

ORIGINAL RESEARCH ARTICLE

Environmental monitoring of heavy metals in aquatic macrophytes by atomic absorption spectrometry analysis—AAS in Cascavel River basin, Guarapuava, PR

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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

1. 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, toxicity at low concentrations and potential for bioaccumulation in the aquatic system^[1]. The release of methane through human activities to the environment has increased over the years^[2], where its concentrations are gradually increased and consequently absorbed by organisms and/or sediment^[3].

Heavy metals are inorganic pollutants, pollutants and can alter the physical, chemical or biological

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characteristics of natural waters, air, soil, plants and food^[4], and can be absorbed in river sediments or accumulated in benthic organisms, sometimes in toxic levels^[5], and contaminate the food chain by leaching to groundwater or by plant absorption and bioaccumulation^[6], being associated with neurotoxicity, nephrotoxicity and hepatotoxicity in humans^[7].

In general, several plants have the ability to adapt and survive in contaminated environments^[8], 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. 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 effluent.

Among the various plant species that have proliferated in the urban stretch of the Rascavel 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^[9], a plant native to the southeastern coast of Brazil^[10], which multiplies mainly by fragmentation of the canopy, being reproduction by seeds very rare^[11], 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 Rascavel 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^[12]. Thus, it is considered that the analysis of the occurrence of heavy metals in dense egeria along the urban basin of the Rascavel 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 Rascavel 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 studie^[13].

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.

2. Methodology and characterization of the study area

This work has as spatial cutout the urban stretch of the Rascavel River basin, located in the center west of Paraná, in the municipality of Guarapuava—PR. The Rascavel 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^[14] and has a territorial area of 3,117.598 km². The total population of the municipality is 180,364 inhabitants^[15] of which 152,993 (91.43%) reside in the urban area. The municipality, according to Thomaz^[16], is an area of the extratropical zone, which favors temperatures with mesothermal character, predominating annual temperatures between 16° and 20 °C, 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^[17].

Initially, a study of the urban stretch of the Rascavel 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 Rascavel 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 ($\mu\text{s}\cdot\text{cm}^{-1}$), 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, uncentro 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 h and manually wetted with the use of a gral and pistil. The biomass was weighed on an analytical balanc.

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 0.1 g 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^[18]. 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^[19], Braile and Cavalcanti^[20] and Santos^[21], these metals being commonly present in industrial effluents.

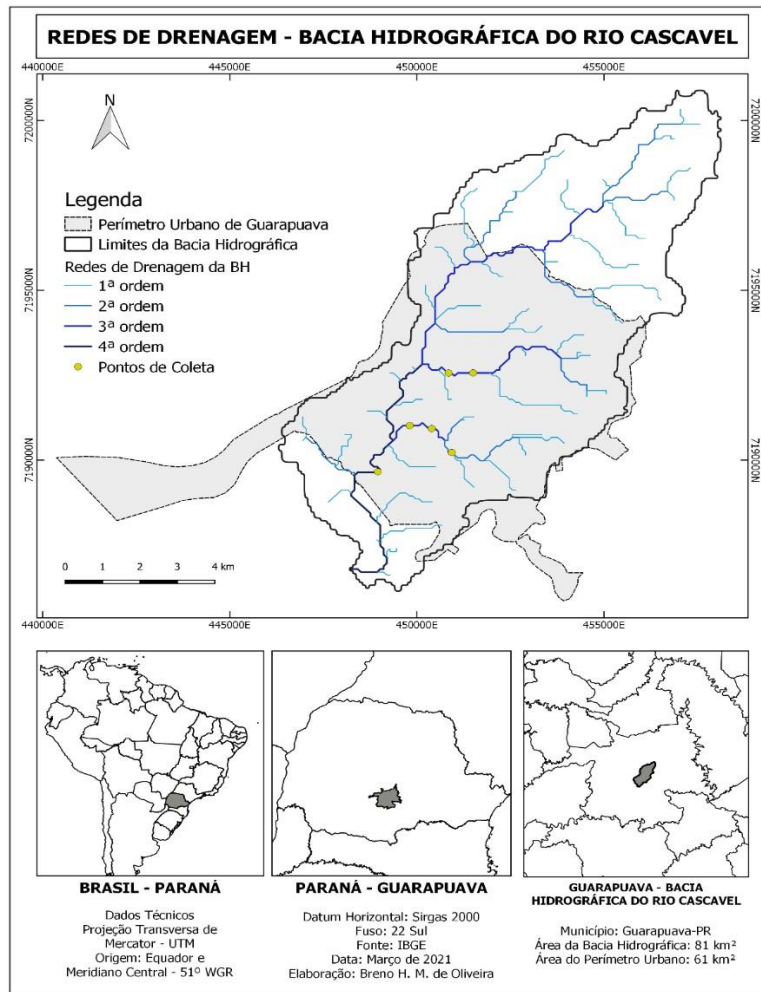


Figure 1. Egeria densa collection points in the urban stretch of the Rascavel River basin, Guarapuava—PR (Source: prepared by the authors).

