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Economic Activities of Banana Cultivation and Phosphorus Contribution to a Brazilian RAMSAR Estuarine System

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Abstract

The Ribeira River valley, region with important banana cultivation and P mining, presents economic activities that exert environmental impact on the Cananéia-Iguape Estuarine-Lagoon Complex (CIELC), located at the river downstream and member of the Biosphere Reserve and the Ramsar list of wetlands. The aim of this work is to verify how much the influence of fertilizers used on riverine banana crops can impact the Ribeira River nutrient concentrations and reach the estuarine system considering the phosphogypsum mining contribution. For it, the amount of fertilizer used and lost by banana cultivated area was estimated and also the nutrient concentrations (N and P) in a salinity gradient were determined. The use and loss of nutrients from fertilized areas were calculated using Google Earth Pro to distinguish the planted plots and the number of banana plants. It was verified that nutrients from fertilizing were estimated as 200 kg of N per ha and 80 kg of P per ha year^{-1} considering its different mobility in the soil and the needs to support 744.5 tons of bananas produced in this area. Considering that 10% of P and 30% of N from fertilizer are lost to the hydrological system, around 5 tons/year for P and 44 tons/year for N are transported. Phosphate values (maximum 13.02 μmol L^{-1}) present in a freshwater downstream and the highest values of nitrate (maximum 14.59 μmol L^{-1}) at the Valo Grande (artificial channel) demonstrating a N/P (2/1) ratio imbalance influenced by anthropogenic activities and confirming P contribution to estuarine system.

Keywords

Fertilizer, Eutrophication, Phosphogypsum, Nutrients, Banana Growing Area, Ramsar Convention

1. Introduction

Coastal regions constitute areas of interface between the ocean and the continent with human interests of occupation. Their special characteristics congregate human influence and the natural processes that occur in each segment of the coastline; therefore, these coastal regions are often locals to countless anthropogenic activities. For Mommaerts et al. (1987), the optimization of coastal areas for multiple uses demands that any interests must be accommodated within a framework of rules which ensure that environmental disturbances are minimal, or reversible, and that marine resources are conserved. The Cananéia-Iguape Estuarine-Lagoon Complex (CIELC) (São Paulo, Brazil) is a region with high hydrological complexity which presents differences in terms of human occupation and land use in its northern and southern sectors. In addition, this area is included on the Ramsar list (https://rsis.ramsar.org/ris/2310) as an important wetland requiring protection (Braga et al., 2023a).

The Ribeira River is 470 km long and begins in the state of Paraná and enters the state of São Paulo, passing through approximately 23 cities, going from the plateau to the lowlands of the plains, where it passes through an extensive wetland. It reaches the Atlantic Ocean in the municipality of Iguape, where it has its mouth. In its lower portion, it is called the Ribeira de Iguape River. This river flows through the Ribeira Valley, where there are communities of farmers, indigenous quilombolas and caiçaras. Banana culture is expressive in this area as agricultural activity. In its final portion, it meets the Atlantic Ocean at the original mouth of the river in Iguape. With the construction of the Valo Grande channel in 1856, part of the river's waters flowed into the Mar Pequeno, located between Comprida Island and the continent, to the southern, where it is between the islands of Cananéia and Comprida. Further south, there is the Ararapira Channel, which is far away from the waters of the Ribeira de Iguape River (**Figure 1**).

In this lowland region, one of the morphological units (Ross, 2002) that stands out is the Cananéia-Iguape coastal plain system, which, in addition to its physical and morphogenetic properties, is home to important biodiversity. It is part of an estuarine region of great biophysical complexity, with mangrove ecosystems alongside marine sandbanks cut by river plains. In this area, flat, sandy terrains of the hydromorphic family develop, presenting shallow water tables (Ross, 2002 *op cit.*). This area is of great natural fragility in relation to human occupation due to its type of sandy and unconsolidated soil and biodiversity that needs to be preserved, since it is considered to be surrounded by Preservation Units (APAs, APAM Parks). Currently, the erosion processes of the sandbanks have intensified, especially to the south of the system, on Cardoso Island and south of Cumprida Island.

The distinction between the northern and southern sectors of the CIELC considering environmental hydrological and sediment properties as demonstrated by some authors (Braga et al., 2023a; Sutti et al., 2023; Bastos Braga, 2023; Chiozzini et al., 2023; Millo et al., 2024) evidence the human level of influence on the system besides the action of natural hydrodynamic. In the northern sector, the river travels a long distance through land that is home to urban centers and to agricultural and mining activities. The Iguape region, located in the northern of the CIELC, receives waters directly from the Ribeira River that are loaded with nutrients that have drained from agricultural areas and particulate material resulting from erosion and pesticide use. In addition, it also receives contributions from mining activities, located at Cajati region where the order of magnitude of the annual production of phosphate rocks 500,000 t, which represents around 8% of Brazilian production (Prominer, 2009). This area is located in the highlands, which leach phosphorus (P) into the hydrological system by a Ribeira River's affluent. There are around 330,000 inhabitants in the Ribeira River valley (IBGE, 2018), 71% of whom make up the urban population and ~20% of whom make up the rural population. There are 23 cities in the region where the population is distributed, and the main activities are agriculture, livestock and industry. This region preserves an important area of the Atlantic Forest (SEADE, 2010).

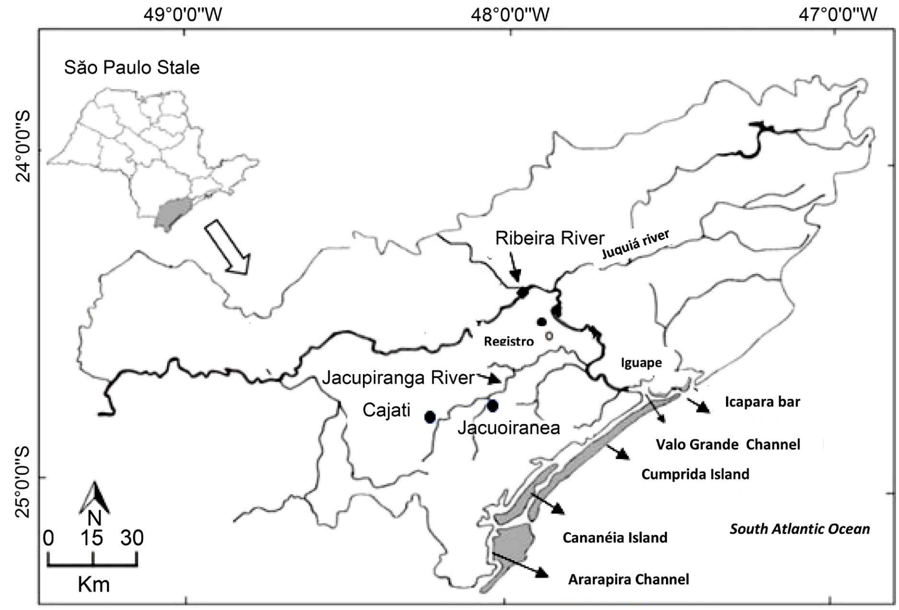


Figure 1. Location Ribeira River Valley (Ribeira and Jacupiranga rivers) and Cajati, Jacupiranga cities located in the plateau and Iguape and Cananéia cities as a part of the CIELC region.

Banana cultivation is one of the predominant agricultural practices in the medium to downstream river valley (**Figure 2**), one of the most important in Brazil, along with phosphogypsum mining and buffalo breeding represent the main economic activities. The Ribeira River is the final destination of the residuals from human activities, and the estuary is the receptacle of dissolved and particulate material. In 2019, banana production in the state of São Paulo reached 1.1 million tons, and it represented 19.3% (~US$ 400 million) of the production of fresh fruit in the state. It was estimated that this activity would reach 1.03 million tons in an area of 51,600 hectares in 2020 and that the region of Registro city would represent 65% of the state's total production.

Figure 2. Aspects of banana cultivation on the banks of the Ribeira de Iguape River (a and b) and Ribeira de Iguape river mouth and Icapara bar (CIELC) (c). (source: camiloaparecido-blog.terra.com.br accessed on 04/07/2013).

Agricultural practices, such as the use of fertilizers (nitrogen, phosphorus and potassium), pesticides and herbicides with the aim of supporting crop production, lead to the water bodies located close to plantation areas becoming polluted, especially when there are no effective controls in place regarding these practices. Other rural practices, such as those involving livestock—for example, buffalo breeding—are also located near the riverbank. Regarding the history of the region, after the decline of metals mining at the Iguape region in the 17th century, the growth of rice crops started to increase; at that time, there was growth in demand for high-quality rice in the European market (Braga, 1998) and the phosphate mining began around 1930 (Silva-Sánchez & Sánchez, 2018). With the objective of securing a greater flow of this product, construction of the Valo Grande Channel began in 1825; the channel was a means of connecting the Ribeira River and the Mar Pequeno, a construction ended in 1852 (Diegues, 1973). The load of suspended particulate material (SPM) was 1,000,000 m^3/year (GEOBRÁS, 1966). The main use intended for the Valo Grande Channel (non natural) was facilitating the movement of rice crop production to the old port. By the time, the work was completed, the channel was four meters wide, two meters deep and three kilometers long. A few years later, an intense process of erosion had begun, and as a consequence, a large number of sediments were being carried in the direction of the Mar Pequeno Channel (Nascimento Junior et al., 2008; Giannini et al., 2018; Prado et al., 2019). Therefore, part of the water of the Ribeira River flows into the estuarine system, altering the hydrochemical characteristics of the CIELC, mainly in its northern sector. It is estimated that the average annual discharge of fresh water into the system is 773.56 m^3/s, with a minimum value of 99 m^3/s in August (dry period) and a maximum of 11,751 m^3/s in March (wet period) (Bérgamo, 2000).

In the 1930, the city of Cajati grew economically as a result of P mining activities; however, these activities have resulted in lots of phosphate being carried into the River Jacupiranguinha, which is connected to Jacupiranga River, which then flows into the Ribeira River in the part of the river between Registro and Iguape city (Cunha, 2010); Environmental Agency of São Paulo State, Brazil (CETESB, 2013). In addition, the cities located along the riverbank also contribute N and P inputs such as those derived from sewage, cattle, agricultural processes and other sources.

According to IBGE (2016), 6,962,134 tons of bananas were produced in Brazil in 2015 and the plantations occupied an area of 516,960 ha. The main states with the highest banana production are Bahia (16%), São Paulo (16%) and Minas Gerais (11%). The largest area occupied by the plantations is 15% in Bahia and 11% in São Paulo. The cultivation of the *Cavendish* variety of banana is predominant at São Paulo (Coltro & Karaski, 2019). Toward the southeast of São Paulo state is the region most important for banana production; this includes Iguape, Cajati, Registro and Jacupiranga cities.

