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Use of Caffeine for the Evaluation of the Anthropic Influence over the Upper and Middle Iguaçu River Basins

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Abstract

Many parameters are usually used as gauges to describe water quality worldwide, such as the concentrations of phosphorus, forms of nitrogen, dissolved oxygen (DO), among others. Though legislative limits for the concentrations of these substances are in place, such is not the case for caffeine. Caffeine is a pharmacologically active alkaloid, from the xanthine group, which can be used as a chemical tracer for anthropic influence over water resources. The objective of this study was to analyze the pollution indicators over the Iguaçu River, one of the main rivers in Southern Brazil, through the examination of nutrients, DO and their correlations to caffeine. The water samples were collected from 10 sampling sites along the river course, unevenly spaced to better represent the different environmental scenarios present in its basin, extracted from 2014 to 2017. Caffeine was detected and quantified through high-efficiency liquid state chromatography. Results show that both nutrient and caffeine concentrations increased in intensely urbanized areas, specially from IG2 to IG5 sampling sites. Downstream from IG6 the contaminant concentrations decreased mainly due to higher river flows and lower population density. Caffeine was detected in 82% of the samples, indicating that most of the sampling sites were under anthropic influence.

Keywords

Water Resources, Water Quality, Caffeine, Urban Areas

1. Introduction

Water resources are of great importance for society, being essential for the supply of drinkable water for human beings, as well as for maintaining the health and balance of the environment. In spite of that, many human activities have been causing the degradation of aquatic environments [1] transforming access to water into a decisive factor for social and technological human development [2].

Urban development is promoted by the economic growth associated with the conversion of rural and farmlands into urbanized settings [3]. Driven by the rapid regional urbanization process, urban centers are constantly expanding, blurring the lines between rural and urbanized areas.

The quantity and quality of the water present in water bodies have been increasingly hampered by the uncontrolled demographic growth in watersheds, which alters the physical, chemical, and biological characteristics of the water resources [4]. The natural balance of ecosystems has been put in check by the fast increase in industrial activity, which has introduced a gamma of new contaminating compounds on all environmental compartments. As a result of this movement, the availability of water of enough quality has diminished significantly [5].

Thus, to describe water quality, many parameters are used as gauges, hinged upon specific legislation [6], such as maximum concentrations for phosphorus, forms of nitrogen among others [7]. Nevertheless, many other substances are still to be legally covered, an example of such is caffeine.

Nitrogen, a parameter that has its limits legally defined, can be present in different forms: as ammoniacal nitrogen ($N\text{-}NH_3/N\text{-}NH_4^+$), nitrate, nitrite, or organic nitrogen. The natural concentrations of these compounds are low and originate from phytoplanktonic production and biological degradation of organic matter. High concentrations of ammoniacal nitrogen in surface waters may indicate contamination by domestic or industrial wastewater, or fertilizer influx [8] [9].

Phosphorus compounds can be identified as orthophosphate (PO_4^{3-}), which is the most relevant form of phosphorated in the environment. The main sources of phosphorus in natural waters are wastewaters that contain phosphorylated detergents, domestic or industrial sewage, animal excretion, and fertilizers of agricultural use. Though they do not represent a direct threat to the sanitary conditions of an aquatic ecosystem, in high concentrations, along with nitrogen, they can lead to uncontrolled growth of microorganism populations, a process called eutrophication [10]. These algal blooms (defined as the spread of harmful algae and cyanobacteria) are a major problem related to aquatic environments, as they can lead to further degradation of water resources [11].

Due to its exclusive human use and it's not presenting toxic effects on the environment, caffeine has been used as a chemical tracer to identify the anthropic influence on aquatic environments. Its presence suggests the existence of other toxic compounds [12].

The results found by [13] indicated that the analysis of caffeine concentrations may be a viable approach to environmental monitoring. These presented a high correlation to traditional water quality parameters, pointing to the anthropic influence over water bodies.

Caffeine is a pharmacologically active alkaloid, from the xanthine group, which is usually found in energy drinks, coffee, soft drinks, and pharmaceuticals. Alkaloids are cyclic organic compounds that have nitrogen in a negative oxidation state and have a limited distribution among animals [14].

