Influence of agriculture on surface water quality in three lentic environments in a conservation unit of Brazil

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Abstract

The use of agricultural inputs (AIs) without technical criteria can affect the quality of water sources and impact the biota present in these environments. This research sought to verify whether there was contamination in the surface water bodies of three lentic environments in a fully protected conservation unit in Brazil, called Estação Ecológica de Águas Emendadas (ESECAE), originating from agricultural activity near its perimeter. The ESECAE is the source of water bodies that flow into important hydrographic basins in Brazil and South America. Water quality parameters (WQPs) related to the use of AIs were selected and evaluated to assess compliance with regulatory provisions regarding the priority use of water at the study site. The analysis of the results revealed that in some situations, these parameters exceeded the normative limit in some samples and that, in general, the transport of contaminants originating from rainfall occurred. Total phosphorus (TP) values were high, exceeding regulatory concentration limits in multiple analyses. Consequently, eutrophication processes were verified in these environments. The eutrophic environments favored the proliferation of aquatic macrophytes, such as the invasive species *Hyparrhenia rufa*. TP concentrations increased during the dry season in these environments. In this context, a process related to the dynamics of phosphorus in aquatic lentic environments under certain conditions was observed. In conclusion, this research highlights the importance of monitoring WQPs in different periods to better assess water quality and to understand contaminant dynamics.

Keywords Brazil · Environment · Agriculture · Conservation units · Water resources · Quality parameters

Introduction

The modernization of Brazilian agriculture began in the 1960s because of the so-called "Green Revolution" and led to an increase in production based on increased productivity caused by the consumption of AIs. This process was concentrated in the South, Southeast, and Central-West regions of Brazil and based on the monoculture of exportable products, such as soybeans and sugarcane; however, this revolution did not reach the poorer regions in the North and Northeast, where small properties focusing on food polyculture prevail. According to Hespanhol (2000), following government incentives, agricultural production in the Central-West region grew substantially after 1970, especially for soybeans, wheat, sugarcane, and corn. This expansion took place in the Cerrado biome, which is predominant in the Central-West region. The Cerrado biome is the second largest biome in Brazil in terms of territorial extension and biodiversity. The practice of modern agriculture in the Central-West Cerrado has generated high levels of productivity in agricultural fields but led to significant environmental problems.

AIs can change the quality of air, soil, and water sources, influencing the biota present in these environments. Pesticides and fertilizers are the main contaminants in aquatic environments, as they contain chemical products that can cause environmental imbalance. Agricultural activities are considered important sources of phosphorus and nitrogen for aquatic systems (Campos 2010). However, depending on the type of soil for agricultural use, there is a need to supplement

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other plant nutrients, which can also compromise the quality of water sources. Pesticides and their derivatives can reach aquatic environments via direct application, spray drift, surface runoff, and leaching. These processes originate in areas where pesticides are applied. Spray drift is any application that does not reach the desired location and can occur by evaporation, slippage, and/or displacement to other areas by the wind. Leaching pesticides through the soil profile can cause groundwater contamination and affect surface water. According to Spadotto et al. (2010), the processes involved in the environmental transport of pesticides depend on their physicochemical properties and form of application, the soil characteristics, and the environmental conditions.

Thus, a continuing concern of AI use in agriculture is contamination of the hydrological system. Three main factors influence the behavior of AIs in soil: the chemical structure and properties of the compounds; the physical, chemical, and biological characteristics of the soil; and the environmental conditions. The compounds have a complex distribution that is influenced by the dynamics of the partitioning processes between phases. The effect and intensity of the effect resulting from the use of AIs in the environment depend on the retention, transfer, transport, and transformation processes that occur in each compartment of the soil−water–plant−atmosphere system. Knowledge of the chemical and physical properties of the contaminants is necessary to predict where the highest concentrations of AIs and/or their derived compounds are likely to be found in the different components of the ecosystem. The adoption of models for assessing the risk of contamination of aquatic ecosystems can reduce the difficulties of monitoring because sites with high vulnerability can be selected for assessment. However, the best way to assess the potential impact of AIs is to conduct well-designed field monitoring studies with frequent and regular sampling.

It is important to monitor water quality based on parameters related to the agricultural activities practiced in the local area. Research on AIs used on rural properties constitutes a starting point for defining these parameters. Carmo (2001), in their study of the hydrographic basin of the Descoberto River (on the border between the Federal District and the state of Goiás, in Brazil), suggested the need for water monitoring to reduce or contain the occurrence of various elements in fertilizers, pesticides, and fungicides. In this sense, the study of the ESECAE is essential due to its environmental importance. In Brazil, with many different environmental conditions, there have been few studies involving AI surveys and the corresponding influence on the quality of surface water. In the case of pesticides, there is a lack of studies due to the lack of laboratories that can perform related analyses, and they are concentrated in the southeastern and southern regions of the country. Another issue is the difficulty of access to the sampling sites in conservation units and the

complex logistics for collecting, packing, and transporting these samples for analysis. For the ESECAE region, no studies with this approach were found.

The ESECAE is located to the northeastern part of the Federal District and is bordered by rural properties. The main watercourses in the area are the Vereda Grande and Fumal streams, originating from a single drainage area called Vereda Grande. This area is the source of two different hydrographic basins: Tocantins-Araguaia and Paraná. Additionally, Bonita Lagoon is part of the ESECAE and occupies a noncontinuous area to the west of its largest extension. Due to its multiple bodies of water, the area was named Águas Emendadas, which means "Waters Stitched Together" in Portuguese.