Excess fertilizers (N and P) applied to the soil and drained into the water system can cause eutrophication (excessive algal growth in water bodies); this can affect oxygen availability as a result of high oxidation of biomass, thus harming other organisms in the aquatic biota going from the river to the estuary. In the case of banana crop, the application of N fertilizer is completed during three phases of the growth cycle, namely the planting, formation and production phases (Brazilian Agricultural Research Corporation (EMBRAPA, 2003). N fertilizer is of paramount importance, and it is usually recommended that 160 to 400 kg of the mineral are applied per hectare per year (EMBRAPA, 2003). When it comes to phosphate fertilizer, P supports the growth of vegetation and roots and the P added is practically fixed (unmoved) it must be put in the planting hole; when the soil is analysed, levels vary from 40 to 120 kg of P_2O_5/ha (EMBRAPA, 2003). According to Godoy et al. (2006), the demand for phosphate fertilization is lower for banana crops in this region, as there is no lack of it in the soil because P compounds are retained in the soil at high levels. The land along the Ribeira River Valley use evidences the agriculture (**Table 1**), mining, reforestation, livestock rearing and tourism activities.

Table 1. Amount of area (ha) planted, pasture, reforestation, livestock /city, Comparison 2008/2018, Cati, 2008 and LUPA Project (http://www.cati.sp.gov.br/projetolupa).

Crop ha/City 2008/2018	Iguape	Registro	Cajati	Jacupiranga
Banana	1086.40/938.3	3178.9/3.490.1	5042/3095.1	3678.3/4.348.2
Reforestation	107/321.7	19770.9/361.5	1393.2/220	2638/2621
Pasion fruit	354/56	50.7/16.7	34.8/4	30.8/43.8
Rice	104/356.9	272.8/151.3	nd	149.5/134
Pasture	15,261/13015.9	nd	9898.9/5869.6	12,700/13439.2
Palm tree	8490/400	432.8/654.1	168.6/675.8	111.1/119.3
Beans	13/1.2	12.9/3.3	3.9/nd	22.4/19.5
Corn	8/15.1	24/18.8	nd	9.9/41.6

Banana cultivation takes place in tropical and subtropical areas around the world, and in Brazil, the Ribeira River valley is the most important area for this activity. The use of fertilizers is important in maintaining productivity, given that the region has a high precipitation index. The loss of nutrients applied to the soil reaching the river is expected in the riverine cultivation, and the other sources of contributions are naturally included in the nutrient river inputs. It is by flowing into the rivers that these substances reach the estuarine system, and there is seasonal influence in the way they spread from the northern to the southern sectors of the CIELC. This work intends to identify the wide range of nutrient contents found in this important hydrological system and to examine the anthropogenic influence on this region, mainly by considering the presence of banana crops and mining activities in the highlands and their influence on estuarine waters.

2. Methods

The studied area is located on the southern coast of São Paulo state, Brazil, in a hydrological system named the Cananéia-Iguape estuarine-lagoon complex (CIELC). This system is included on the Ramsar list (https://rsis.ramsar.org/ris/2310) and is a member of a Biosphere Reserve (UNESCO, 2005; Braga et al., 2023b). The southern region (Cananéia and Ararapira Channel), is enough preserved, maintaining a sanctuary for native animals and vegetables. In the northern area, around Iguape and Registro cities there is an intense use of the soil for banana cultivation, and industrial phosphorus mining activities, sewage disposal and livestock rearing also takes place. These activities contribute to the supply of nitrogen and phosphate nutrient inputs into the hydrological system, which later reach the CIELC. It is of paramount importance to mention that the Ribeira River receives phosphorous contributions in its final portion (i.e., downstream) in the form of water from Jacupiranga River. which runs through the city of Cajati where a phosphogypsum mining company is located. The Jacupiranga River is 52 km long, formed by the Guaraú and Jacupiranguinha rivers, and it discharges on the right bank of the Ribeira River. Regarding water use in the Jacupiranga River's sub-basin, most water use is related to industrial consumption, with a demand of 1.628 m^3/s, followed by the demands of irrigation, 0.714 m^3/s, and urban demand at 0.206 m^3/s (CETEC, 1999). The land around the Jacupiranga River is used in many different ways; there are rural agricultural areas (mainly banana cultivation and the breeding of bulls and buffalos), and there are also coastal communities installed in both the urban and rural regions (Cunha, 2010).

Most of the existing urban properties and urban developments do not respect limits regarding the water bordering vegetation set by the Brazilian Law (Lei 4771) of the Forestry Code (BRASIL, 1965). Along the length of the Jacupiranga River, there are vast areas without bordering vegetation; in some areas, the soil is at risk of erosion and exposed, with sand ravines reaching heights of at least two meters. Besides being a vulnerable area with regard to rural and urban drainage, the river receives wastewater from the city of Jacupiranga and the release of household wastewater (Cunha, 2010). According to the Surface Water Report of CETESB

(2013), water samples collected from the Jacupiranguinha River (located near to Cajati city) and Jacupiranga River (located near the Jacupiranga city) have shown concentrations of total P ranging from bad to acceptable quality.

The Jacupiranga-Jacupiranguinha River runs through the cities of Jacupiranga and Cajati. These cities present the following characteristics:

- Jacupiranga (SP): The main economic activity of the city is agriculture, mainly represented by banana plantations (Cunha, 2010; SEADE, 2010). Data from Cati (2008) reveal that there are around six million banana plants occupying an area of 3680 hectares in this area. The urban area of this city is located on the right side of the Jacupiranga River margin, far from its lowlands. The Jacupiranga River flows to the right side of the Ribeira River, close toits downstream, with a drainage area of 534 km^2.
- Cajati (SP): Located 13 km from the city of Jacupiranga, this city has as its main economic activities mining and banana cultivation. This city is considered the most important mining center of the Vale do Ribeira region, and the extraction of apatite started in 1930. This started with the Moinho Santista Group, which won the right to undertake mining explorations in 1938 and held the patent for cement production; later, the Mining Company of Serrana S/A was founded. In May 2010, the Vale Company acquired the assets of Bunge Fertilizantes (Silva-Sánchez & Sánchez, 2011). The part of the company currently responsible for exploration is *Vale Fertilizantes*, which in 2016 was allowed to expand its digging area. This company is number one in Brazil when it comes to the production of dicalcium phosphate, and the expansion of the area to be explored will allow mining to continue until 2036. Thus, the company will contribute to supporting the local economy and ensure the availability of dicalcium phosphate, which is a product used for animal nutrition. *Vale Fertilizantes* is responsible for 50% of this market and while expanding its exploration area, the company will also be responsible for protecting the fauna and flora within this area (Brasil Mineral, 1984).

2.1. Area of Banana Cultivation

In order to estimate how many plants are grown in the riverine area, 29 lots of banana cultivation were identified along the banks of the Ribeira River in 2015 (**Figure 3**) using the program Google Earth Pro® to map and calculate the plantation area. The polygons of 29 areas were delimited and subdivided into subareas, being that paths, rural constructions and visible areas without plants were not included in the estimated calculation of banana crop. Varying levels of density regarding the number of plants in each area/subarea (a minimum of 1300 plants/ha and a maximum of 2500 plants/ha) were also taken into account. The total area estimated covered around 744.4 hectares, with an average of 1800 plants/ha and an approximate number of 1,340,100 plants in total. After these calculations had been made, this information was used to estimate how much fertilizer was used and, consequently, how much of it (approximately) was leaching to the hydrological system.

Figure 3. Identified Areas/sectors of banana crops, used in this study and located at the Ribeira river between the Registro and Iguape cities (SP). (GOOGLE EARTH PRO-11/01/2015).

2.2. Environmental and Chemical Analyses

The water samples were obtained in 5 points in the low river and 12 points in the CIELC (**Figure 4**). The sampling was performed in August 2012, February 2013, September 2013 and February 2014. The hydrological and biogeochemical parameters were determined to support the evaluation of the influence of nutrients inputs on nearby bodies of water (Ribeira River and CIELC) mainly considering two sources (banana crop and minaning). The water was sampled using Hydrobios® bottles and a van Dorn collector. Temperature values were obtained by use of a protected reversal thermometer with a precision of ±0.02˚C. Salinity was determined using an inductive Backman® RS-10 salinometer with a precision of ±0.01. Dissolved oxygen (DO) was determined by titration following the Winkler principle described in Grasshoff et al. (1983), using a dynamic titrator Metrohm® Titrando, with a precision of 0.02 mL L^{-1}. Hydrogenionic potential (pH) was measured using an Orion® pH meter with a precision of ±0.01, calibrated using NBS buffer solutions. Dissolved phosphate and silicate were determined using a colorimetric method described in Grasshoff et al. (1983), with a precision of ±0.02 μmol L^{-1}. Dissolved nitrate and nitrite were determined using a colorimetric method described in Grasshoff et al. (1983), adapted by Braga (1997) using an AutoAnalyzer-II Bran-Luebbe® with a precision of ±0.02 M. N-ammonium was determined using a colorimetric method (Solórzano, 1969; Aminot & Chaussepied, 1983) with a precision of 0.05 M. Dissolved inorganic nitrogen (DIN) is the addition of nitrate, nitrite and ammonium. Turbidity was measured using a nephelometer. Suspended Particulate matter (SPM) and Suspended Particulate Organic Matter (SPOM) were measured by a gravimetric method described in Strickland and Parsons (1972), with precision of 0.1 mg L^{-1}.

Analytical quality control (QC) was executed for all determinations. The inductive salinometer was calibrated using IAPSO-OSIL® standards for low (10L-series) and high (P-series) salinities. For DO QC, standardizations performed with 0.01 N potassium iodate standard solution reported values with relative standard deviation always lower than 0.5%. A TRIS-HCl solution prepared in artificial seawater according to the method of DelValls and Dickson (1998) was used to verify the accuracy of the pH measurements (8.094 at 25˚C) and the observed standard deviation was less than 0.01. For nutrients (nitrite, nitrate, phosphate, silicate and ammonium) QC was performed using certified reference materials (KANSO® - SCOR/JAMSTEC, Japan), to low and high concentrations, and the relative standard deviations obtained were always less than 1.0% to nitrate, nitrite, phosphate and silicate, and less than 2.0% to ammonium. In spectrophotometric methods, such as those used for nutrient analysis, the detection limit and precision are represented by the same value. None of the quantifications performed presented a value below the quantification limit of the methods.

