effects on ecosystems, as well as obtaining data for proper environmental management, contributing with information to governmental bodies and interested institutions for the implementation of strategies to control environmental pollution.



Legenda
Drainage networks of bh
Guarapuava urban perimeter
Limits of the hydrographic basin

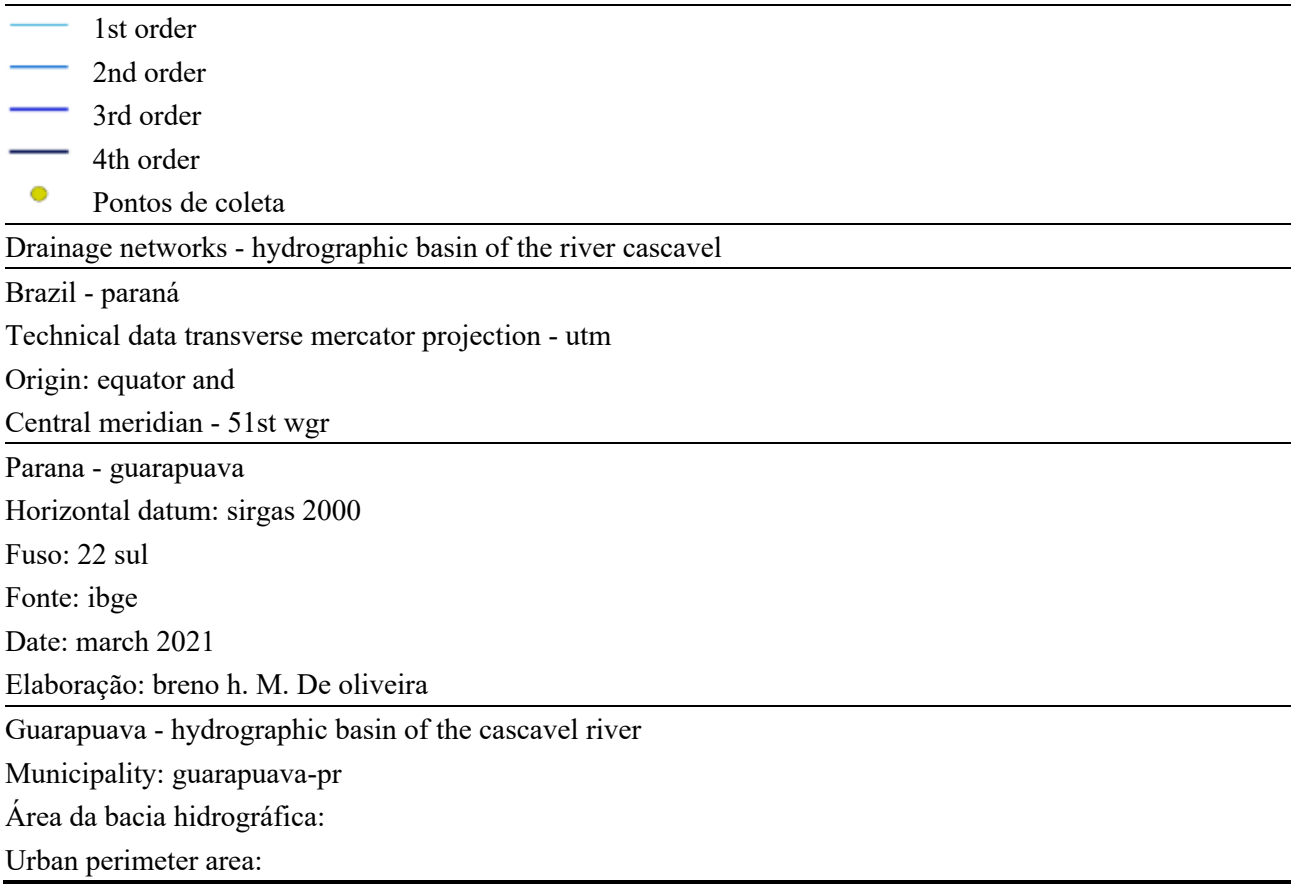


Figure 1. egeria densa collection points in the urban stretch of the cascavel river basin, guarapuava-pr.
Source: prepared by the authors (2021).