Other emerging compounds analyzed are hormones. The presence of estrogens in the environment indicates the discharge of urban and rural wastewaters. The natural forms of these compounds are produced within the human organism and are excreted through feces and urine daily, while the synthetic forms are only excreted by individuals who undergo medicinal hormonal procedures, such as birth control or hormonal replacement therapy [15].

There are many other substances that are not considered during environmental monitoring, which are named compounds of emerging concern [16]. For decades, the presence of such compounds, pharmaceuticals, personal care products, and endocrinal disruptors, have raised scientific awareness due to their undesirable, and sometimes unknown, ecological effects [17]-[24].

The area was chosen for this study, the Iguaçu River basin, has been targeted by many environmental discussions, mainly due to the fact that it is home to over three million people. It is divided into three major sub-basins, being the Upper Iguaçu sub-basin the one which has been more thoroughly researched to determine the degradation of this area [25]-[34].

Therefore, this paper aims to evaluate the concentrations of the nutrients, caffeine and female sexual hormones present in the waters of the Iguaçu River, caffeine.

2. Materials

Study Area

This study was performed in the Iguaçu River, in the state of Parana, in Southern Brazil. This river is formed by the junction of the Irai and the Atuba rivers, on the eastern border of the municipality of Curitiba, the State's capital and largest city. It flows through 1.320 km, crossing the three plateaus of the state, until it discharges onto the Parana river, on the border of Brazil with Paraguay. Its main tributaries are the Irai, Atuba, Passauna, Barigui, Verde, Passa Dois, da Varzea, Chopin, Palmital, Cavernoso, Adelaide, Gonçalves Dias, Castro Alves, Ampere and Silva Jardim rivers [35].

The land use of the 421 square kilometers of urban areas of the Upper Iguaçu basin is distributed as: 46% as low-density urbanization, 37% medium-density urbanization, 9% of industrial zones, and 8% of high-density urbanization.

Due to the larger proportion of urban settlements of the complete Iguaçu river basin being located in the Upper Iguaçu sub-basin (**Table 1**), 9 out of the 10 sampling sites are within this sub-basin, only the IG9 site is in the Middle Iguaçu basin.

Out of the 10 sampling points studies within the complete Iguaçu River basin, 9 of them are in the Upper Iguaçu sub-basin (**Figure 1**), which is in the Metropolitan Region of Curitiba (MRC), due to its great urban influence (**Table 2**). The last sampling location is within the Middle Iguaçu watershed.

Table 1. Points monitored in the Iguaçu River, upper and middle iguaçu basin, Paraná, Brazil. With its drainage areas (km^2), coordinate location in UTM and distance from each spring point in km.

Point	Drainage area km^2	UTM (m)		Spring distance (km)
		Latitude	Longitude	
IG1	282.88	7,184,651.35	686,974.22	21.82
IG2 (E/D)	625.53	7,180,287.79	682,025.92	28.97
IG3	1283.65	7,167,578.84	674,659.45	45.03
IG4	2122.22	7,167,597.18	660,896.97	65.32
IG5	2577.76	7,167,732.33	649,296.46	79.12
IG6	3048.69	7,169,311.30	637,420.05	93.64
IG7	3662	7,173,883.51	611,572.87	129.47
IG8	6050	7,137,918.39	561,142.42	230.34
IG9	24,500	7,099,293.64	487,354.43	384.43

Source: Adapted from [36].

Table 2. Monitoring dates of collections in the Iguaçu River, upper and middle Iguaçu Basin, Paraná, Brazil.

Collection	Date
C1	MARCH 31st, 2014
C2	JULY 22nd, 2014
C3	OCTOBER 13th, 2014
C4	MARCH 02nd, 2015
C5	JUNE 01st, 2015
C6	NOVEMBER 30th, 2015
C7	MARCH 14th, 2016
C8	JUNE 06th, 2016
C9	NOVEMBER 21st, 2016
C10	APRIL 03rd, 2017