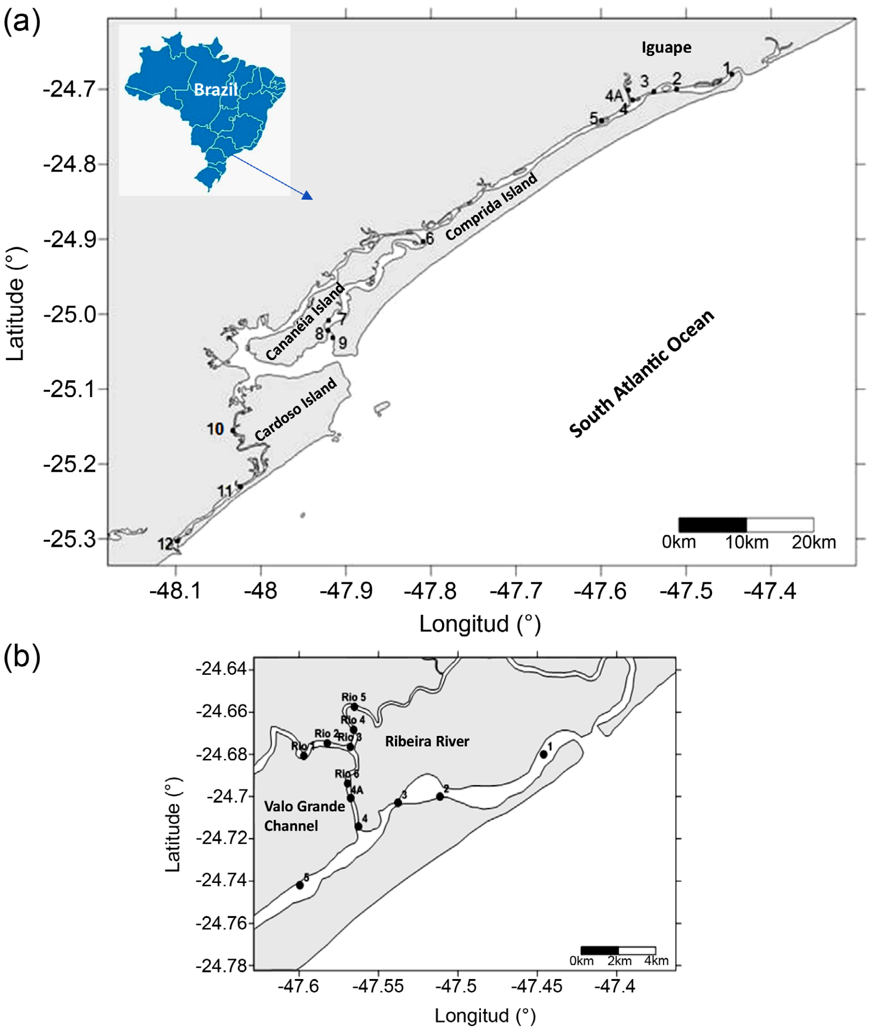
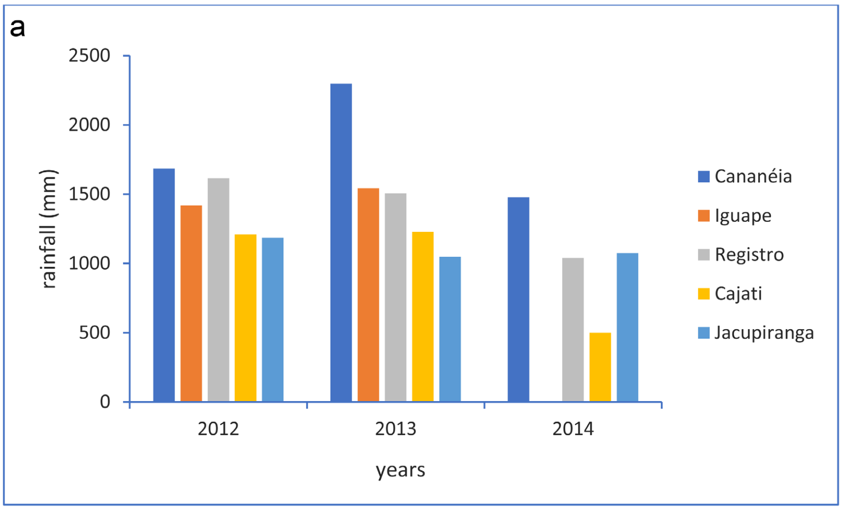
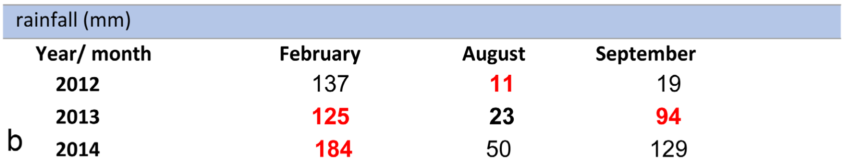


Figure 4. Location of the sampled points in the CIELC and Ribeira River, São Paulo, Brazil. General position of the stations sampled (a), detail of the Ribeira river points and Valo Grande artificial channel (b).

3. Results

The rainfall in the region represents an important factor in leaching nutrients to the hydrological system. The annual precipitation in 2012, 2013 and 2014 in the cities of the Ribeira de Iguape river and Cananéia in the southern area are presented in **Figure 5(a)** observing that in 2014, the Cajati region presented the lower value in function of dryness (~500 mm), however the two coast cities (Cananéia and Iguape) presented high annual rainfall, considering that in Iguape 2014 occurred a problem with data acquisition. The monthly rainfall in the region studied in 2012, 2013 and 2014 in the sampling months is presented in **Figure 5(b)**. A special case occurred in 2012, which showed exceptional precipitation in June and July that reached values of between 180 and 200 mm (Centro Integrado de Informações Agrometeorológicas, CIIAGRO, 2020, http://www.diagro.sp.gov.br) maybe in function of La Niña phenomenon (NOAA, 2012). Also, it is important to note that February 2013 followed an extreme rainy January.





rainfall (mm)

Year/ month	February	August	September
2012	137	11	19
2013	125	23	94
2014	184	50	129

Figure 5. Annual rainfall in 2012, 2013 and 2014 a) in the cities of: Cananéia, Iguape, Registro, Cajati and Jacupiranga (Iguape presented a lack of data in 2014) and Cajati showed some periods of dryness in 2014); b) Monthly precipitation in the region at the sampling period. Source: http://ciiagro.org.br/mensal/cmensal.

3.1. Banana Cultivation

The identified areas of banana cultivation located in the Ribeira River margin between Registro and Iguape cities are shown in **Figure 6**, where it is possible to verify that areas D, E, O, S and BR2 are the biggest—with more than 40 hectares of cultivated land. The distance between area A (near to the bridge located in the city of Registro) and area BR1 is approximately 26 km (estimated distance along the Ribeira River). The distance between area A and the Jacupiranga River bar is 40 km (estimated distance along the Ribeira River). The distance between area A (near to the bridge located in the city of Registro) and the R1 station (the first river sampling point) is 68 km.

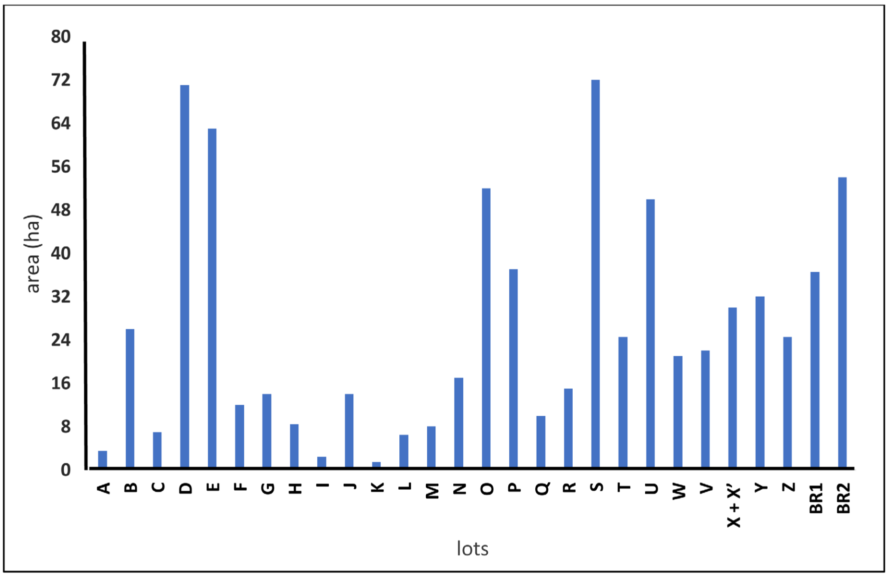


Figure 6. Areas of banana culture (lots) located near to the Ribeira do Iguape River between Registro and Iguape cities (SP).

3.2. Characteristics of Each Area

In general, the planted plots with banana growing included in this study have different sizes. All have a potential to contribute N and P inputs into the riverine system as a result of leaching, although the level of leaching is dependent on the size of each cultivar and the climate conditions.

In relation to the extension, Figure 7(a) shows the banana cultivation area named A, located on the left bank of the river and which is the closest to the Registro city bridge and has slightly more than 3.5 ha, and the intensity of farmland cultivated in this area ranges from 1300 plants to 2500 plants per hectare.

Figure 7(b) shows areas B and C located right after area A; they are divided into a total of 28 planted plots within a total area of 32 ha, and the number of plants varies from 36,000 to 65,000 in area B and, 9000 to 17,000 in area C. Figure 7(c) shows area D, which is located on the right side of the riverbank, whereas area E is on the left side of the riverbank. There are some points in area D where some plants are too close to the river (less than 40 metres from the water's edge); area D covers a total of 71 ha, and the number of plants in this area varies from 92,000 to 177,000 plants. Area E is located on the left side of the river; it comprises 51 lots within an area of more than 63 ha; its total number of plants varies from 82,000 to 157,000 plants depending on the intensity of cultivation. Figure 7(d) presents areas F, G, H and I, all of which are located on the left side of the river. Area F comprises eight lots in an area of 12 hectares of cultivation, where the number of plants may vary from 15,000 to 30,000. It is important to mention that some lots in area F do not contain any plants, representing 10% of the total area. Area G (with 24 lots) comprises approximately 14 hectares of cultivated land, in which some plants are 64 to 140 m from the river and the number of plants varies from 17,000 to 34,000. Between 8 to 10% of the total area is without plants. Area H, with four lots in an area of 8.6 ha, contains some plants located around 55 m distant from the river and a total of 11,000 to 22,000 plants depending on farming intensity. Area I, with four lots in an area of 2.4 ha, contains between 3000 and 6000 plants in accordance with the intensity of cultivation. Figure 7(e) shows J, K, L and M areas. Area J is divided into five lots comprising approximately 14 hectares of planted areas. It may contain between 18,000 and 35,000 plants depending on the density of cultivation, and its distance to the river is close to 50 m. Area K, with three lots within an area of 1.5 hectares of planted areas, contains from 2000 to 4000 plants depending on the density of crops grown. Its total distance from the river reaches 157 m. In this sector, 5% of the total area has a lack of plants. Area L, which is divided into seven lots with a planted area estimated at 6.5 ha, contains a number of plants ranging from 8000 to 16,000, in accordance with total crop cover, and a distance to the river of 157 m. 5% of the total area has a lack of