Legenda

Drainage networks of bh

- Guarapuava urban perimeter
- Limits of the hydrographic basin
- 1st order
- 2nd order
- 3rd order
- 4th order
- Pontos de coleta

Drainage networks—hydrographic basin of the river cascavel

Brazil—Paraná

Technical data transverse mercator projection—utm

Origin: equator and

Central meridian—51st wgr

Parana—Guarapuava

Horizontal datum: sirgas 2000

Fuso: 22 sul

Fonte: ibge

Date: march 2021

Elaboração: breno h. M. De oliveira

Guarapuava—hydrographic basin of the Rascavel River
 Municipality: Guarapuava-PR
 Área da bacia hidrográfica:
 Urban perimeter area:

The parameters used for the measurement of heavy metals in organic matter were in accordance with Kabata-Pendias, Pendias^[31], Brazil^[7], Fao^[23] and Malavolta^[24]. 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 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.

3. Results and discussion

3.1. 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^[25]. 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^[26], 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^[27].

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^[28]; 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.

Table 1. Mean values of temperature (°C), conductivity ($\mu\text{s}/\text{cm}$), pH and total dissolved solids (mg), arithmetic mean and standard deviation between sampling points in the urban stretch of the Rascavel River, municipality of Guarapuava, PR. Surveys conducted between November 2018 and July 2019 (Source: prepared by the authors).

Ponto	Temperature °C	Conductivity $\mu\text{s}\cdot\text{cm}^{-1}$	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

Regarding conductivity, the sample points presented mean and standard deviation of 105.1 ± 15.2 $\mu\text{s}\cdot\text{cm}^{-1}$, being those natural waters present conductivity values in the range of 10 to 100 $\mu\text{s}\cdot\text{cm}^{-1}$ in

environments polluted by domestic or industrial waste, the values can reach 1000 $\mu\text{s}/\text{cm}$. 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 affirm that as dissolved solids are added to a water body, the electrical conductivity of the water increases, as observed in the analysis points.

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 Rascavel River basin towards the eeteestação 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.

3.2. Quantification of heavy metals in dense egeria by sample point:

According to Tuna et al.^[29] 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^[30] affirms that magnesium does not cause significant problems for human health. In addition, this metal is commonly found in plants.

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^[31]. Without reference parameter. Surveys conducted between November 2018 and July 2019 (Source: prepared by the authors).

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

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^[32].

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^[33].

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^[31]. Without reference parameter. Surveys conducted between November 2018 and July 2019 (Source: organized by the authors).

Ponto	Cr (mg/kg) median teor 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

3.3. 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^[34].

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^[35]. 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.

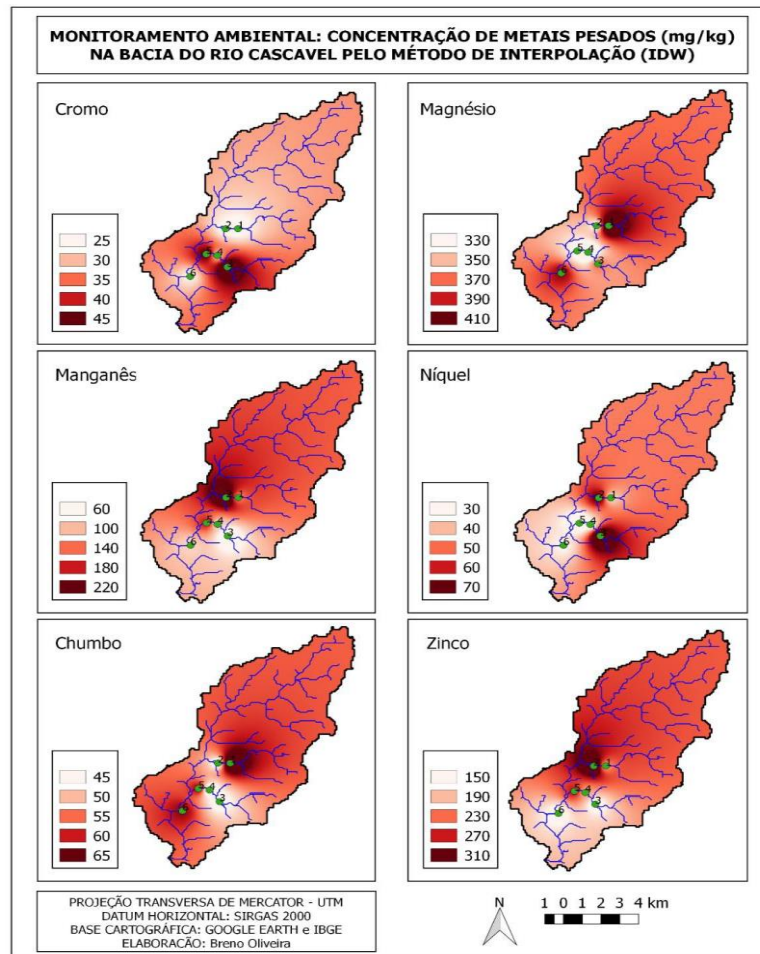


Figure 2. Concentration of heavy metals, generated by the interpolation of the data by the inverse distance weighting (IDW) method (Source: organized by the authors).

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

Chrome

Magnésio

Nickel

Chumbo

Zinco

Transverse mercator projection—utm horizontal datum: sirgas 2000

Cartographic base: google earth and ibge

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 Rascavel 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.

4. 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 Rascavel 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^[22], 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 Rascavel 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.

Conflict of interest

The authors declare no conflict of interest.

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