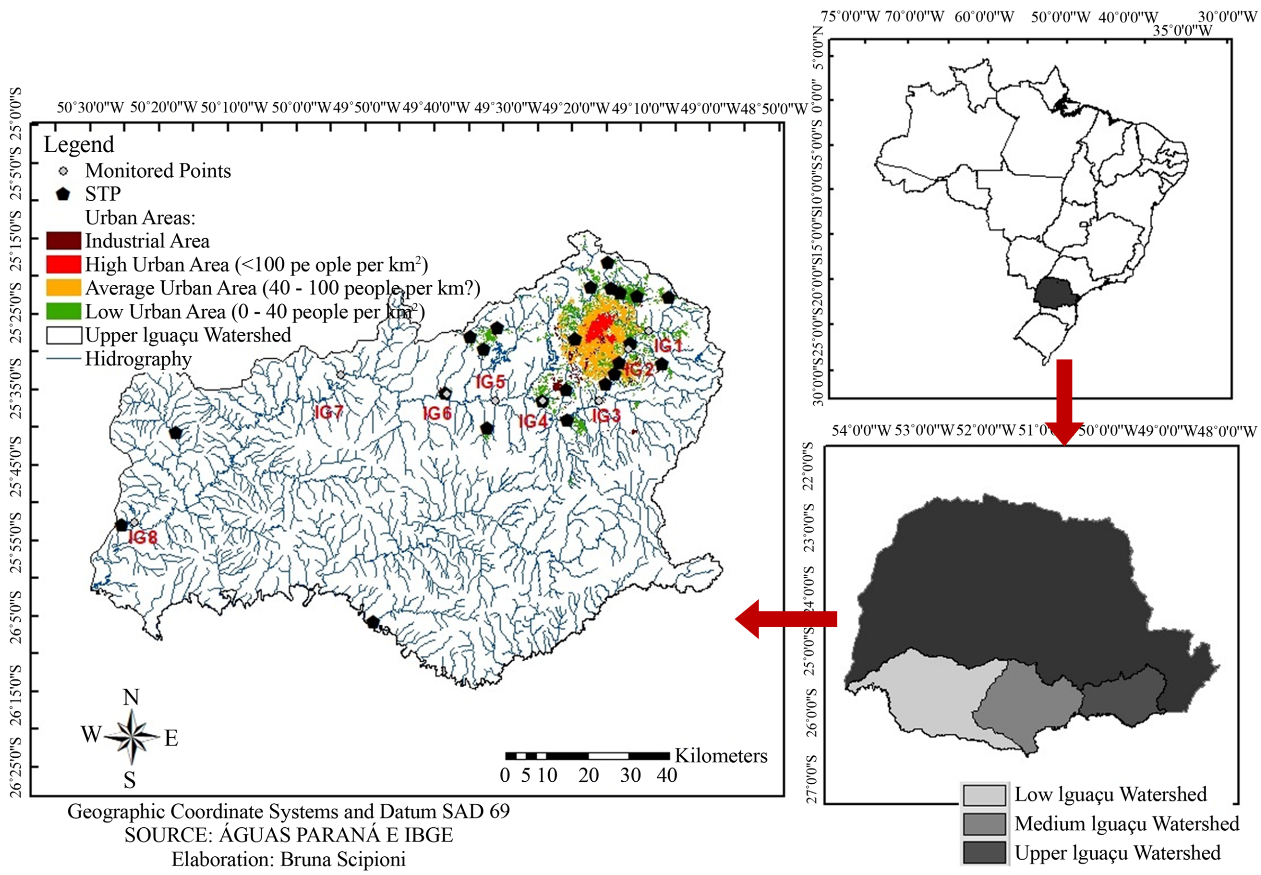


Figure 1. Location map of monitored points, urban areas, and domestic effluent treatment plants (WWTPs) in the upper Iguaçu sub-basin, Paraná, Brazil.

The location of the IG1 sampling site is within a low-density urbanized region. IG2 is located right on the confluence of the Irai and Atuba rivers. It is divided into sides with different characteristics, being IG2E representative of the Irai river and IG2D of the Atuba river. The area around the IG3 is defined by lower density urbanization from that of IG2, but it is influenced by the discharges of three different wastewater treatment plants (WWTP), these being the WWTP Belem, WWTP Iguacu and the WWTP Padilha Sul [37].