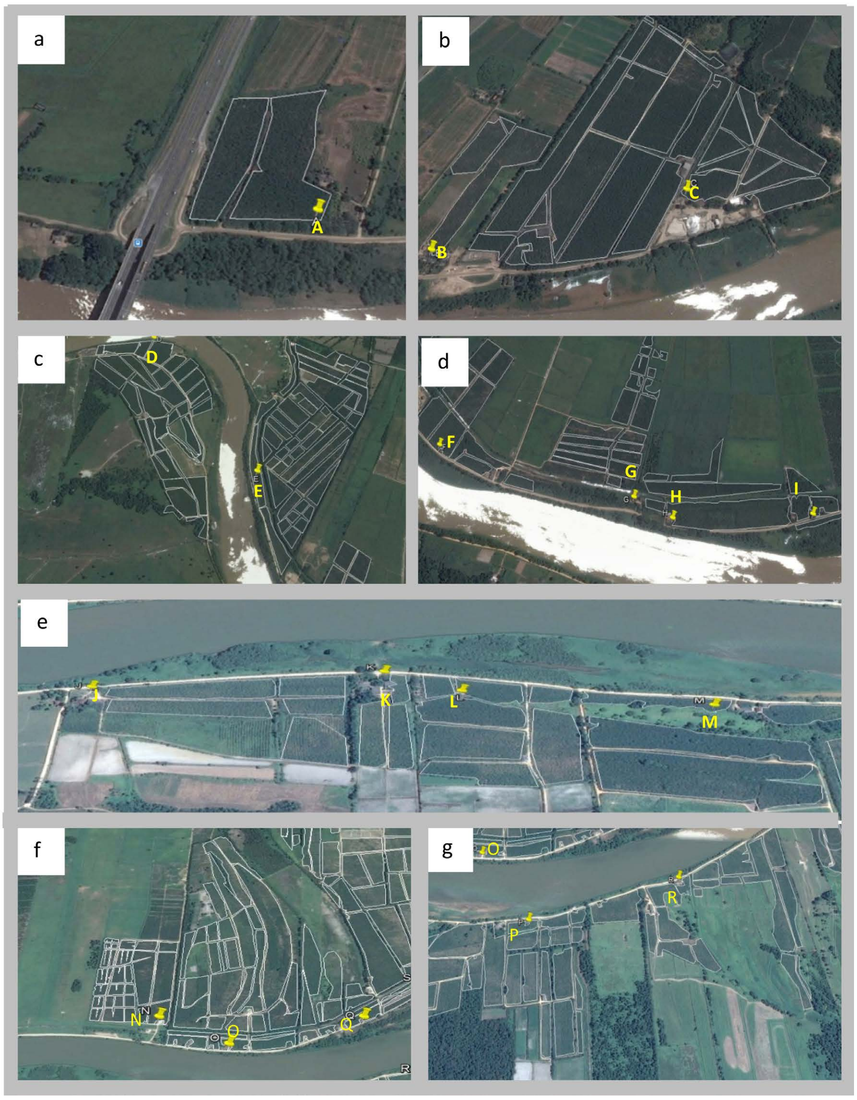


Figure 7. Banana culture areas (a) lot A; (b) lots B and C; (c) lots D and E; (d) lots F, G, H and I; (e) lots J, K, L and M; (f) lots N, O Q; (g) lots Q, P and R.

plants. Area M (four lots) is an area of eight hectares containing from 10,000 to 20,000 plants in relation to its cultivation density, and the distance to the river is 170 m. **Figure 7(f)** shows area N, located on the left bank of the Ribeira River and divided into 27 lots, which comprises a cultivated area of 17 ha. There are 22,000 to 42,000 plants in this area, depending on its cultivation density, and its distance from the river is 160 m. Area O is divided into 30 lots with a planted area of 52 ha; however, 15% of it should be discounted due to the lack of plants. This area can grow from 67,000 to 130,000 plants, in accordance with its cultivation density, and the distance to the river reaches 30 m in some parts. Divided into 11 lots, area Q presents an area of 10 hectares with plants, with 20% of its total area discounted because of the lack of plants. Its capacity for growth is from 67,000 to 130,000 plants, taking into account its density of cultivation, and the distance to the river is approximately 140 m. **Figure 7(g)** shows the areas located on the right side of the riverbank. Area P is divided into 26 lots, representing a planted area of approximately 37 ha; therefore, this area could support from 48,000 to 94,000 plants, depending on its crop density. It was observed that 10% of the total area had no plant presence, and the distance to the river is 78 m. Area R, divided into 16 lots, has approximately 15 hectares of planted areas, which numbers from 19,000 to 38,000 plants depending on its crop density. 2% of the land lacked plant cover, and it sits at a distance of 45 m from the river.

Figure 8(a) shows areas S, T and U, which are located on the left side of the river. Around 15% of area S's total area is without plants. Areas S and T contain plants located more than 200 m from the river. For areas U and W, the plants were located some 30 to 35 m from the river at some points. **Figure 8(b)** shows area V, which is located on the right side of the river and contains areas of cultivation located between 5.5 and 200 m from the river. Area X, on the right side of the river, and X', located on the left side of the river, both contain areas of cultivation located at a distance of 30 m from the river; they are presented in **Figure 8(c)**. This figure shows that in area X, 20% of the total area had no presence of plants. In the case of area BR2, which is located on the right side of the river which in its final portion is also very wide (**Figure 8(d)**), and area BR1, which is located on the left side further down the river and divided into 21 lots, some of these lots are at a distance of 60 m from the river (**Figure 8(e)**). Finally, area BR1 and the mouth of the Jacupiranga River—located at Lat. 24˚37'14.59"S and Long. 47˚43'49.48"W and which flows into the Ribeira River—are shown (**Figure 8(f)**). The distance between area A (near to the bridge of the city of Registro) and area BR1 is approximately 26 km, if traveling along the river, while the distance between area A (near to the bridge of the city of Registro) and the Bay of the Jacupiranga River is 40 km. The distance between area A (near to the bridge of the city of Registro) and the R3 sampling station is 68 km. The location in latitude and longitude of each area is present in **Table 2**.

According to EMBRAPA (2003), N fertilization of banana crops takes place in three phases of the growth cycle, which are planting, formation and the production phase. N fertilization is of paramount importance, and it is usually recommended at a level of 160 to 400 kg of mineral N/ha/year. In the case of P, the fertilization encourages vegetation and root growth and normally the P is practically unmoved in the soil. At this region the content of P varies from 40 to 120 kg of P_2O_5/ha in the soil and the demand for phosphate supplementation is lower for the banana crops as observed by Godoy et al. (2012).

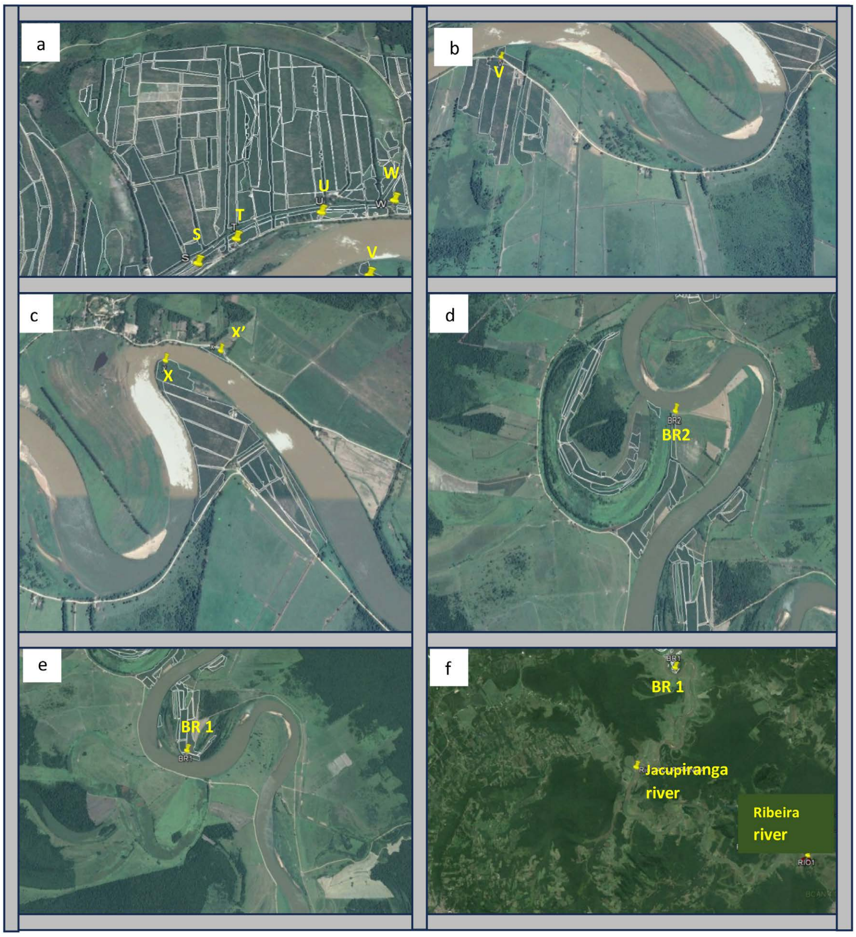


Figure 8. Banana culture areas (a) lots S, T, U and W; (b) lot V; (c) lots X and X'; (d) lot BR2; (e) lot BR1; (f) Jacupiranga river, R1, R2, R4 and R5.

Table 2. Indication of the areas and lots in each area, coordinates (Lat. and Long.), river distance, size of the areas and plants estimative in each area.

Area ha/lots	Lat. S	Long. W	River distance (meters)	Size (ha)	Plants estimative
A/2	24˚29'15.29"	47˚49'56.11"	176	3.5	4.600 - 8.900
B/19	24˚29'14.54"	47˚49'26.64"	116	26	35,000 - 65,000
C/9	24˚29'9.14"	47˚49'26.24"	107	7	9000 - 17,000
D/35	24˚29'13.67"	47˚48'50.43"	40 - 80	71	92,000 - 177,000
E/51	24˚29'52.72"	47˚48'22.31"	60 - 90	63	82,000 - 157,000

Continued

F/8	24°30'25.62"	47°48'7.23"	110 - 130	12	15,000 - 30,000
G/24	24°30'32.29"	47°47'37.25"	64 - 140	14	17,000 - 34,000
H/4	24°30'34.84"	47°47'31.78"	55	11.4	11,000 - 22,000
I/4	24°30'34.15"	47°47'11.94"	106	2.4	3000 - 6000
J/5	24°30'40.64"	47°46'42.39"	50	14	18,000 - 35,000
K/3	24°30'39.54"	47°46'25.00"	120	1.5	2000 - 3000
M/4	24°30'43.57"	47°46'5.69"	170	8	10,000 - 20,000
N/27	24°30'27.05"	47°46'1.69"	160	17	22,000 - 42,000
O/30	24°30'33.05"	47°45'49.86"	30	52	67,000 - 130,000
P/26	24°30'44.35"	47°45'42.08"	78	37	48,000 - 94,000
Q/11	24°30'28.00"	47°45'27.88"	144	10	13,0000 - 25,000
R/16	24°30'38.08"	47°45'19.30"	45	15	19,000 - 38,000
S/41	24°30'21.05"	47°45'18.09"	240	72	79,000 - 93,000
T/25	24°30'16.50"	47°45'11.55"	256	24.5	31,000 - 61,000
U/41	24°30'11.98"	47°44'56.37"	30	50	64,000 - 124,000
V/14	24°30'25.24"	47°44'49.15"	5.5-200	22	29,000 - 56,000
W/30	24°30'10.27"	24°30'10.27"	35	21	27,000 - 52,000
X+X'/20	24°30'7.97"	47°43'42.30"	30	19.3	40,000 - 80,000
Y/20	24°30'53.09"	47°42'25.96"	30	32	41,000 - 80,000
Z/25	24°31'13.04"	47°41'47.58"	20	24.5	32,000 - 62,000
BR1/21	24°33'13.57"	47°42'0.16"	60	36.5	47,000 - 91,000
BR2/32	24°32'0.07"	47°43'42.30"	45	54	70,000 - 135,000

Banana cultivation in the cities of Registro and Iguape is estimated at 744.5 hectares. Fertilizer application is estimated at between 130 and 270 tons ha^{-1} year^{-1}, considering a N average of 200 kg ha^{-1} year^{-1} and taking into account 30% of loss (Cati, 2008); thus, the river could receive, on average, 3.7 t/month. P application is estimated at 80 kg ha^{-1} year^{-1}, reaching 53.6 tons year^{-1}; in this way, on average, 446.6 kg/month could reach the river. It is important to note that the biogeochemical interaction of these elements in the soil and water by the suspended particulate matter association (SPM) results in different availability in the river water.