One issue that needs to be studied is the effect of rural properties adjacent to conservation units. Agricultural activity is intensive and involves the permanent use of AIs. Thus, contamination may be occurring in the surface waters of the ESECAE. However, no noticeable changes in surface water quality were found. The only change observed was the proliferation of the aquatic macrophyte *Hyparrhenia rufa* in Bonita Lagoon and its increase during dry periods. According to Lacerda (2008), in the ESECAE region, the following soil types predominate: red latosoil, red−yellow latosoil, and cambisoil. Latosols are characterized by low water retention, a low ion exchange capacity, and a high infiltration capacity and are ancient, deep soils over 10 m thick (Campos 2005). In principle, the soil of the ESECAE has a high infiltration capacity, which would facilitate contamination. The ESECAE's water source is important for the biological community and for the population. This importance encompasses regional, national, and even continental aspects. The existence of a large agricultural area within the boundaries of the ESECAE could lead to the broad dispersion of AIs, which can infiltrate the soil and contaminate groundwater and surface water. Thus, due to these conditions, surface water pollution may occur, a hypothesis that justifies this work. The assessed hypothesis was that the surface water resources in the ESECAE are contaminated due to agricultural activity.

Materials and methods

Delimitation of the study area

The hydrographic basin was chosen as the unit of delimitation of the study area. The Federal District Hydrographic Map—2016 (DF 2016) and the Level Curves Map of the Federal District (DF 2013), which were georeferenced, were used to outline five hydrographic subbasins. These subbasins encompassed the entire ESECAE area and a minimal drainage area around it, to which materials and substances could

flow, especially AIs from adjacent rural properties. For this activity, a geoprocessing program called ArcGIS® 10.5 was used, in addition to other tools in a geographic information system (GIS). The outlined subbasins were transferred to a properly georeferenced digital image of the ESECAE region obtained from LANDSAT (LANDSAT OLI 8 2018). These hydrographic subbasins are shown in Fig. 1.

Figure 1 shows the outlined hydrographic subbasins, the adjacent agricultural lands, and the locations of the surface water collection points in the study area. Showing this information in a single figure supports the analysis of the influence of agricultural activity on ESECAE water resources and the assessment of the relevance of collection points. It is clear that the hydrographic subbasins delimited around the Bonita Lagoon and those that encompass the water courses that originate from the Vereda Grande include agricultural areas, which may influence the quality of water sources.

Definition of criteria and analysis parameters

Water usage

To initially define the criteria and analysis parameters, the main uses of water in the ESECAE were researched to verify the existence of norms related to these uses. Then, the WQPs described in these standards, which could be related to the presence of AIs, were selected. The maintenance of biological communities is among the main priorities of water allocation in the ESECAE. These communities range from microscopic organisms such as microalgae and bacteria to even larger animals, such as the Lobos-Guará (*Chrysocyon brachyurus*) and Jaguars (*Panthera onca*). The general water supply constitutes another main use in the area. According to DF (2019), the Environmental Sanitation Company of the Federal District, CAESB, uses ESECAE's water to supply the populations of Planaltina, Arapoanga, Mestre D'Armas, and Sobradinho, regions located in the Federal District. There are two water catchment points at the ESECAE, one on the Brejinho stream and the other on the Fumal stream. The water collected from these springs is sent to the Pipiripau Water Treatment Station in Planaltina/DF, where it is treated, stored, and distributed (Tables 1 and 2).

Table 1 Geographic coordinates of surface water collection sites

Collection point	Latitude (S)	Longitude (W)	Elevation (m)
1	− 15° 35′ 52.444″	− 47° 37′ 16.463″	1015
2	− 15° 35′ 42.102″	− 47° 40′ 6.731″	937
3	− 15′ 34″ 33.781″	− 47° 41′ 11.230″	954
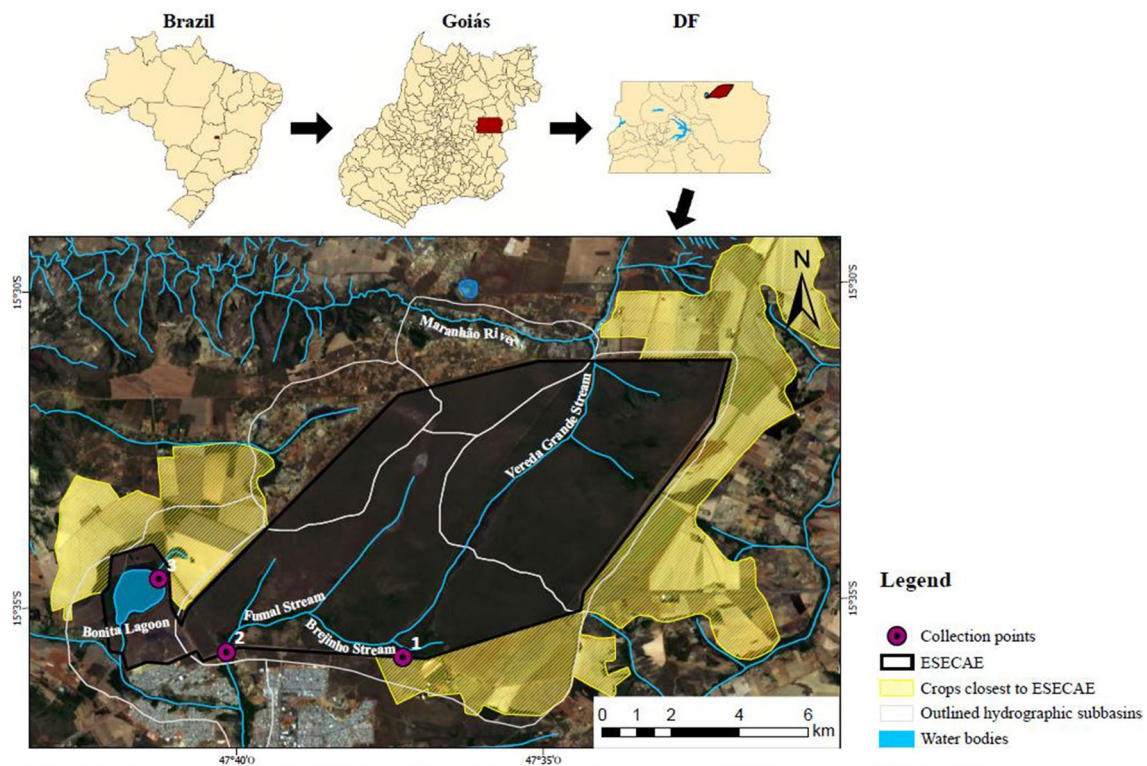
Fig. 1 Map of the ESECAE region with delimitations of hydrographic subbasins, closest crops and location of surface water collection points