The area of influence of the IG4 covers almost the whole of the urban gathering of the MRC. IG5 to IG9 is within less urbanized regions, which are characterized by having large rural areas and having few, and small, urban centers. The IG4 and IG5 sampling sites are located in the municipality of Araucaria, IG6 in Balsa Nova, IG7 in the town of Porto Amazonas, IG8 in the city of São Mateus do Sul and the last site, IG9, is in União da Vitoria.

3. Methods

3.1. Sampling

The determination of temperature, dissolved oxygen (DO), and pH of the samples were performed on-site by the multi-parameter probe Hanna HI 9828.

The samples were, then, filtered using 0.45 μm cellulose acetate membranes. Analyses of the concentration of ammoniacal nitrogen, nitrate, nitrite, dissolved orthophosphate, and total phosphorus were performed on the same day of the collection and followed the methods described in the Standard Methods for the Examination of Water and Wastewater [38].

Solid-state extraction (SSE) was applied for the determination of the concentrations of caffeine and estrogenic compounds. **Figure 2** depicts a flow chart which explains the process of isolation, pre-concentration, and separation of the compounds of interest.

For the evaluation of the concentrations of caffeine and estrogens, solid-state extraction (SSE) was applied. For this, it was performed the isolation, pre-concentration, and separation of the compound of interest, according to what is presented by the flow chart depicted in **Figure 2**.

The preparation of the samples was performed following the method developed by [29]. They were detected by high-efficiency liquid state chromatography with an arrangement of photodiodes detectors, model Agilent 1260, quaternary pump of 600 bars of pressure, and a column of octadecylsilane (Eclipse Plus C18) with a length of 250 mm, a pore diameter of 5 μm and an internal diameter of 4.6 mm.