3.3. Hydrological System

3.3.1. Ribeira River

The Ribeira River showed water composition that varied in the four sampling periods. The hydrological and hydrochemical properties of the Ribeira River water are presented in Figure 9.

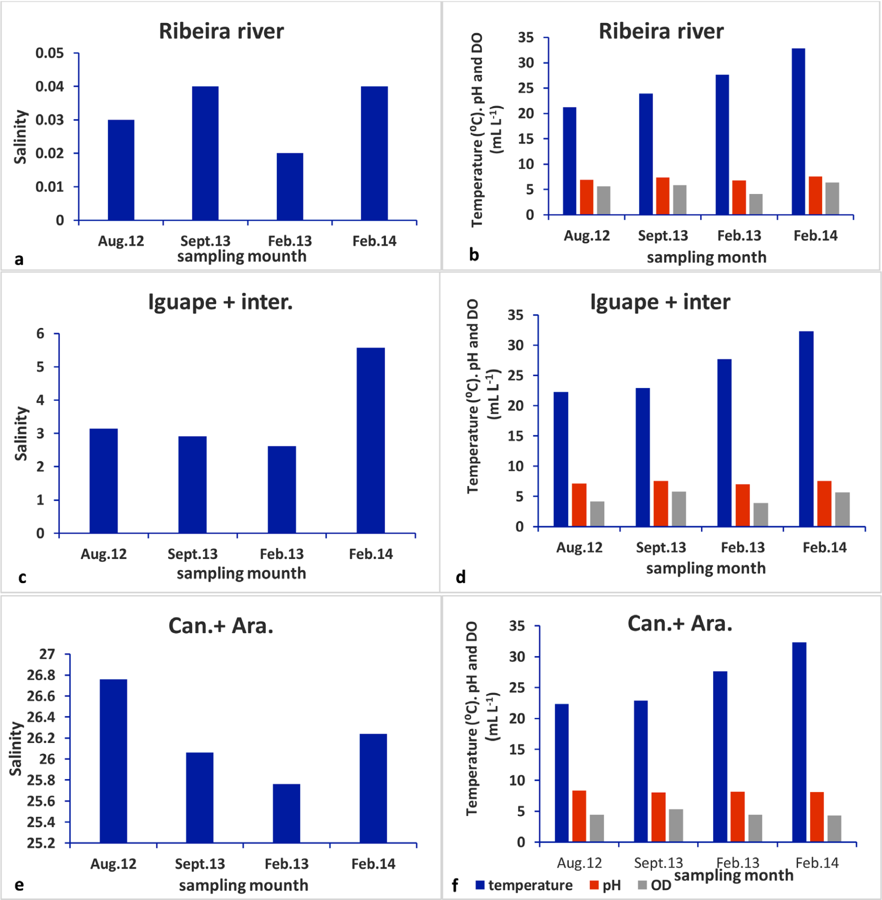


Figure 9. Average values (August 2012, September, 2014 and February 2013 and 2014) of salinity and temperature, pH, DO, respectively in Ribeira river (a, b) Iguape and intermediate region (c, d) and Cananéia and Ararapira Channel (e, f).

The temperature in the Ribeira River presented its lowest values in winter (August 2012) and in spring (September 2013); the values increased in the downstream stations, with R4 presenting the highest values (25.10˚C). In summer, February 2014 presented the highest temperature values, all of them over 30˚C, while February 2013 also presented high temperature values in water. The salinity in the river water was characteristic of freshwater (<5) even downstream. The pH values were below 7 only in the winter sampling period, with the highest value in R4 (6.96). In spring sampling, the highest values were observed in R5 (7.82), while in summer the highest values were observed in R1 (7.26). Dissolved oxygen (DO) presented values always over 4 mL L^{-1}, and the lowest values were observed in the spring period in the stations upstream (R1, R2 and R3). The highest values were observed in the summer period. The nutrient concentrations (N and P) presented high values, showing the most important N concentrations in the spring and summer period. In spring, R1, R2 and R3, in the upstream region, showed high N concentrations, while in summer, R4, R5 and R6 (the downstream stations) presented the highest N concentrations. In relation to P concentrations, the opposite seasonal behaviour was observed, i.e., the highest values were observed in the winter period at all stations, with the highest value at R6 (13.02 µmol L^{-1} P-Phosphate).

3.3.2. Cananéia-Iguape Estuarine-Lagoon Complex (CIELC)

The water data ranges of temperature, salinity, pH, dissolved oxygen, N-ammonium, nitrite, nitrate and DIN (dissolved inorganic nitrogen), phosphate, SPM, and turbidity are shown in **Table 3**, where it is possible to distinguish different sectors (Ribeira river, Valo Grande Channel, Iguape (northern region), Pedra do Tombo (medium of the system), Cananéia (southern region) that following an increasing gradient of salinity and coincidently an increasing degree of environmental preservation. In relation to the water temperature, the maximum (33.45˚C) was observed in summer 2014 at the Iguape, while the minimum was similar (~21˚C) in all sectors with 20.75˚C in the Valo Grande Channel, under direct influence of the river input and 20.25˚C in Ararapira channel in winter. The salinity follows in an increasing gradient from the river sector (freshwater) to the Cananéia region, reaching a maximum of 31.00 in the spring period (2013) near Cananéia where the seawater influence is greater as a result of the hydrodynamic across the Cananéia bar. The pH values recorded in the northern sector, which is influenced by the river presenting some values <7.00, in contrast to those in the southern sector (>7.5), which has a marine influence and also showed values above 8.0. In general, DO showed high enough values to support oxidative processes (>4.00mL L^{-1}) except in winter (2012) in the Iguape, northern sector, which presented an extremely low value (1.14 mL L^{-1}). In spring (2013), at Iguape and also at Pedra do Tombo (intermediate station), the values were < 4.00mL L^{-1}.

Table 3. Values of hydrological and hydrochemical parameters along the CIELC considering the limits (max. and min.) values observed in winter (2012), spring (2013) and summer (2013 and 2014).

7 Local	Ribeira river	Valo Grande	Iguape	Intermediate (st.6)	Cananéia	Ararapira
Temperature (˚C)	21.10 - 33.20	20.75 - 32.70	21.40 - 33.50	21.60 - 32.82	21.20 - 32.82	20.25 -33.45
Salinity	0.02 - 0.05	0.03 - 0.05	0.25 - 12.35	10.03 - 16.54	20.21 - 31.00	22.16 - 32.86
pH	6.83 - 7.74	6.23 - 7.77	7.01 - 7.87	7.55 - 8.00	7.94 - 8.42	7.36 - 8.63
DO (mL L^{-1})	4.04 - 7.26	4.14 - 6.07	1.14 - 6.40	3.78 - 5.62	4.05 - 5.62	3.31 - 5.45
N-amm. (µmol L^{-1})	0.29 - 6.22	0.69 - 3.45	0.15 - 5.00	0.05 - 5.08	0.08 - 4.40	0.14 - 5.83
Nitrite (µmol L^{-1})	0.06 - 0.25	0.09 - 0.22	0.09 - 0.22	0.01 - 0.20	0.02 - 0.27	0.03 - 0.23
Nitrate (µmol L^{-1})	9.97 - 12.87	10.26 - 14.59	1.21 - 11.26	0.06 – 7.50	0.04 - 4.29	0.06 - 0.67
DIN (µmol L^{-1})	9.47 - 16.10	12.99 - 17.01	2.19 - 15.43	0.25 - 9.00	0.18 - 8.71	0.29 - 4.58
Phosphate (µmol L^{-1})	3.06 - 13.02	3.21 - 12.06	1.77 - 9.08	0.50 - 3.64	0.48 - 6.24	0.04 - 2.51
SPM (mg m^{-3})	5 - 155	4 - 85	10 - 139	6 - 43	22 - 83	23 - 113
Turbidity (NTU)	5 - 42	8 - 74	5 - 135	1 - 32	2 - 22	0 - 23

In relation to the water trophic condition (the nutrient values), the N-ammonium concentrations, the highest values (6.22 μmol L^{-1}) were observed in Ribeira river. In general, the average values diminished enormously in the summer and spring periods **Figure 10(a)**. Nitrate was the main inorganic member of the dissolved inorganic nitrogen (DIN) pool. The nitrate values associated with the river water (low salinity) were the highest (> 9 μmol L^{-1}) in all periods in the northern sectors, and a dilution was observed in the direction of the southern region (**Figure 10**). DIN values reached 17 μmol L^{-1} with highest contribution of nitrate, while nitrite maintained lowest values (<0.27 μmol L^{-1}). In relation to phosphate, the northern region presented the highest values of dissolved inorganic phosphorus (phosphate), with values reaching 13 μmol L^{-1} in the winter and spring periods. Most effective dilution was observed in the rainy period (summer) and in the direction of the southern region.