Table 2 Measurement methodologies and equipment used in qualitative and quantitative assessments of the selected water quality parameters

Water quality parameter	Measurement methodology	Measurement equipment
Nitrite	SM 4500 NO_2– B	Spectrophotometer—Brand: Hach; Model: DR5000
Nitrate	SM 4500 NO_3– D	Spectrophotometer—Brand: Hach; Model: DR5000
Total ammoniacal nitrogen	SM 4500 NH_3– D	Selective ion meter—Brand: Hach; Model: HQ440D
Total sulfate	SM 4500 SO_4–E	Spectrophotometer—Brand: Hach; Model: DR5000
Sulfide (H_2S not dissociated)	SM 4500 S_2–D	Spectrophotometer—Brand: Hach; Model: DR5000
Total boron, dissolved copper, total phosphorus, total manganese, and total zinc	SM 3120–B	Atomic spectrometer ICP−OES—Brand: PerkinElmer; Model: Optima 7300 DV
Pesticide	USEPA Method SW-846—8260 C—2006	Gas Chromatograph—Brand: PerkinElmer; Model: Clarus 600

SM denotes standard methods, which is a set of procedures described in the document Standard Methods for the Examination of Water and Wastewater (SM 2017). The acronym USEPA refers to the United States Environmental Protection Agency (USEPA 2006), which establishes chemical analysis procedures. The characters following these abbreviations indicate the chapter in which the procedure is described

Adjacent rural production and AIs used

To select WQPs for assessing the use of AIs, it was necessary to research the agricultural crops adjacent to the ESE-CAE and the types of inputs used. The existing agricultural crops were soybean and corn and were adopted as references for the assessment of AIs and to define the WQPs. There are two well-defined seasons in the study region: rainy summer (October–April) and dry winter (May–September). The cultivation of these grains and the application of fertilizers and pesticides are performed at the end of the dry season, which is in September. Then, the development of these crops begins in October, with the beginning of the first rains during the rainy season. The agricultural area close to the ESECAE is shown in Fig. 1.

The AIs used for soybean and corn crops in the region around the ESECAE are sold in the municipality of Formosa in the state of Goiás. No agricultural supply stores sell AIs for the cultivation of grains in Planaltina/DF. The municipality of Formosa is the closest location to buy these inputs. In view of this finding, a survey was conducted in eight agricultural stores in Formosa to determine the most commonly used AIs for the cultivation of soybeans and corn, with a focus on pesticides and fertilizers. These stores were consulted from March 2018 to January 2019. The data obtained are shown in Table 3.

Evaluation sites

Surface water collection sites were chosen based on certain guidelines. We selected locations in lentic environments contained within a subbasin with soybean and corn plantations, which might be influenced by drainage and the leaching of AIs from these crops. Additionally, an attempt was made to choose the collection sites closest to the studied plantations. However, the limiting factor was accessibility because these areas are surrounded by bushes that are close together and are far (on foot) from places accessible to vehicles. Roads pass by only a few locations with water sources.

Three sites were chosen to collect surface water, all at the ESECAE. The choice of these locations was consolidated from previous visits to different locations based on the aforementioned guidelines. The locations of the three collection points are shown in Fig. 1. The georeferencing of the water collection sites was performed using a Garmin handheld GPS. To assist in the survey, the Offline Maps application was used to record observations, navigation data, and the name of each site. The geographic coordinates of the collection sites are shown in Table 1. The water at all collection points is first used to maintain biological communities, and the instrument used to regulate water usage was CONAMA Resolution N° 357/2005, which performs well in freshwater (BRAZIL 2005).