Methodology and characterization of the study area

This work has as spatial cutout the urban stretch of the cascavel river basin, located in the center west of paraná, in the municipality of guarapuava - pr. The cascavel river has a drainage area of 81.03 km², with a 4th order fluvial hierarchy, and has more than 40% of its basin occupied in the urban area of guarapuava (67.86 km²). The municipality is located in the center-south region of the state of paraná, in the third paraná plateau or guarapuava plateau (maack, 2002) and has a territorial area of 3,117.598 km². The total population of the municipality is 180,364 inhabitants (ipardes, 2018), of which 152,993 (91.43%) reside in the urban area. The municipality, according to (thomaz, vestena, 2003), is an area of the extratropical zone, which favors temperatures with mesothermal character, predominating annual temperatures between 16º and 20ºc, with cold winter and summer enlivened by the altitudes. According to köppen's classification, the climatic type is "cfb", corresponding to the temperate climate, rainy and moderately hot summers (ayoade, 1983).

Initially, a study of the urban stretch of the cascavel river basin was carried out for the selection of collection points, evaluation of access to the site and logistics. Six aquatic macrophyte collection sites were chosen in the urban environment, strategically located considering the different geomorphological characteristics, as well as the use and occupation of the soil in the vila carli, alto cascavel and olarias neighborhoods (figure 1). The collection points were identified by their geographic coordinates.

The identification of potential sources of contamination consisted of the survey of potential

sources of heavy metals within the urban drainage area of the cascavel river basin. Foram coletadas 48 amostras (sendo 12 amostras por campanha) da planta aquática egeria densa em seis pontos ao longo do trecho urbano do rio cascavel, entre novembro de 2017, janeiro, abril e julho de 2018; sendo realizada com a utilização de luvas e material inerte para coleta do material. Samples were removed where the water level was sufficiently high to keep the plant submerged and prey to a stable substrate, in good physiological state. The physical and chemical parameters of water quality measured in the field were water temperature (c), specific conductivity (µs.cm-1), ph and total dissolved solids (mg/l), using a hanna multiparameter probe - model hi 769828.

The samples were washed in the laboratory, directly in running water, in order to remove sediments and invertebrates, being later stored in plastic bags, catalogued and identified in the hydrology laboratory, unicentro geography department. Before being subjected to analytical determinations, the samples were washed, dried in an oven with air circulation at a temperature of 30°c for 48 hours and manually wetted with the use of a gral and pistil. The biomass was weighed on an analytical balance (bioprecisa, fa-2104n).

To analyze the presence of heavy metals, the procedures were performed using the faas technique "flame atomic absorption spectrometry", at the laboratory of trace analysis and instrumentation, linked to the department of chemistry - unicentro, in duplicate. Samples of 0.1g of egeria densa were prepared for wet digestion with nitric acid in a digestion block for subsequent quantification of the metabolites by flame atomization atomic absorption spectrometry (faas) in varian equipment model spectraaa220, equipped with an oxy-cathode lamp, in an air/acetylene flame, by the direct method and a melt corrector in flame analysis with oxy-cathode lamps, procedure carried out according to (Santos et al, 2006). The concentrations of these metals are expressed as a function of dry weight (mg/kg). The choice of the analysis of the heavy metals Zn (zinc), Mg (magnesium), chumbo (Pb), Cr (chromium), Mn (manganese) and Ni (nickel) was based on studies by dean (1972), braile and Cavalcanti (1993) and Santos (2012), these metals being commonly present in industrial effluents.

The parameters used for the measurement of heavy metals in organic matter were in accordance with kabata-pendias, Pendias (2001), Brazil (1998), Fao (1992) and Malavolta (1994). The definition of water quality refers to the type of use to which it is destined, and stipulates the quality standards in resolution 357 of the national council of the environment (Conama, 2005) and its modifications in resolutions 410 of 2009 and 430 of 2011. The parameters are defined in acceptable limits of substances present according to water use.