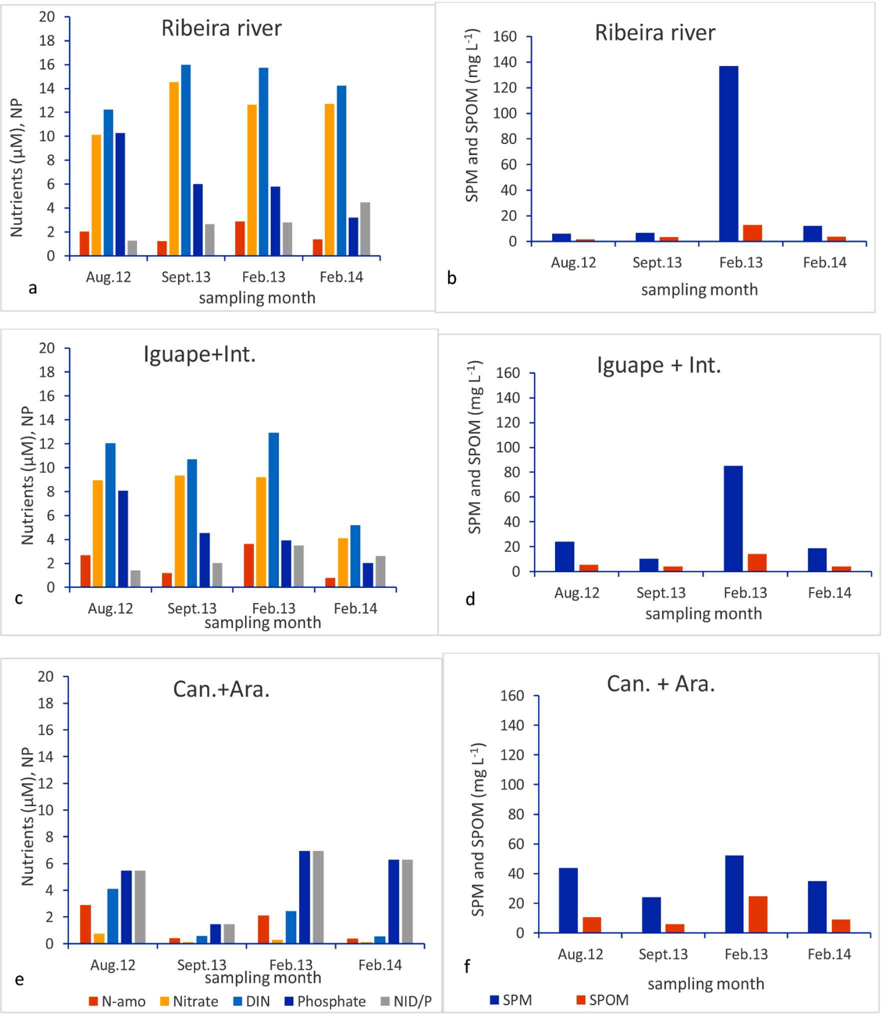


Figure 10. Average values (August 2012, September,2014 and February 2013 and 2014) of N-ammonium, nitrate, dissolved inorganic nitrogen (DIN) phosphate and N/P, respectively in Ribeira river (a, b) Iguape and intermediate region (c, d) and Cananéia and Ararapira Channel (e, f).

In relation to the particulate phase, regarding SPM, the lowest values were recorded in the river (~5 mg L^{-1}) and under freshwater influence in this region due that the river mainly transports fine sediments and, in minor quantities in winter. Sand is most common material and with particulate organic matter (SPOM) in the direction of the southern region in function of the marine influence and, especially in the summer 2013 sampling period due to the intense phytoplankton production and growth contribution. However, the highest values were observed in the Iguape region in function of the silting with presence of high total particulate matter. On the other hand, the highest values of turbidity were observed in the Ribeira River in winter (41 NTU), and in general, mainly in the September sampling period at Valo Grande and Iguape reaching 135 NTU. Then, the turbidity was higher in the northern sector than in southern.

In relation to the nitrogenous compounds (DIN = N-ammonium + nitrite + nitrate) in the hydrological system, N-ammonium and nitrite reaching normal values (maximum of 6.22 and 0.27 μmol L^{-1}, respectively) and nitrate was the main form reaching values >10 μmol L^{-1} in the northern region (Ribeira river, Valo Grande channel and Iguape) decreasing in direction to southern with some values <0.18 μmol L^{-1}. In the case of the phosphate, the highest values (>13 μmol L^{-1}) were observed also in the northern sector with a similar decrease to the southern reaching values <0.50 μmol L^{-1}. The N and P sources are influenced by natural processes intensifying by anthropogenic activities diminishing naturally southward.

4. Discussion

Completing about 50 years after the signing of the RAMSAR Convention on wetlands and interactions with agricultural activities (Finlayson et al., 2022) some aspects such as food systems and the political and economic issues that are important drivers for an efficient improvement in earth exploitation still seems incipient. Issues involving the RAMSAR Convention on wetlands and the interaction with agriculture without linking policy responses to the drivers of agriculture were addressed in a review of more than 400 documents by Finlayson et al. (2024) showing that there are a diversity of agricultural systems around the world and the improvement of the relation among the actors of management is necessary. On the other hand, multiple land use activities, besides agriculture, are associated in the exploitation of ecosystem services, and the environmental degradation continues to occur through unplanned interventions and pollution generation that deteriorate the natural system. The conflict in the uses of coastal areas and especially wetlands need to be well understood in terms of the attribution of different values of environmental disturbance (scores) that should be associated with each activity (agriculture, mining, urbanization, livestock, etc.) to contribute to the environmental management and preservation plan. In view of these observations, the studied aim regions lived succession of activities and were influenced by ancient metal mining operations that occurred on the plateau, rice cultivation and currently banana cultivation, and also the exploration of phosphogypsum, which is quite active along a tributary of the Ribeira River. Thus, our data could contribute to improving knowledge of the environmental drivers in this region.

This study is located in an area considered a member of a Biosphere preservation and a RAMSAR site, where agricultural activities have been taking place since the 19th century with the planting of rice that led to the opening of Valo Grande for the flow of agricultural production of that time. In any case, changes have occurred and will occur in different areas considering the population and economic demands, not only in this study area, but in different wetlands where the balance between the use of ecosystem services must dialogue with the needs of environmental preservation. This work addressed the behavior of some hydrochemical parameters that can help in the evaluation of the impact of agricultural areas and other types of land use with preservation measures and the possible "scores" attributed to the drivers of a system, also being useful in model construction.

Considering the suspended organic matter, the values of suspended particulate organic matter (SPOM) and DO show points where oxygen reached low values, but there was no indication of hypoxia, except in station 2 (Iguape) in the first sampling period, in winter 2012, where this period in Brazil was the hottest winter since 2007 (la Nina influence) (CPTEC/INPE, 2012). The values of DO were enough to assure a good condition for oxidation process, indicating that there are some areas, namely Iguape and Pedra do Tombo in winter, where the decomposition of organic matter is more intense and the circulation process is less effective (Sutti et al., 2023; Chiozzini et al., 2023), and it is verified that the organic load is the highest. Hydrogen potential (pH) values lower than 8 were only observed in the northern of the system, in regions where there was a lower buffering capacity due the presence of fresh and brackish waters, and pH values reached around 8 in the southern of the system (Braga et al., 2023b). As salinity increases to values above 5, the content of N and P decreases, reaching the expected values for estuarine waters with a lower anthropogenic influence.

On observing the data for September (2013), spring period, the values of SPM were high in the southern region of the system. This may be due production of organic particulate matter by primary production of phytoplankton and increase of sediment resuspension.

In the Northern, the unbalanced entrance of P-phosphate influences the N/P ratio indicating a strong anthropogenic influence in the region. What is the further outcome of this to the CIELC if the dilution process becomes ineffective? The acidification or the increase of pollution acts on the phosphorus behavior in sediment as shown by Braga, 2023b. In the present work, it was verified that the maintenance of the efficiency of the dilution process southward is also associated to the decreasing anthropogenic charge that reaches the sector near to Cananéia Island, and that besides receiving the influence of marine hydrodynamics. The environmental properties vary between the sectors of this system mainly in relation to salinity, nitrate and phosphate contents, and turbidity. The influence of the river's contribution to the CIELC is also evident as shown by Sutti et al. (2023), Bastos & Braga (2023).

Banana cultivation around the world is an important activity by which to maintain the agro-economy, and the main world producers are India (30.80 million tons), China (11.22 million tons), Indonesia (7.26 million tons) and Brazil (6.75 million tons) (Food and Agriculture Organization of the United Nations (FAO, 2020). In Brazil, São Paulo state was the largest banana producer in 2019, accounting for 1,120,000 tons, followed by Bahia (1,040,000 tons), Minas Gerais (820,113 tons), Santa Catarina (719,571 tons) and Pernambuco (437,262 tons) (Instituto Brasileiro de Geografia e Estatística (IBGE, 2020). In São Paulo, the Ribeira River valley is the most important banana-producing region, with an area of 34,500 hectares and overall production of about 952,700 tons (Nomura et al., 2013).

The use of fertilizers is essential to maintaining the health of a plantation, and the amounts of fertilizer required must be calculated by taking into account the estimated amounts of N, P and K that will be lost as a result of leaching (Silva & Borges, 2008; Silva & Rodrigues, 2013; Liu et al., 2015; Nomura et al., 2017). In this study, N and P were observed along the hydrological system considering the terrestrial inputs and the differences in the biogeochemical cycles of each nutrient element. Leaching and volatilization are means by which nutrients can be lost from soil, and drainage conditions can also have an impact. Observing the maximum river flow value of 1751 m^{-3} s^{-1} and the minimum of 99 m^{-3} s^{-1} shown in Bérgamo (2000), an average flow of 774 m^{-3} s^{-1} was obtained based on this author. Considering these values, it is possible to calculate the fluxes of these elements in the hydrological system. Regarding the seasonal conditions (**Table 2**), in February, 2014 (summer), precipitation presented its highest value (184 mm), while in August (2012) it was at its lowest (11 mm), and there was evidence of differing effects on leaching and the dilution capacity of the river water. In relation to these distinct values, an estimation of N and P transport based on nitrate and phosphate data was proposed. This facilitates a relation with the data of the most referred work for the region (Cunha, 2010) to have on idea of time evolution in the use of N and P in banana cultivation and the water quality of the CIELC related to dissolved N and P. Other studies of banana cultivation, such as Faithful and Finlayson (2005) and Aryal et al. (2011), showed a seasonal difference/effect in the loss of N and P, which may most likely be linked to the characteristics of the local soils.

The program of banana fertilization in the studied region occurs from end February to May and from August to November to avoid the rainy period (December–January) (Godoy et al., 2012). The fertilization period coincided with the highest N values (DIN), which were observed in September in the water. **Table 4** shows the high concentration of nutrients (nitrate and phosphate) present in the river water. The highest nitrate concentration was 14.59 μM in September 2013, moderately rainy and 13.02 μM of phosphate in August 2012, exceptionally drier month. This reflects the fact that this time of the year is the beginning of the rainy season; as a result, the use of fertilizers in banana cultivation is not so recommended as proposed by farmers to avoid the loss of fertilizers via leaching, surely other factors associated to the plant development are considered to proposed these periods. In some plantations in Central America and Africa, the recommendation is to apply fertilizer while avoiding the most intense rainfall period (Aryal et al., 2011). In any case, the high phosphate values in the driest period may indicate another contribution of P that is not only from agriculture.