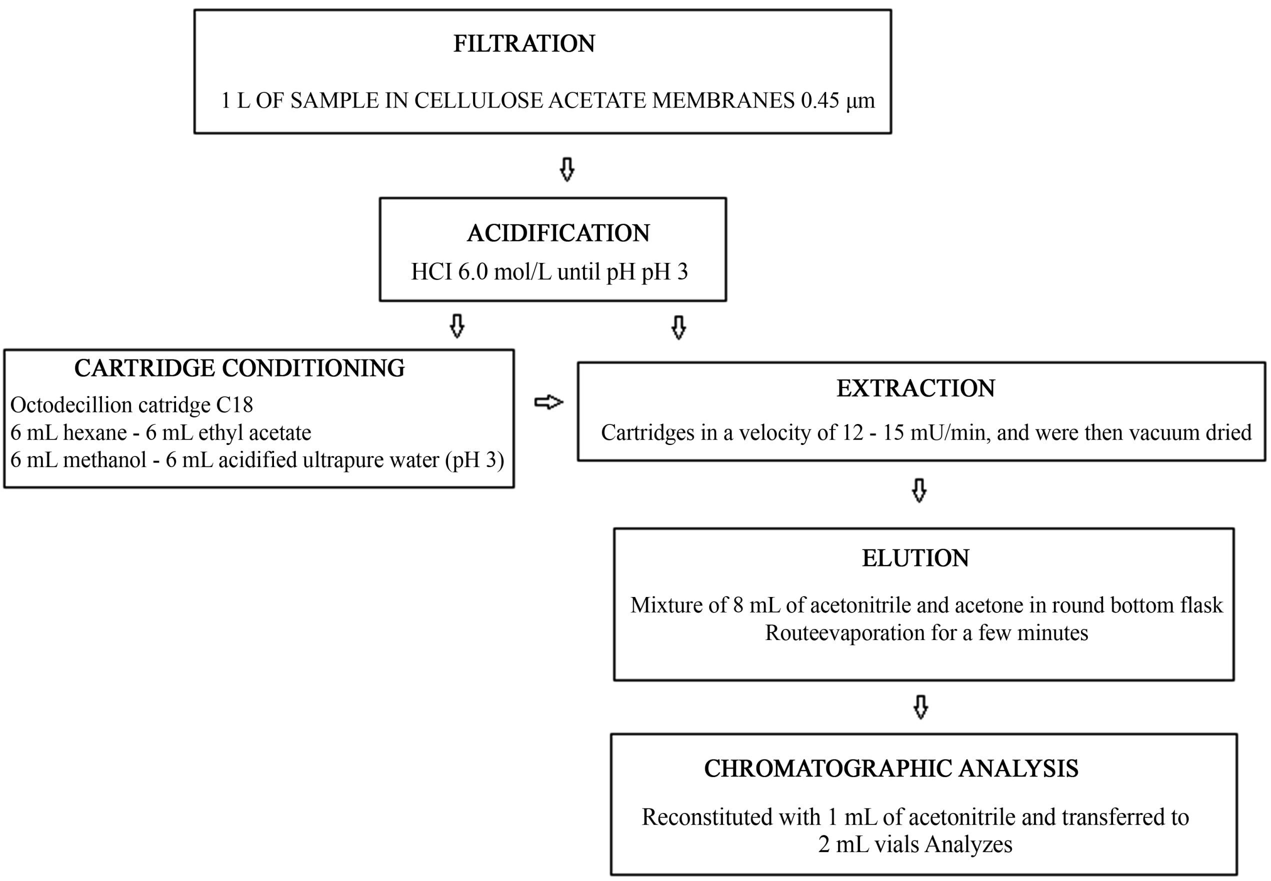


Figure 2. Flowchart of solid phase extraction method for phase chromatography.

Isocratic elution in a constitution of 1:1 to the mobile phase was performed with water with an adjusted pH of 3.5 and acetonitrile.

3.2. Hydrological Data

Data of 5 pluviometric gauge stations, spreading over the region of the Iguaçu River basin, from 2014 until 2017, was obtained through the Parana Meteorological System [39].

For the better visualization of the rainfall along the sampling sites, and encompassing each sampling campaign, **Table 3** shows the accumulated values of rainfall of the last 5 days before each campaign.

There are two related ways to define a water resource, either by the quantity or the quality of its water. The dilution, transport, and dissolution of dangerous or benign substances to living organisms demonstrate the quantity of water influences its quality [40]. **Figure 3** illustrates the flows along the sampling period, to better comprehend the behavior of the measured parameters and your dilutions.

4. Results

A reduction in DO concentrations between IG2D and IG6 was observed (from 3.37 mg·L^{-1} to 5.45 mg·L^{-1}), which could be related to the discharge of domestic sewage at the sampling points. The decomposition of labile organic matter, existent in domestic wastewater, consumes DO on the water, diminishing its concentration. DO concentration reduction along the river interferes with the natural processes of the aquatic environment, such as photosynthesis.

Table 3. Accumulated precipitation values in millimeters from the 5 days prior to collection at each monitored point of the Iguaçu River, Upper Iguaçu Basin, Paraná, Brazil.

Sample Date	IG1 - IG5 (MRC)	IG6 - BALSA NOVA	IG7 - PORTO AMAZONAS	IG8 - S. MATEUS DO SUL	IG9 - UNIÃO DA V.
S1 (3/31/2014)	13.20	7.80	12.20	10.80	12.40
S2 (7/22/2014)	17.80	8.20	8.00	16.20	24.40
S3 (10/13/2014)	0.00	0.00	0.00	0.00	0.00
S4 (3/02/2015)	9.40	3.40	5.00	15.80	20.80
S5 (6/01/2015)	23.60	22.60	57.00	48.60	31.60
S6 (11/30/2015)	30.00	21.80	12.40	23.60	46.40
S7 (3/14/2016)	21.40	0.00	22.40	13.00	24.80
S8 (6/06/2016)	43.20	10.20	13.00	14.20	5.40
S9 (11/21/2016)	6.80	3.80	8.60	19.20	3.00
S10 (4/03/2017)	5.40	2.40	0.00	0.40	0.20

Source: [39].