Results and discussion

Physical parameters of water

The hydrographic basin is understood as a fundamental geographic unit for the management of surface and groundwater resources and is also used for actions related to environmental planning (gorayeb, pereira, 2014). The use of the hydrographic basin as a unit of analysis of environmental systems, presents a more appropriate conception to work with the systemic approach, starting from the perspective of the tripod formed by the environmental, social and economic dimension (albuquerque, 2015), making it possible to deal with the components and dynamics of the interrelationships necessary to the planning of land use and environmental conservation.

Because it is an open system with energy input (hydrological cycle) and material export (water, solutes, sediments, etc.), the importance of adopting hydrographic basins for urban planning has been discussed in areas such as hydrology, geology and other environmental areas, which began to discuss them during the nineteenth century. This advance is of great importance, as it serves as a basis to justify the delimitation of these areas as "ideal" for the proper purposes of urban planning (mirandal et al, 2017).

Table 1 shows the values obtained for the physical parameters of the water of the points chosen for sampling, by arithmetic mean and standard deviation. The ph and total dissolved solids were found to be adequate in relation to the values recommended by conama, 2011; for special class 1, which establishes ph values between 6 to 9 and up to 500 mg/l for total dissolved solids. However, we emphasize that there was a decrease even lower in ph which, without oxygen, can influence the solubilization of heavy metals in sediments and cause their undesired introduction into the food chain (gonçalvez, 2016).

Regarding conductivity, the sample points presented mean and standard deviation of 105.1±15.2 $\mu s \cdot cm^{-1}$, being that natural waters present conductivity values in the range of 10 to 100 $\mu s \cdot cm^{-1}$ in environments polluted by domestic or industrial waste, the values can reach 1,000 µs/cm (funasa, 2014). It is probable that the increase in the values of the electrical conductivity in points 1 and 2 are related to the clearance of domestic effluents upstream of the analysis points. Philipi júnior et al. (2004) affirm that as dissolved solids are added to a water body, the electrical conductivity of the water increases, as observed in the analysis points.

Ponto	Temperature C	Conductivity $\mu s \cdot cm^{-1}$	Ph	Total dissolved solids (mg)
25°22'53.43 "s 51°28'56.54 "w	19.7	132.3	6.4	70.3
25°22'57.75 "s 51°29'14.40 "w	20.5	112.6	6.3	62.6
25°24'10.96 "s 51°29'17.48 "w	19.3	107.6	6.1	57.6
25°23'46.47 "s 51°29'34.57 "w	18.4	96.0	6.0	47.3
25°23'44.06 "s 51°29'56.36 "w	18.1	99.6	6.0	48.6
25°24'26.47 "s 51°30'29.98 "w	18.3	83.0	6.3	40.3
Arithmetic mean and standard deviation	19.5±0.8	105.1±15.2	6.1±0.2	54,4±10.1

Table 1**.** Mean values of temperature (c), conductivity (µs/cm), pH and total dissolved solids (mg), arithmetic mean and standard deviation between sampling points in the urban stretch of the cascavel river, municipality of guarapuava, pr. Surveys conducted between November 2018 and July 2019.

Source: prepared by the authors (2021).

The decrease in conductivity and total dissolved solids in the sample points at the right, corresponding to the lower topography of the study area, at the end of the urban stretch of the cascavel river basin towards the eteestação de tratamento de esgoto, may indicate a process of natural dilution and accumulation of elements along the urban stretch. However, further research and more samples are needed to analyze this process.

Quantification of heavy metals in dense egeria by sample point

According to tuna et al, 2006, heavy metals are stable and persistent environmental pollutants,

since they cannot be degraded and, depending on the physical and chemical characteristics of the aquatic environment, they reaggregate, disperse or are mobilized and deposited in sediments, constituting a potential hazard due to the bioavailability characteristics they can acquire. The choice of the evaluated targets was based on the identification of potential sources of pollution in the proposed study area.