The demand of banana crops for phosphate is low, according to Godoy et al. (2012), as there is no lack of this nutrient in the soil of this region. In addition, P compounds are retained in the soil at higher levels than N compounds and the P biogeochemistry properties allow bigger adherence to the particulate matter favoring the lower contribution of dissolved P to the river by washing. The highest P content found was 13.02 μmol L^{-1}, in August 2012; this may be attributed to phosphate entering the tributary of Jacupiranga River via the mining of phosphate rock in the exploration site at Cajati. The Jacupiranga River flows into the Ribeira River at a distance of about 30 km from the R3 river station. There is a sedimentation system for suspended material in lagoons to retain the solids from the mining exploitation, however the signature of phosphate continues evidencing the P input. Other studies conducted around the world have confirmed that the mining of phosphogypsum impacts the water bodies close to such sites (Rutherford et al., 1994; Borrego et al., 2004; Oliveira et al., 2007).

The estimated quantity of N lost from banana plantations (30%, according to Godefroy et al. (1970, 1975)) in the water sampling regions between Registro and Iguape is shown in **Table 4**. A value of 44 tons a year corresponds to 1% of the total N that flows along the river's course. Regarding the data for P in **Table 4**, it can be seen that the values of P vary a lot from one sampling station to another, differently to the N samples. It was observed in a study conducted in Mexico that the concentration of phosphate (0.5 mg L^{-1}) measured in surface water in an area of banana cultivation was lower when compared to an adjacent area of pasture land (1 mg L^{-1} - 32 μmol L^{-1}) in three seasons of the year, namely dry, tropical rainy and moderate rainy; in addition, the soils there were mainly loamy-clay: Gleysoils and fluvisols, and frequent flooding occurred in non-drained areas within this region (Aryal et al., 2011).

The highest values of P obtained in this work correspond to the water sample taken in the lower region of the Jacupiranga River, a region influenced by effluents from the mining of phosphate rock in the city of Cajati. The highest estimated value, 9.035 tons a year, is comparable to those determined by Cunha (2010) of 7918 tons of P a year. The estimated 10% of P lost per year from banana crops in the area between Registro and Iguape works out as 5.36 tons of P a year, which is equivalent to 0.5% of the total P that flows along the river's entire length.

Meybeck (1982) measured values of N-nitrate and P-phosphate in unpolluted rivers in different regions (Arctic, subarctic, temperate, tropical and desert areas) and obtained values according to this work when sectors of the studied system present a preservation condition. The Kazan and Back Rivers in the Arctic region showed values without detected nitrate and up to 2 μg L^{-1} for phosphate, while in the subarctic and temperate region, the Iceland River presented 0.7 μg L^{-1} for nitrate and 20 μg L^{-1} for phosphate. The Glomma River showed 0 μg L^{-1} for nitrate and 6.8 μg L^{-1} for phosphate, while the Volga River showed 0 μg L^{-1} for nitrate and 11μg L^{-1} for phosphate. In tropical regions, the Solimões. Negro and Amazonas rivers showed 1 μg L^{-1} for nitrate, and the phosphate values were 15 μg L^{-1} for the Solimões River, 6 μg L^{-1} for the Negro River and 12 μg L^{-1} for the Amazonas River. In the desert region, the Orange River presented values of 9.1 μg L^{-1} for phosphate, while for nitrate showed no significant values.

Table 4. N and P loss transport estimation through the rivers, during winter and summer with water collected at the river station 3 and Registro city (November. 2013), both taken from the Ribeira do Iguape River in comparison to the work of Cunha, 2010, water collected from Jacupiranguinha River. (Estimate loss by agriculture in the banana area: N (t $year^{-1}$) = 44.22; P (t $year^{-1}$) = 5.36).

Season	River Flow (m^3 s^{-1})	Nitrate Conc. (μmol L^{-1})	Nitrate Load (g s^{-1})	N Transp. (t $year^{-1}$)	Phosphate Conc. (μmol L^{-1})	Phosphate Load (g s^{-1})	P Transp. ($year^{-1}$)	N/P
River St. 3[¥]								
Winter (2012)								
August	774	10.07	109.17	3443	11.95	286.49	9035	0.84
Spring (2013)								
September	774	14.17	153.62	4845	5.82	139.53	4400	2.43
November	774	12.64	137.04	4322	6.45	154.63	4876	1.96
Summer (2014)								
February	774	12.28	133.13	4198	3.18	76.24	2404	3.86
Registro[¥¥] (2013)								
November	774	18.17	196.99	6212	4.49	107.64	3395	4.05
Jacupiranguinha [¥¥¥] (2010)								
October	42	37.14*	21.85	689	193.00*	251.08	7918	0.19

*Data from Cunha (2010), in μmol L^{-1}; ¥: point downstream; ¥¥: point upstream; ¥¥¥: river near the mining.

In the same work (Meybeck, 1982), it is stated that the rates of the exportation of nitrate can vary from less than 10 kg km^{-2} $year^{-1}$ in subarctic regions (the Nelson. Kazan and Back Rivers) to 200 kg km^{-2} $year^{-1}$ in tropical regions (the Sumatra. Borneo and Papua Rivers). The level of phosphate (orthophosphate) was low in natural waters, varying from 1 to 24 μg L^{-1}; these water samples were filtered (waters from Brazilian rivers), and the orthophosphate P-PO_4^{3-} was the prominent form that was found.

Watersheds in the lowland rivers, such as the Don and Ythan in Scotland, which are under a huge influence of agricultural activity, have levels of N-nitrate higher than 600 μmol L^{-1}, while the level of phosphate increases to more than 5 μmol L^{-1} in their estuaries. On the other hand, rivers with their tributaries in mountains, where soils are lacking in minerals, that then flow through areas with low populations and low levels of agricultural activity into estuaries such as the Inverness, Cromarty and Dornoch Firths', have shown much lower levels of these nutrients, with nitrate presenting levels between 3 and 8 μmol L^{-1} and phosphate presenting levels between 0.07 and 0.28 μmol L^{-1} (Balls, 1994). In this study, the highest value of phosphate (13.02 μmol L^{-1}) was observed in the Ribeira River, and this was the result of anthropogenic influence due mainly to phosphogypsum mining. It was also confirmed that nutrients spread along the CIELC in the direction of the southern region; dilution of these nutrients is evident until the Cananéia region, and this is particularly pronounced for phosphate, whose highest values are present in the northern region.

The exportation of nutrients via the soil-water interface increases due to the use of land, and it occurs at higher rates when fertilizers are intensively used in agricultural activities. Former works by Young et al. (1996), Mckee et al. (2000); Brodie and Mitchell (2005) state that compared to forests, pastures can increase the loss of nutrients (i.e., nitrate and phosphate) tenfold, and for plantations aimed for market production this loss can be twenty times higher. Many agricultural experiments (Dowdell, 1982; Hilhorst et al., 2001; Delgado, 2002), suggest that in general, agricultural cultures use only 50% of the N applied to them. The remaining N will be lost via volatilization (ammonia), denitrification and leaching (Boumans et al., 2005).

Khatik et al. (2011) conducted a study in Jalgaon in the Indian district of Maharashtra and examined an area where banana crops were intensively cultivated. They evaluated the residual content of nitrate in the soil and its further horizontal and downward movement within the soil profile; on reaching ground waters, concentrations between 16.8 mg L^{-1} and 79.7 mg L^{-1} were found. In the cited work, the authors assert that in many tropical countries not much information is validated or standardized when it comes to the quantity of fertilizers applied to cultivated land and the subsequent pollution of water bodies close to them. This lack of information may be due to the belief that the use of fertilizers is below levels that would cause alarm in these countries; therefore, it may be believed that they do not pollute the environment (Olarewaju et al., 2009).

Mitchel et al. (2009) conducted a study in Australia and compared three rivers (Tully, Murray and Hull) from 1987 to 1995; nitrate concentrations were analyzed in different plantations (sugar cane and banana), confirming that nitrate levels peak at the rainy season. This is in line with findings from the present work, which showed an average >12.00 μmol L^{-1} of nitrate during the beginning of the rainy period (September 2013). In relation to the impact of the use of fertilizers, Mitchel et al. (2009) observed that banana crops were responsible for a 25% increase in the levels of nitrate in the river (the level of nitrate found was 46 μg L^{-1}); this was attributed to the timing of the application of fertilizers' and the rainy season. In relation to other inputs, such as N-ammonium and phosphate, these were not found to occur at levels as remarkable as those for nitrate. The estimate regarding nitrate exportation to the Tully River, which covers an area of 1683 km^2 (Brodie et al., 2001) and flows through regions with sugarcane crops and banana crops, was approximately 502 t year^{-1} (Mitchel et al., 2009). Another study, also performed in the Tully River region (Faithful & Finlayson, 2005) showed that high concentrations of nitrogenous nutrient inputs took place due to the outflow of banana crops, reaching a flux of 9.2 kg/N and 0.8 kg/P right after a single storm. The estuarine region of the Baixada Santista in Brazil, which is under the strong influence of industry, has levels of nitrate higher than 90 µmol L^{-1} and levels of phosphate higher than 24 µmol L^{-1}, according to Braga et al. (2000).

The current work shows a high concentration of nutrients in the Ribeira River stations in relation to nitrate, whose highest value is 12.87 µmol L^{-1}, as well as for phosphate, whose highest value is 13.02 µmol L^{-1}. N-ammonium showed higher values in the stations close to the Valo Grande Channel; this is in line with the fact that 70% of the river's flow pours into this area, as mentioned by Bérgamo (2000). Salinity shows values from 0.02 to 0.05, typically from river water.

Data from a report on the condition of surface water by the Environmental Control Company of the São Paulo State (CETESB, 2013) show that the average content of nitrate found in the sampling and monitoring points in the Ribeira River (northern area) had values between 0.23 mg L^{-1} (16.4 µmol L^{-1}) and 0.26 mg L^{-1} (18.5 µmol L^{-1}) in 2013. Data from 2008 to 2012 show average values of 0.29 mg L^{-1} (20.7 µmol L^{-1}) and 0.32 mg L^{-1} (22.9 µmol L^{-1}). N-ammonium presented average values for 2013 of 1 mg L^{-1}, while the average for the four previous years (2008-2012) was around 0.55 mg L^{-1}. In the present study, the values reached a maximum of 6.22 µmol L^{-1} (~0.44 mg L^{-1}) in the river water and in the northern region of the system (in summer 2013 and 2014); this decreased to 0.08-4.40 µmol L^{-1} I (max, of 0.31 mg L^{-1}) in the southern region (Cananéia).