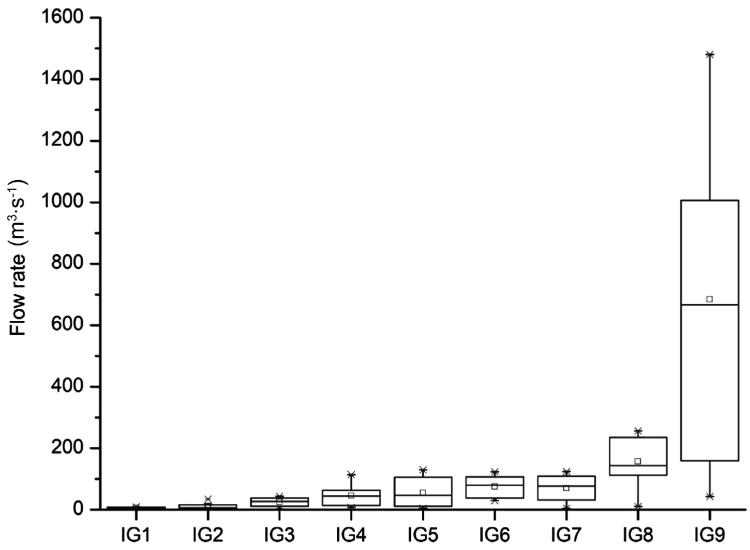


Figure 3. Average flow rates observed, considering all collections, for each point sampled in the Iguaçu River, upper and middle Iguaçu Basin, Paraná, Brazil.

DO concentration presented a steady growth subsequent to the IG7 sampling point (8.58 mg·L^{-1}). The reason for such behavior could be that the labile organic matter suffered prior decomposition by the time it arrived in this region, leading to the river experiencing a period of rehabilitation, which is corroborated by the rise of the DO concentration and the drop in the concentration of other parameters.

Figure 4 shows the variation of the average concentration of ammoniacal nitrogen. Considering the location of the sampling points along the river, the sites IG2E and IG2D present changes in the water quality as a result of urbanization. The highest concentrations were measured on the IG2D sampling point, as a consequence of the influence, it suffers from the discharge of WWTP that employs up-flow anaerobic fluidized sludge bed reactors as treatment solution [37]. Such a process does not aim to remove nutrients such as phosphorus and nitrogen, focusing only on the removal of organic matter, which influences greatly the concentrations of these nutrients. On the other sites, high concentrations of ammoniacal nitrogen are related to regions with more substantial demographic gatherings. In less populous regions (starting at IG7), concentrations presented a downward tendency.

Reference [41] shows not only the relation of high concentrations of ammoniacal nitrogen with aquatic environments lacking oxygen, as well as with external sources of nitrogen, such as residential or industrial wastewater, or animal excretion. Thus, variations in concentrations of ammoniacal nitrogen might be due to anthropic sewage discharge which degrades biologically, diminishing DO concentration, as an important indicator of eutrophication in rivers (**Figure 5**).

The pH of the samples varied in the range of 6.5 and 7.5, which complies with Class 2 rivers. For such a classification, the limit for the ammoniacal nitrogen concentration is 3.7 mg·L^{-1}, while for Class 3 rivers, this limit is 13.3 mg·L^{-1}.

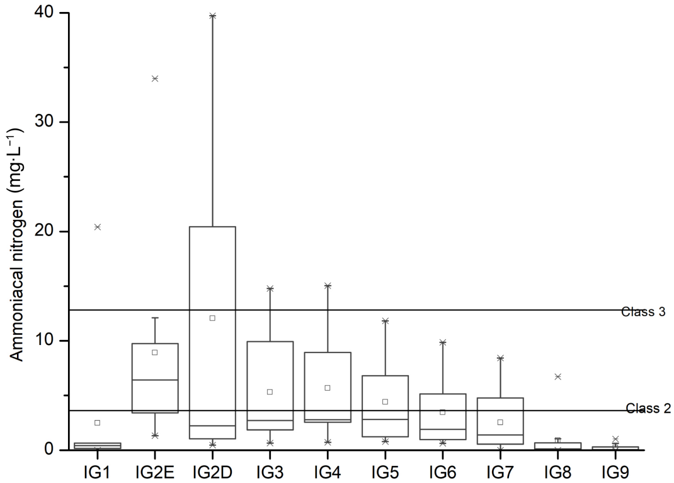


Figure 4. Ammoniacal N concentration (mg·L^{-1}) along with monitoring points in the Iguaçu River, upper and middle Iguaçu sub-basins, with highlighted river framing classes.