The use and management of soils are indicators for the management of water resources and the health of a river basin, since the quality of water bodies is the result of the actions that occur along their streams. In relation to table 2, the occurrence of zinc and nickel showed critical concentrations for plants. Magnesium showed values above the norm, however, torres, 2005 affirms that magnesium does not cause significant problems for human health. In addition, this metal is commonly found in plants.

Ponto	Zn (mg/kg) media teor normal 1-100 Critical conc. 100-400	Ni (mg/kg) media teor normal 0.02-5 Critical conc. 10-100	Mg (mg/kg) média teor normal 30-100* mg (mg/kg) média teor normal 30-100* mg (mg/kg)
25°22'53.43 "s 51°28'56.54 "w	149-95-290-207	16036.561-27	554-382-242-285
25°22'57.75 "s 51°29'14.40 "w	183-318-482-283	2643.5-38-38	488-352-376-297
25°24'10.96 "s 51°29'17.48 "w	159-68-161-166	11.5-59-20-49	390-379-271-289
25°23'46.47 "s 51°29'34.57 "w	191-146-172-219	17.549.547-40	484-370-482-289
25°23'44.06 "s 51°29'56.36 "w	178-96-307-227	12.5-38-10-54	461-351-317-274
25°24'26.47 "s 51°30'29.98 "w	153-89-227-95	68.5-71-55-36	420-415-327-229

Table 2. average values found for Ni, Zn and Mg in egeria densa, in the municipality of guarapuava, pr and respective normal values and critical concentration (kabata-pendias & pendias, 1992; *knezek & ellis, 1980). Without reference parameter. Surveys conducted between November 2018 and July 2019.

Source: prepared by the authors (2021).

In relation to table 3, the occurrence of chromium showed to be below the critical concentration for plants. However, the residues have a high power of contamination and chromium easily reaches the groundwater table or even reservoirs or rivers, which are the water supply sources of the cities (cetesb, 2005).

Ponto	Cr (mg/kg) median theor normal nd conc. Critical 75-100	Mn (mg/kg)media teor normal 0.02-5 Critical conc. 10-100	Pb (mg/kg)median teor normal 0.20-20 Critical conc. 30-300
25°22'53.43 "s 51°28'56.54 "w	50-40-65-49	48-113-30-45	75.550.5-67-33
25°22'57.75 "s 51°29'14.40 "w	33-63-8-6	96-143-11158	72.5-55-68-32
25°24'10.96 "s 51°29'17.48 "w	63.545.5-10-5	124-105-7692	70-47-54-20
25°23'46.47 "s 51°29'34.57 "w	1259.5-18-13	137-260-186120	88.552.5-79-34
25°23'44.06 "s 51°29'56.36 "w	77-65-35-1	166-221-155-93	86.548.5-66-26
25°24'26.47 "s 51°30'29.98 "w	6244.5-0-0	296-232-192230	7540-59-21