Table 3 Agricultural inputs most used for soybean and corn crops in the ESECAE region

Agricultural inputs	
Fertilizers	Pesticides
Compounds containing nitrogen, phosphorus and potassium—NPK. Micronutrients: boron, zinc, manganese, and copper. Agricultural plaster ($CaSO_4$). Agricultural limestone (CaO and MgO)	Glyphosate, methomyl, imidacloprid, fipronil, cletodim, azoxystrobin, tebuconazole, atrazine, carbendazim, lufenuron, thiamethoxam, propiconazole + diphenoconazole, azoxystrobin + cyproconazole, s-metolachlor, carbendazim + tiram, fludioxonil, metalaxyl, and 2,4-D

Definition of WQPs

The CONAMA Resolution N° 357/2005 (BRAZIL 2005) was used to collect WQP data based on different classifications of salinity, namely, fresh, brackish, or saline, and water quality according to end use. Thus, maximum values were established for each WQP. In the case of freshwater, the classes were special, class 1, class 2, class 3, and class 4. The classes were established based on the CONAMA Resolution N° 2 readings on December 17, 2014, and the standard of the Federal District Water Resources Council (CRH/DF 2014), which governs the classification of surface water bodies in the Federal District according to predominant uses and gives reference values. Collection point 1 was grouped into the special class. Collection points 2 and 3 were grouped into class 2.

The WQPs selected depended on the AIs used and the regional water uses (BRAZIL 2005). Thus, the WQPs measured were related to chemical products from the researched AIs, as listed in Table 3, and were analyzed. It is noteworthy that the table for freshwater class 1 was used to select the WQPs for the special class, as no parameters are explicitly defined for this class. Article 13 of the CRH/DF (2014) standard indicates that in special class waters, the natural conditions of the body of water must be preserved. For the collection points classified as class 2, the table for freshwater class 1 was also used, given that this class encompasses all the parameters of class 2, as described in article 15 of the aforementioned standard.

The selected WQPs are displayed in Table 4, with information about their origins. Notably, to measure the total ammoniacal nitrogen parameter at the normative limit, it was necessary to obtain the hydrogen potential (pH). This measurement was performed at each collection point using a digital device and was recorded with the total ammoniacal nitrogen concentration at the respective collection points.

Sample collection and evaluation of WQPs

The collection and transport of samples and the qualitative and quantitative determination of the WQPs were tasks performed by Conágua (Conágua 2019). The storage and preservation of the samples were conducted following the set of procedures described in the chemical analysis manual called Standard Methods for the Examination of Water and Wastewater (SM 2017). Thus, for each group of WQPs selected and described below, the following procedures were performed.

- Total manganese, total zinc, total boron, and dissolved copper: The sample was stored in a borosilicate glass container with a capacity of 200 mL. Sample preservation was performed with a 1.5-mL solution of nitric acid and a pH lower than 2. Samples were then stored in a refrigerator at 4 °C. The dissolved copper sample was filtered before preservation through a 0.45-μm aperture membrane filter. The filtered samples were preserved and stored according to the aforementioned procedure.

- Nitrite, nitrate, total sulfate, sulfide (H_2S not dissociated), and pesticides: The sample was stored in a borosilicate glass container with a capacity of 200 mL. Then, it was preserved in a hermetically sealed container at 4 °C. For sulfide, before cooling, 0.2 mL of 2 M zinc acetate was added per 100 mL of sample, and sodium hydroxide was added to the sample so that the pH was greater than 9.

- Total phosphorus and total ammoniacal nitrogen: The sample was stored in a borosilicate glass container with a capacity of 200 mL. For preservation, sulfuric acid was added to the sample to lower the pH to less than 2. Then, the sample was stored at a temperature of 4 °C.

Table 4 Selected water quality parameters and their origins

Selected water quality parameters	Origin
Total boron	Boron micronutrients
Dissolved copper	Copper micronutrients
Total phosphorus	NPK compound
Total manganese	Manganese micronutrients
Nitrate	NPK compounds. Nitrogen oxidation product
Nitrite	NPK compounds. Nitrogen oxidation product
Total ammoniacal nitrogen	NPK compound. It Includes NH_3 e $^+NH_4$
Total Sulfate	Agricultural gypsum
Sulfide (H_2S not dissociated)	Agricultural gypsum (reduction of sulfate in water)
Total zinc	Zinc micronutrients
Atrazine	Atrazine
2,4-D	2,4-D
Glyphosate	Glyphosate

The equipment and methodology used in the qualitative and quantitative assessments of the selected WQPs are described in Table 2.

Collection was performed at each water collection point, and there was a single measurement for each WQP. The collection campaigns were implemented on four dates, all in 2019. The first (collection 1) was carried out on February 15, the second (collection 2) on May 3, the third (collection 3) on September 13, and the fourth (collection 4) on December 19 (Table 5). The concentration data obtained for each parameter at each collection point were organized according to the temporal sequence of water collection and are listed in Table 6. With the data from those evaluations, it was verified whether the chosen parameters fell within the permitted ranges based on the relevant standards.

The transport of these substances was analyzed by comparing their concentrations in the dry and rainy seasons. The concentrations of parameters that did not reach the minimum limit detectable by the measurement equipment were important in this analysis. Therefore, despite not having a determined value, the findings were used to indicate an increase or decrease in abundance in relation to the determined values from successive measurements. A description of the climatic conditions associated with each water collection period was necessary to optimize the analysis. This information is shown in Table 7.