In relation to dissolved phosphate, the data obtained by the Environmental Control Company (CETESB, 2013), indicated average values of 0.15 mg L^{-1} (4.8 µmol L^{-1}) and 0.16 mg L^{-1} (5.2 µmol L^{-1}) for the Iguape points in 2013 and average values of 0.19 mg L^{-1} (6.1 µmol L^{-1}) and 0.26 mg L^{-1} (8.4 µmol L^{-1}) for the four previous years (2008-2012) in Ribeira river. In the present study, considering upstream sampled stations of Ribeira river, the highest value in the river water was 13.02 µmol L^{-1} (~0.41 mg L^{-1}) in winter (2012); this decreased in the southern region, where values reached 0.48 µmol L^{-1} in Cananéia and 0.04 - 2.51 µmol L^{-1} (max, 0.08 mg L^{-1}) in the Ararapira channel.

It is of paramount importance to mention that in the monitoring point for the Jacupiranga River. showed P value of 2.4 mg L^{-1} (77 µmol L^{-1}) as the average for the period from 2008 to 2012, while an average of 3.8 mg L^{-1} (122 µmol L^{-1}) was reported in 2013. In relation to the total P, the quality in the Jacupiranqa river in 2012 was unacceptable as presented by CETESB (2013).

The values of nitrate and, above all, phosphate observed in the waters of the different sectors of the Ribeira River, as observed in this study, show evidence of enrichment in these elements; however, these values were not as drastic as in the observation points of the environmental risk. Regarding the concentration values in the southern region of the system considering seasonal variations, the highest values can be seen in the river water in winter (2012), and attenuated values are observed in the other periods (spring and summer) (N/P>1) (**Table 4**). The higher values, which are associated with the flow of the Ribeira River, are not solely caused by banana cultivation; the mining of phosphogypsum has the biggest impact on levels of phosphate in this region confirmed by N:P molar ratio <1 in the critical points.

Significant volumes of nitrogen and phosphorus can be discharged into surface waterways when mineral fertilizers are utilized excessively, which encourages an excessive development of algae and aquatic plants (Dai et al., 2019). Soil erosion from agricultural lands, exacerbated by poor land management practices and deforestation in developing countries like Brazil. Indonesia, and Nigeria, also contributes to water pollution. Irrigation methods can potentially contaminate agricultural water. Irrigation systems that are poorly maintained can result in water waste and soil erosion, which can transfer contaminants into surrounding water sources (Aliste et al., 2022).

However, in the studied case the sector related to agriculture crop not reveal so clear the introduction of an excess of N and P, but the unbalance promoted by excess of P are highlight with the Jacupiranga river contribution as observed in the winter (dry period-August 2012) where the high P values were observed associate to low salinity values and low rainfall. In abstract, the dilution is effective southward with a gradient increase of salinity (**Figure 11**).

Historically, the occupation of the Ribeira valley (a largest area) was related to discovery of gold in the first half of 16th century especially alluvial gold contributing to the transform the Ribeira river in an avenue transporting minerals and a small agricultural surplus in the initial periods, more recently the presence of magnetite and apatite in this area improved the mining activity (Lino, 1983).

A special regard of the Ribeira Valley is based on being a home of a largest area of Atlantic Forest concentrating 40% of the conservation units in the state of São Paulo for being home to the largest remaining continuous portion of this forest. The Ribeira Valley has historically been characterized as one of the least developed regions in the state of São Paulo, with low human development rates, high unemployment and low per capita income, as well as land conflicts, frequent floods (Brasil Mineral, 1984).

In relation to the Ramsar convention, it was cited in some works the agricultural impact in the wetlands, but though nutrient runoff has been recognized as a primary contributor to degraded water quality, Ramsar (2018) has provided no direct guidance on fertilizer use and wetlands as evidenced by Finlayson et al., 2024.

Despite a greater appreciation for the ecosystem services that wetlands provide (Davidson et al., 2018), wetland loss and degradation continue around the world, as expressed in the Convention's Global Wetland Outlook (Gardner & Finlayson, 2018).

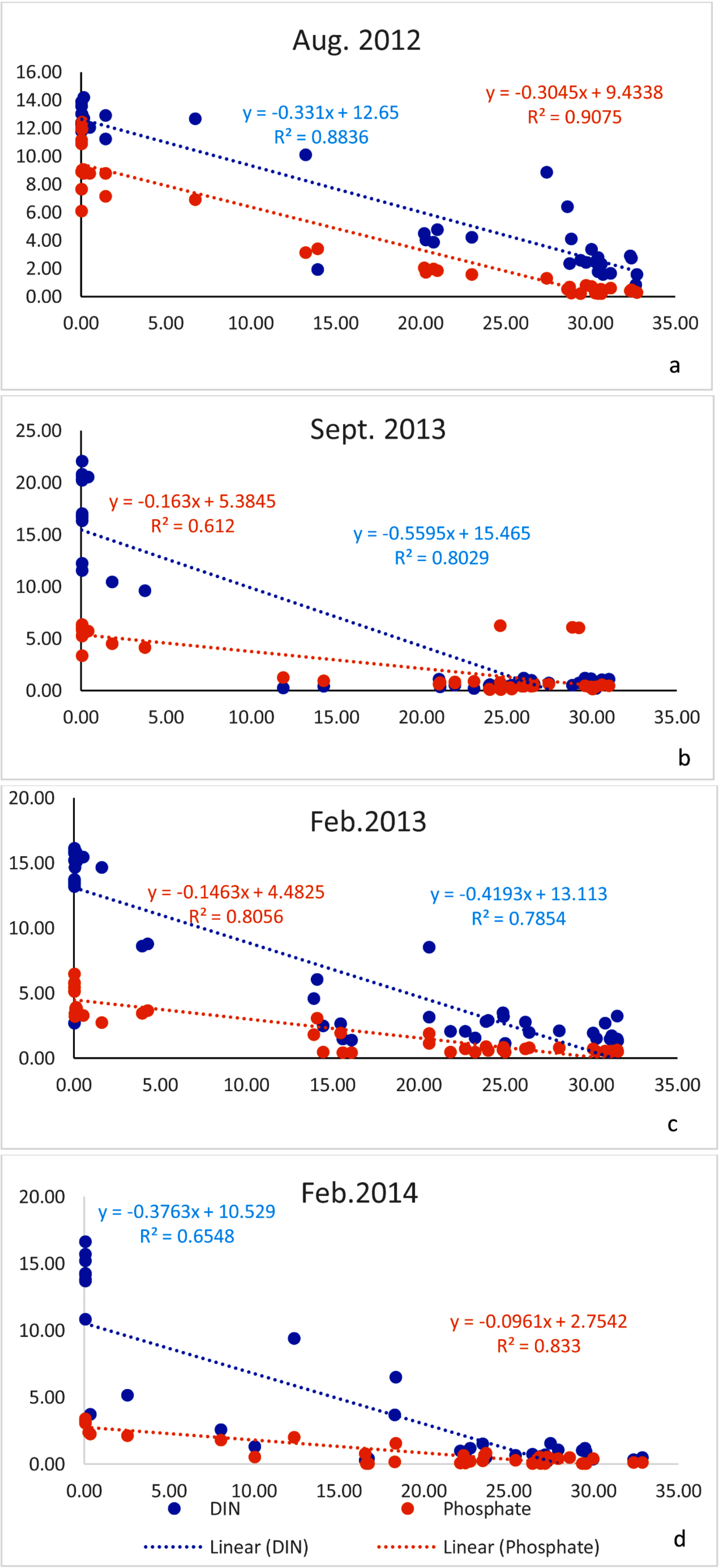


Figure 11. Hydrochmemical dilution from northern to southern region (Ribeira River to Cananéia city) considering the seasonal variation: winter 2012 (a), spring (b) and summer 2013 (c) and 2014 (d).

5. Conclusion

The values of P-phosphate in most of the points in the northern part of the CIELC were between 9 and 13 μmol L^{-1}. This concentration range is too high to have originated only from agricultural activities following the estimated loss charge from the riverine cultivated area. There is another anthropogenic contribution, namely mining exploration, which is responsible for high P-phosphate contribution (jacupiranguite and apatite) that is mined for their use in the production of phosphoric acid, while phospho calcium is mined for its use as a mineral supplement in animal feed. The N input seems to not correspond at the same source from P. In northern part of CIELC, the dilution of these nutrients following the introduction of salt water is low by the northern bar (Icapara bar), because it is silted up and there is a bigger freshwater influence in this sector due to river inflow via the Valo Grande Channel, the artificial channel. Thus, dilution is not effective enough to take the nutrients N and P to their natural limits of concentration. More effective dilution was verified southward of this sector, at the intermediate station near Cananéia Island in the central and southern sectors. The influence of low precipitation was seen in August 2012; however, its influence was not significant enough to cause any reduction in the concentration of these nutrients, particularly the P concentration. This confirms the presence of additional sources of this nutrient besides the soil leaching from agricultural practices.

Taking into account the areas of banana cultivation further above the Ribeira River, between the cities of Registro and Iguape, it was estimated that an area of approximately 744.5 hectares had been planted. For crop development and growth, it would be necessary to apply 200 kg of N ha^{-1} $year^{-1}$ and 80 kg of P ha^{-1} $year^{-1}$. However, the mobility and retention of these nutrients is very different. The high mobility of N influences the hydrological system, in which values of it were constantly high. P has a higher retention rate in soil; for this reason, leaching from the agricultural soil does not explain the high values found downward the hydrological system—this indicates an additional input beyond that from agricultural activities and the sewage system from the riverine cities.

The contribution of N and P to the CIELC from banana cultivation is estimated to occur at a rate of loss of 10% for P and 30% for N, according to Godefroy et al. (1970, 1975).

Taking the average river flow of the Ribeira River as a reference point, it is shown that there is a potential for the transportation and exportation of both P and N to the marine system, but not enough to justify the P input only by fertilizer use in the banana culture. This unbalance and the excess of P may influence biogeochemical processes in the coastal zone, and it may even cause eutrophication. In abstract, the estimate loss of P is 44 t year-1 only considering the banana culture contribution to the downstream of Ribeira river while the loss calculated is based on concentration in water and taking into account the average flow of the river is in the order of 5 t year-1 for P. In this way, even not so significant locally, these values are cause for concern when compared to other values from around the world.

Regarding the increasing levels of P that reach the estuarine system and taking into account our calculation of P loss by agricultural activities, it is noticed that mining activities are also responsible for the increased levels of P, evident in stations after input from the Jacupiranguinha River coming from the mining area. These levels of P should be monitored and evaluated in environmental management and conservation plans.

Finally, indirect drivers (food production, governance, policies) and direct divers as salinity sediments, water quality, nutrient inputs could construct a closest interaction. The eutrophication is an important risk for the wetland associated with agriculture activities, but P mining offers an important risk mainly associated with sanitary conditions. In front of it, the agriculture practices in the studied region offer the minor impact risk among all recent activities concerning nutrient contributions.

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Credit Authorship Contribution Statement

Katia Leite Agostinho—Investigation; methodology; writing; discussion, review & editing. **Vitor Gonsalez Chiozzini**—Methodology; chemical analysis, discussion. **Elisabete de Santis Braga**—Supervision; resources; project administration; funding acquisition; investigation; discussion, writing—review & editing.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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