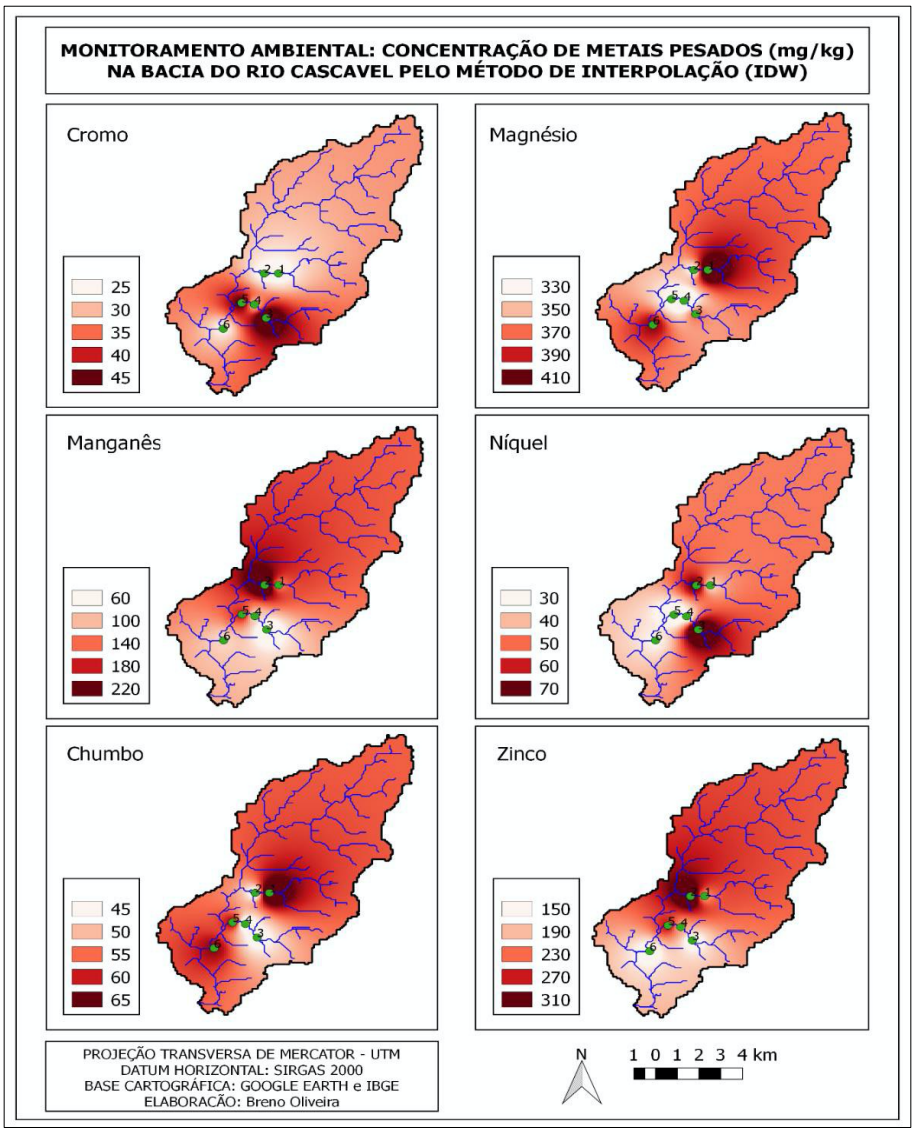
Table 3. Average values found for Cr, Mn and Pb in egeria densa, in the municipality of guarapuava, pr and respective standard values and critical concentration (Kabata-pendias & Pendias, 1992). Without reference parameter. Surveys conducted between November 2018 and July 2019.

Source: organized by the authors (2021).

Only points 4, 5 and 6 at the right are found with critical amount of manganese. The prickly pear cactus is within the critical limit of occurrence in all the points of analysis. In addition to natural weathering processes, the main sources of prickly pear are automobile exhaust, industrial flames, foundries, fertilizers, pesticides, pigments and atmospheric deposition in gasoline that contains it as an additive (sharma, bubey, 2005).

Polluting sources in the urban stretch of the river cascavel, guarapuava, pr

The intensification of anthropic activities in the urban stretch of the river cascavel, guarapuava, pr occurred without planning or control, being associated with nutrient loading due to the contribution of domestic and industrial waste and chemical fertilizers used throughout the study area, leading to a condition of imbalance in the system. In addition, as well as the point pollution caused by clandestine sewage, the diffuse pollution from rainfall and surface runoff contributes as an important source of deterioration of the quality of urban drainage water (song et al, 2017).



Environmental monitoring: concentração de metais pesados (mg/kg)
Na bacia do rio cascavel pelo método de interpolação (idw)