Table 5 Maximum values of the water quality parameters selected according to the CONAMA Resolution N° 357/2005 and the freshwater class 1 standard (BRAZIL 2005)

Selected water quality parameters	Maximum value
Total boron	0.5 mg L^{-1}
Dissolved copper	0.009 mg L^{-1}
Total phosphorus	0.020 mg L^{-1}
Total manganese	0.1 mg L^{-1}
Nitrate	10.0 mg L^{-1}
Nitrite	1.0 mg L^{-1}
Total ammoniacal nitrogen	3.7 mg L^{-1}, pH ≤ 7.5
	2.0 mg L^{-1}, $7.5 < $ pH ≤ 8.0
	1.0 mg L^{-1}, $8.0 < $ pH ≤ 8.5
	0.5 mg L^{-1}, pH > 8.5
Total sulfate	250 mg L^{-1}
Sulfide (H_2S not dissociated)	0.002 mg L^{-1}
Total zinc	0.18 mg L^{-1}
Atrazine	2 µg L^{-1}
2,4-D	4.0 µg L^{-1}
Glyphosate	65 µg L^{-1}

Results and discussion

Fertilizers are used to supply nutrients that are deficient in the typical soil types of the Cerrado biome and are necessary for the cultivation of soybeans and corn. Agricultural plaster ($CaSO_4$) provides sulfur in the form of sulfate (SO_4^{2-}). Agricultural limestone (CaO and MgO) is used to mitigate the acidity of the Cerrado soil and neutralize the action of available aluminum to an insoluble form that is unavailable to plants. Aluminum is a toxic element for the development of plants and is present in excess in the Cerrado biome. Regarding the damage caused using fertilizers, it is noteworthy that compounds containing nitrogen and phosphorus can contribute to eutrophication in aquatic environments. The chemical reduction of sulfate leads to the formation of H_2S, which is a gas with an unpleasant odor. Excess limestone in water causes an unpleasant taste. These compounds are harmful to human health. The toxic action of nitrates and nitrites can lead to methemoglobinemia and nitrosation of amines, inducing carcinogenic effects; these impacts can be extremely detrimental to human health (De Saint-Blanquat 1980).

According to data from the Brazilian official agencies AGROFIT (2018) and IBAMA (1996), among the pesticides cited in the survey, 72% of the products were classified as very dangerous or highly dangerous for the environment, 66% are highly persistent in the environment, and 11% fell into both categories.

The WQPs selected according to the CONAMA Resolution N° 357/2005 and the freshwater class 1 standard (BRAZIL 2005) are shown in Table 4, as are their relationships with the agricultural inputs researched. Table 5 shows the maximum values of the WQPs selected (BRAZIL 2005).

The quantitative evaluations conducted are shown in Table 6. The concentrations of total boron, dissolved copper, sulfide (H_2S not dissociated), and pesticides (atrazine, 2.4-D and glyphosate) did not reach the minimum limits detectable with the measurement equipment and, therefore, these parameters were not included in the analysis. The minimum detectable limits of these parameters are lower than the maximum values that can be detected by the CONAMA Resolution N° 357/2005 (BRAZIL 2005).

When comparing the concentrations of these parameters with the maximum values allowed (BRAZIL 2005), it was found that there were cases in which the limit values were exceeded. The normative limit of total ammoniacal nitrogen (sum of NH_3 and $^+NH_4$) was exceeded at collection point 3 (located at Bonita Lagoon) during collection period 3 (dry season). At this point, the concentration of total ammoniacal nitrogen was 0.918 mg L^{-1} and pH = 9.0, which were above the limits (0.5 mg L^{-1}; pH > 8.5). The TP concentration was

Table 6 Quantitative assessment of collection points: (a) collection point 1; (b) collection point 2; (c) collection point 3. The notation with the symbol < (less than) followed by a number indicates that the quantitative measurement of the parameter did not reach the minimum limit detectable by the measurement equipment. The limit is the number shown

(a) Collection point 1

Water quality parameters	Measurements			
	1	2	3	4
Total phosphorus (mg L^{-1})	0.067	0.017	0.125	0.069
Total manganese (mg L^{-1})	0.03	0.036	0.007	0.063
Nitrate (mg L^{-1})	0.6	1.1	0.3	2.6
Nitrite (mg L^{-1})	0.005	0.03	0.007	0.008
Total ammoniacal nitrogen (mg L^{-1})	0.993 pH = 8.20	1.021 pH = 7.20	0.933 pH = 8.10	0.963 pH = 7.10
Total Sulfate (mg L^{-1})	< 2.00	2.28	< 2.00	< 2.00
Total zinc (mg L^{-1})	0.132	0.015	0.012	0.024

(b) Collection point 2

Water quality parameters	Measurements			
	1	2	3	4
Total phosphorus (mg L^{-1})	0.022	0.022	0.055	0.091
Total manganese (mg L^{-1})	0.029	0.044	< 0.007	0.073
Nitrate (mg L^{-1})	0.5	1.1	0.3	2.6
Nitrite (mg L^{-1})	0.006	0.019	0.021	0.008
Total ammoniacal nitrogen (mg L^{-1})	0.961 pH = 6.26	0.977 pH = 7.60	0.941 pH = 8.40	0.982 pH = 6.90
Total sulfate (mg L^{-1})	< 2.00	< 2.00	< 2.00	11.34
Total zinc (mg L^{-1})	0.042	0.067	0.087	< 0.007

(c) Collection point 3

Water quality parameters	Measurements			
	1	2	3	4
Total phosphorus (mg L^{-1})	0.026	0.023	0.038	0.09
Total manganese (mg L^{-1})	0.02	0.025	< 0.007	0.063
Nitrate (mg L^{-1})	0.3	1.1	0.6	1.4
Nitrite (mg L^{-1})	0.021	0.014	0.003	0.008
Total ammoniacal nitrogen (mg L^{-1})	0.973 pH = 7.02	1.079 pH = 7.50	0.918 pH = 9.00	1.23 pH = 7.00
Total sulfate (mg L^{-1})	< 2.00	3.06	< 2.00	10.95
Total zinc (mg L^{-1})	0.064	0.013	0.025	0.009

Table 7 Climatic conditions associated with the temporal sequence of water collection

Time sequence of water collection	Weather conditions
1	Dry weather twenty-eight days into the rainy season. Collection conducted on February 15, 2019, after the first rains began in October 2018
2	Heavy and frequent rains. Collection performed on March 5, 2019, at the end of the rainy season
3	Dry season. Hundredth day without rain. Collection carried out on September 9, 2019
4	Start of the rainy season. Heavy and frequent rains. Collection conducted on December 19, 2019. First rains occurred in October 2019

above the allowable limit at nearly all sites. Except at collection point 1 during collection period 2, the other measurements exceeded the allowable limit (0.020 mg L^{-1} for the lentic environment). These results indicate that these bodies of water are eutrophic, as their TP concentrations are above 0.02 mg L^{-1}, as reported by Campos (2010).

Regarding pesticides, the fact that the concentrations did not reach the lower detection limit does not irrefutably mean that these water courses or even other environmental components are free from pesticide contamination. There may be metabolites that were not considered in the evaluation, including some that may even be unknown, with the potential for harming local biota. Glyphosate was the most cited pesticide in a survey of the literature. The leaching of 2,4-D occurs at an average rate, the GUS index (Gustafson 1989) for work done in Brazilian clays is generally between 1.8 and 2.8. Its half-life (time to reach half its initial amount) is on average 4 to 10 days, a short period. Thus, the chance of 2,4-D reaching the groundwater is moderate. However, this chance may increase with rainfall. Glyphosate displays little mobility in the soil and is generally adsorbed to the soil; its degradation product AMPA breaks down rapidly. Thus, the chance of contamination in surface water is low. A study by Padilla and Selim (2019), who analyzed clayey soil and silty soil, indicated that the adsorption by glyphosate in soil can be widely considered an irreversible process. The degradation of 2,4-D and glyphosate occurs by microorganisms. Atrazine is highly leachable, with a half-life of 30–100 days. However, its nondetection can mainly be attributed to its photodecomposition and to its use in small quantities. According to IBAMA (1996), among these pesticides, only 2,4-D is classified as highly mobile, and therefore, the destination of the other pesticides tends to be the soil.

In this study, a statistical analysis of the data for the evaluated WQPs was not appropriate, considering that a single quantitative evaluation of each parameter was conducted on each collection day. Additionally, the climatic conditions varied during each collection period, which could influence the results obtained. The weather conditions on each water collection day are shown in Table 7.

Regarding the analysis of the transport of these parameters, variations were observed in the concentrations of the WQPs observed. The transport of total manganese occurred during heavy rains (collections 2 and 4) at all points, and the corresponding values were used as a reference for nondetection in the dry period (collection 3). One explanation for this transport is that one of the ways to add manganese to cultures is in the form of chloride or sulfate, which are highly water-soluble compounds. Regarding the evaluated WQPs (Table 4), it is noteworthy that a large portion of the fertilizers found was in the form of salt, an inorganic chemical group; this group encompasses any substance that, when in water, produces a cation different from H^+ and an anion different from ^-OH. For the context of this research, salt is at least partially soluble water in which, and upon dissociation, the formation of components occurs, at least one of which is of nutritional importance for plants. According to the Potash & Phosphate Institute (1995), spraying $MnSO_4$ with

water is a common treatment for soybeans with manganese deficiency. According to Robson (1988), the ion Mn^{2+} is very stable in acidic solutions and does not form complexes as strongly with other organic or inorganic ligands as other micronutrients (Cu^{2+}, Zn^{+2}, Fe^{2+}, and Fe^{3+}). Thus, during leaching, there is no significant retention in the soils due to this interaction, with a greater flow of this substance to surface water bodies.

The concentration of total zinc at collection points 2 and 3 was relatively high during the dry season (collection 3). At the beginning of the rainy season (collection 4), the concentration was relatively low at all points. These findings may be because, according to Jenne (1968), hydrated manganese and iron oxides are the main controls over the fixation of zinc in soils and sediments in freshwater, and sorption or desorption occurs in response to certain factors, such as pH and aqueous concentrations. Zinc can be added to cultures in the form of sulfate, which is very soluble in water.

Nitrate levels increased at all collection points during the period of heavy rain (collections 2 and 4). Thus, associated compounds were transported during these periods. Nitrate is characterized by high solubility in water; it originates directly from fertilization in the form of nitrate and from the decomposition of nitrogen fertilizers, such as urea. In a study of surface water contamination from substances used in agricultural areas, Ghane et al. (2016) concluded that the average daily load of nitrate per unit area of fertilized field was significantly higher than for unfertilized fields because of the higher concentration of nitrate in the fertilized fields.

Regarding nitrite, it was not possible to evaluate its behavior based on the concentration data obtained at the collection points in the various study periods. Nitrite originates from the decomposition of nitrogen fertilizers and is an intermediate decomposition product of nitrogen in aquatic environments, thus requiring a period for formation.