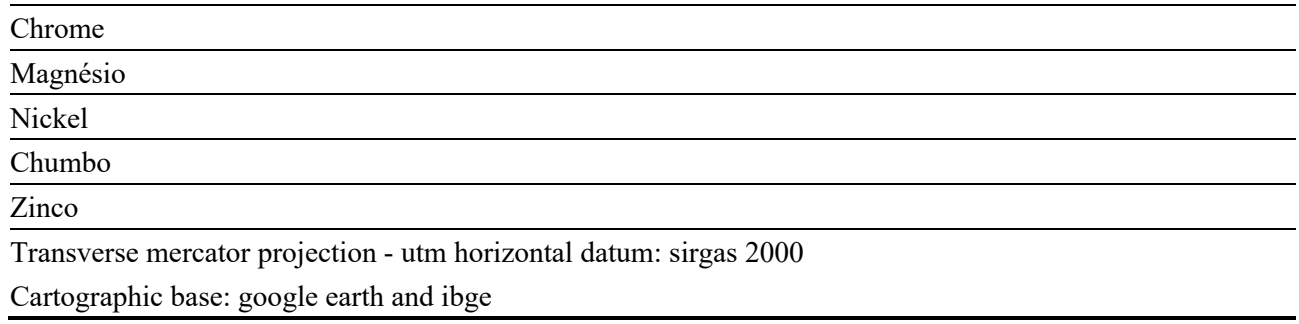


Figure 2 Concentration of heavy metals, generated by the interpolation of the data by the inverse distance weighting (IDW) method.

Source: organized by the authors.

The anthropogenic sources of heavy metals in the study area are probably coming from industrial solid wastes (electroplating and metallurgy, foundries, welding, melting and modeling of alloys, incineration), being more evident in the southernmost points, to the east; and urban (wastewater from fuel and car washing plants, mechanical offices, sludge, sanitary landfills, urban and industrial waste, incineration), in the points chosen upstream; in addition to points with occurrence of pesticides, fertilizers and combustion of fossil fuels, found along the analyzed stretch.

Figure 2 shows that the dispersion of these elements in the urban environment may indicate their presence in the food chain, since these metals can reach and contaminate plants through water and soil (mahmood et al., 2013). The geographic spatialization of the concentration of heavy metals, according to the average values obtained during the 4 samplings and analyses, using the interpolation complement of the qgis software, aims to present the distribution of these concentrations in the entire length of the basin, including areas where they were not sampled.

According to the figure, the elements magnesium and prickly pear were found to have the highest concentrations in points 1 (montant) and 6 (justifying), while in the central points the contamination values are lower. For manganese and zinc, the highest concentrations are in points 1 and 2 (montante), while in the other points these values decrease. The elements chromium and nickel presented the highest concentration values in point 3, while there is a variation between points 5 and 2, respectively, where the concentration appears accentuated.

The points with the highest concentration appear in the darkest red and as the value decreases, the red gets darker, until reaching white where the values are the lowest. Points 1 (montante), 2 and 3 correspond to stretches of the central region, with greater flow of people, vehicles and greater number of residences and consequently, greater generation of domestic effluents, while points 4 and 5 are located in neighborhoods more distant from the center, in areas with irregular occupations. Point 6 is located in the area just behind the other points, a few meters from the municipal sewage treatment plant.

In general terms, the geomorphological characteristics and the use and occupation of the soil along the hydrographic basin of the cascavel river have produced a cycle of contamination, generated by the effluents resulting from domestic-industrial and rainwater runoff, transported by surface runoff, being commonly found zinc, chromium, magnesium, prickly pear, nickel and manganese.

Final considerations

The methodology proposed in this work, of working only with data on methane concentrations, partially meets the defined objective, since when assessing the level of contamination by heavy metals in water bodies and its variability of spatial and temporal concentration, the physical-chemical conditions of the environment and the environmental effects resulting from seasonality should also be taken into consideration.

Despite not having been determined more collection and analysis points distributed along the urban stretch of the hydrographic basin of the cascavel river, in guarapuava, pr, due to the scarcity of the aquatic macrophyte egeria densa in the study area, it was possible to identify the heavy metals zinc, manganese, prickly pear, chromium, magnesium and nickel in its physiological structure. Although the concentrations of heavy metals are considered critical for organic matter according to kabata-pendias and pendias (1992), the plant showed efficiency in the bioaccumulation of these chemical elements.

The methodology showed that the use of egeria densa can be used for biomonitoring studies of heavy metals in polluted urban aquatic ecosystems. We emphasize that the cascavel river is the main recipient of clandestine and industrial discharges in the municipality of guarapuava, pr, being necessary to propose and implement an alternative monitoring program for its basin in an emergency character.

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