Total ammoniacal nitrogen (sum of NH_3 and $^+NH_4$) increased at all points in the period of intense rainfall (collections 2 and 4). This increase was mainly due to the concentration of $^+NH_4$ ions, mostly from fertilizers in the form of phosphate (used to manufacture phosphorus) or sulfate (used to manufacture nitrogen). This ion is characterized by high solubility in water. The largest increase occurred at collection point 3 (Bonita Lagoon) and was potentially related to the large concentrated area of agricultural crops surrounding it. However, the relative variation in the concentration of total ammoniacal nitrogen in the periods of heavy rain (collections 2 and 4) in relation to those with less rainfall (collections 1 and 3) was low. This occurred because ammonium is less likely to be transported by underground drainage, as it is bound to soil particles due to its positive charge, according to Ghane et al. (2016). The adsorption of positively charged ammonium ions occurs on the surface of

negatively charged clay particles (Sieckza and Koda 2016). In the environment, ammonium will reach an aquifer faster in sandy soils and soils with low organic matter contents than in cohesive soils with higher clay and organic matter contents (Sieckza and Koda 2016).

The sulfate concentration increased during the period of heavy rains at the points where the measurement equipment was able to detect its presence, which were collection points 1 and 3 on collection day 2 and collection points 2 and 3 on collection day 4. These collection points are very close to the agricultural area. Sulfate originates mainly from the application of agricultural plaster ($CaSO_4$) as a source of sulfur for agricultural crops. $CaSO_4$ is a salt characterized by relatively low solubility in water. Thus, this input was transported, generating an increase in sulfate at these locations.

Regarding TP, in the interval between collection days 2 (near the end of the rainy season) and 3 (dry season), an unusual situation occurred. The amount of TP increased in the dry season (collection day 3) compared the levels on collection days 1 and 2. The pH also increased. To explain this result, it became necessary to approach concepts and phenomena from different fields of knowledge. At the beginning of the intense and frequent rains (collection day 4), collection point 1 was the only point at which there was no increase in the TP concentration.

The traditional forms of applied fertilizers that contain phosphorus as a nutrient are monoammonium phosphate ($NH_4H_2PO_4$) and diammonium phosphate ($(NH_4)_2HPO_4$), which are salts. Phosphorus components are characterized by low leaching, with almost all the phosphorus translocating in the soil by diffusion (Potash and Phosphate Institute 1995). Diffusion is the movement of ions from a high-concentration solution to a low-concentration solution. The movement of phosphorus is a slow process with low amplitude and depends on soil moisture (Potash and Phosphate Institute 1995). Shen et al. (2011), who researched the dynamics of phosphorus, reported that it has unique properties in soil, such as low solubility, low mobility, and high fixation by the soil matrix.

Iron and aluminum oxides and hydroxides are present in large amounts in heavily weathered tropical soils, especially in clayish soils. The soils of the ESECAE are mostly red latosoil. This soil has a clayish texture and is enriched by sesquioxides (a classification encompassing oxides, oxyhydroxides, and hydroxides) of iron and aluminum.

This process takes place in two layers of a body of water: an oxidizing layer where aerobic process occur and a reducing or anoxic layer. At the start of heavy rain (collection day 4), there is generally an increase in phosphorus in water bodies. Storm events transport large loads of total phosphorus from surface drained fields (Macrae et al. 2007). Simultaneously, there is a flow of substances that serve as oxidizing agents, such as O_2, NO_3^-, and Mn^{4+}, leading to the oxidation of Fe^{2+} to Fe^{3+} in the form of ferric oxyhydroxide. There is recirculation of water between the aerobic and anaerobic layers, resulting in the flow of these oxidizing agents, such as O_2, to the anaerobic layer located at the bottom of a water body, contributing to an increase in Fe^{3+} ions; with the help of microorganisms, these ions adsorb phosphate. This phosphate is relatively insoluble, and over time, precipitation and the accumulation of phosphorus occur in the sediment. During the dry season, the flow of these oxidizing agents ceases, and an anaerobic layer forms near the bottom. The Fe^{3+} of the formed ferric oxyhydroxides is reduced to Fe^{2+}. As these compounds are more soluble, they dissolve in water, and the adsorbed phosphate is released from the sediment into the solution as the pH increases. The arguments presented here are supported by research conducted by Novais and Smyth (1999), Busigny et al. (2016), Cosmidis et al. (2014), Parsons et al. (2017), Liang et al. (2016) and Pantano et al. (2016).

This cyclic phenomenon in water bodies has different designations. It is called, for example, the "iron wheel" according to Busigny et al. (2016) or "phosphorus pump" by Pantano et al. (2016). Its understanding essentially requires a biogeochemical approach, and according to Cosmidis et al. (2014), there are microorganisms and metabolic processes involved in these transformations that have not yet been fully described. The analysis of this phenomenon was initially carried out by Einsele (1936) and then improved by Mortimer (1941). Later, other researchers, such as Lee et al. (1977), Boström et al. (1982) and Jensen and Andersen (1992), analyzed other factors in these transformations. Wilson et al. (2010) stated that the dynamics of the flow of dissolved phosphorus in the water column vary according to trophic status and other biogeochemical conditions. The increase in TP generated by this phenomenon may overshadow the eutrophic nature of lentic environments, as would be the case with sporadic assessments of water quality carried out in periods when high concentrations are not recorded. This situation occurred at collection point 1, where on collection day 2 (drought during the rainy season), the concentration was 0.017 mg L^{-1}, and on collection day 3 (dry season), the value was 0.132 mg L^{-1}. Thus, it is important to monitor this parameter over different climatic conditions to obtain appropriate analysis results. The release of phosphorus from the sediment of surface waters in agricultural areas, which are modified with agricultural inputs, has an important effect on the quality of these waters (Grift 2017).

The concentration of TP in Bonita Lagoon has increased over time. In the work by Leite (1990), under similar collection conditions (an area close to the agricultural area; collection of surface water conducted on the banks of Bonita Lagoon), all concentrations were below 0.010 mg L^{-1}, which was the lower limit of detection of the equipment

used. Gomes (2007) obtained an average concentration of $0.014 \, \text{mg L}^{-1}$ under similar collection conditions. Thus, the euphotic zone is becoming rich in phosphorus and is very productive from the point of view of transforming inorganic carbon into organic species, favoring the proliferation of algae and aquatic macrophytes. Thus, *Hyparrhenia rufa* disseminated (Fig. 2), which, in some places, is confused with the soil surface. *Hyparrhenia rufa* is an invasive grass native to Africa and is known by the popular name of Jaraguá grass. Grift (2017) reported that the input of phosphorus via manure and fertilizers into hydrographic basins should not exceed the output of phosphorus via surface water and animal feed (and manure) exports, and under these conditions, waste loss must be minimized.

Some studies have verified the relationship between eutrophication and the emergence of noncommon species. Tan et al. (2018) showed that sediments rich in phosphorus and nitrogen in eutrophic waters may be the main reason for the rapid expansion of invasive macrophytes. Randall et al. (2019) verified the correlation between phosphorus in the sediments and in the water column in Lake Utah in the USA and explored the corresponding relationship with the proliferation of algae or cyanobacteria. The expansion of invasive aquatic plants can lead to changes in the ecosystem, displacing native species (Brundu 2014) and reducing biodiversity (Hussner et al. 2017).

Thus, in general, the transport of AI constituents and the decomposition of its products are initiated at the beginning of the rainy season (October–April). The transport of these substances is higher during heavy rains, which start in December and can reach groundwater and surface water. An example of changes resulting from agricultural activity occurring in the hydrographic subbasin where the ESECAE is located was the change in the surface water quality in Bonita Lagoon (Collection Point 3) over time.

Among the potential existing methods for sample collection and preservation, the National Guide for Sample Collection and Preservation, prepared by the Environmental Company of the State of São Paulo and the National Water Sanitation Agency, is among the most popular and important. In this method, there are some differences regarding the procedures and materials adopted, such as the sampling volume and the material used to store samples.

Regarding the tolerance limits of contaminants, the limits in this study were compared with the limits of the United States Environmental Protection Agency, and the limits adopted here are generally higher; moreover, there are fewer contaminants with set limits. Additionally, the Environmental Quality Standards Directive for surface waters published by the European Commission has generally lower contaminant tolerance ranges than those adopted in this study. Atrazine and glyphosate were banned in the European Community. Thus, Brazilian environmental legislation is less restrictive than American and European legislation.

A potential tool for predicting pesticide contamination in surface waters, if available, would be modeling programs suitable for the particular conditions of the region under study, such as soil, vegetation, and climate. Thus perform a reliable analysis. The modeling programs satisfactorily portray the behavior of contaminants for regions where they have been developed, tested, and validated.

Conclusion

Actions are necessary to mitigate the loss of environmental quality in these areas, especially educational actions targeted at the populations of nearby agricultural areas. These actions would focus on highlighting the role of the ESECAE as a water source for the supply and maintenance of fauna and flora. The preservation of these areas could be achieved using slow-release fertilizers along with integrated pest management. The rational use of fertilizers, implemented by professionals in agricultural areas and with technological resources supported by precision agriculture, could control the use of these inputs without major losses. Slow-release fertilizers gradually release macronutrients and micronutrients over a certain period, depending on the thickness of the polymer in which they are encompassed and the quantity of losses through leaching and volatilization. Integrated pest management, through pest and disease control techniques, would aid the recovery of the affected area by other means, such as biological control and pruning, thus reducing the need for pesticides. Finally, regarding the initial hypothesis, it was concluded that there was contamination in the studied environments due to agricultural activity. The verified consequence of this contamination was eutrophication.

Among the contributions of this manuscript, two stand out. One is the association between the most commonly used

Fig. 2 Dissemination of *Hyparrhenia rufa* in Bonita Lagoon

AIs and pollution in surface water bodies, with the local hydrographic subbasin as a territorial reference. The other is the method used to evaluate WQPs and their intervals in different climatic periods to better understand the dynamics and behaviors of contaminants in the soil and aquatic environment. One objective of the work was to clarify the proliferation process of the aquatic macrophyte *Hyparrhenia rufa* in Bonita Lagoon, which increased in abundance during dry periods, likely due to the "iron wheel" effect. Moreover, the constituents and decomposition products of AIs of environmental interest in the study area were identified.

Data availability The authors declare that they have no conflict of interest.

Declarations

Conflict of interest The authors have no relevant financial or nonfinancial interests to disclose.

Ethical approval Not applicable for that specific section.

Consent to participate and to publish The authors agreed on the content and all give explicit consent to participate, to submit, and to publish and that they obtained consent from the responsible authorities at the institute/organization where the work was carried out before the work was submitted.

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