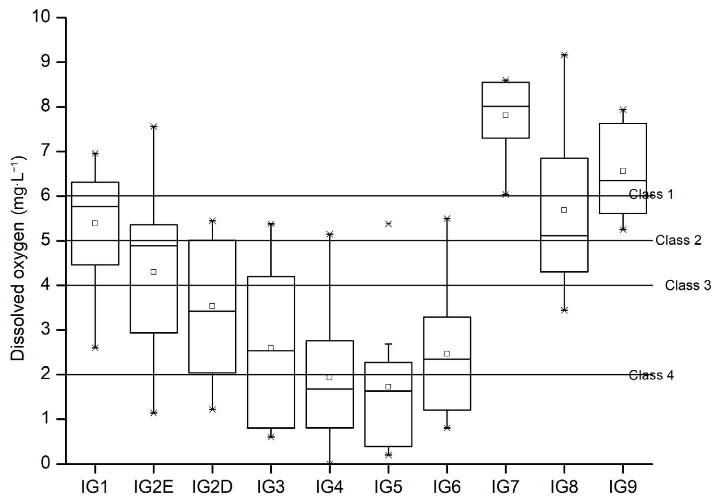


Figure 5. DO concentration (mg·L^{-1}) along the monitored points in the Iguaçu River, upper and middle Iguaçu sub-basins, with the framing classes.

Excepting IG2D (which presented higher concentrations) all the sampling sites located in the MRC presented concentrations consistent with Class 2 rivers in relation to ammoniacal nitrogen. The sampling sites from IG5 to IG9 presented lower concentrations and less anthropic influence.

Orthophosphate ($P\text{-}PO_4^{3-}$) is also considered as an indicative parameter of anthropic influence. Phosphorus may be the limiting factor for the eutrophication of aquatic environments, for the relative scarcity of this element in natural ecosystems, and its essential role in phytoplankton growth [42].

Concentrations of orthophosphate, illustrated in **Figure 6**, could lead to harmful changes to the aquatic environment, such as unnatural eutrophication. Therefore, variations in the concentration of orthophosphate, that ranged from 0.05 mg·L^{-1} to 1.37 mg·L^{-1}. Reference [17] also measured concentration values for orthophosphate on the same waterway, averaging 0.77 mg·L^{-1}, which corroborates the values obtained in this study.

Orthophosphate concentrations were analogous to those of ammoniacal nitrogen, especially the specific rise on IG2D site during the dry period of 2014, mainly due to WWTP discharge, corroborates the anthropic influence on the MRC.

The patterns for both the orthophosphate and ammoniacal nitrogen present a positive correlation (R = 0.6713), indicating that these contaminants might have the same source.

As caffeine is considered a chemical tracer for anthropic influence on urban rivers, the presence of domestic wastewaters, as well as of human influence, is confirmed, as this compound was present in 82% of the samples (**Figure 7**).

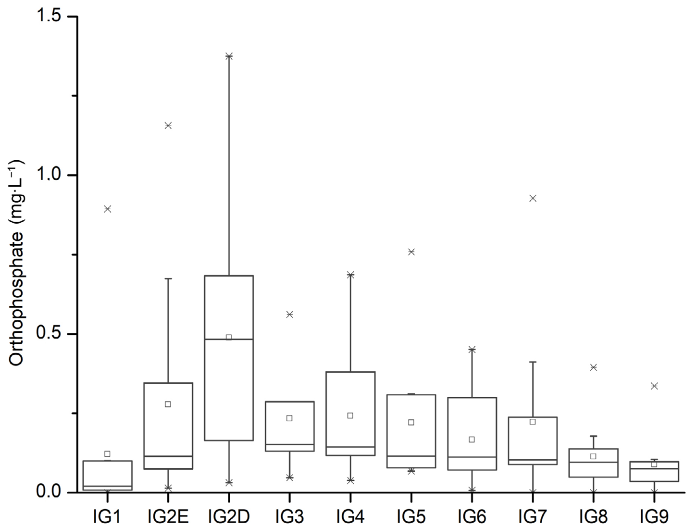


Figure 6. Orthophosphate concentration (mg·L^{-1}) along with monitoring points in the iguaçu River, upper and middle Iguaçu sub-basins.

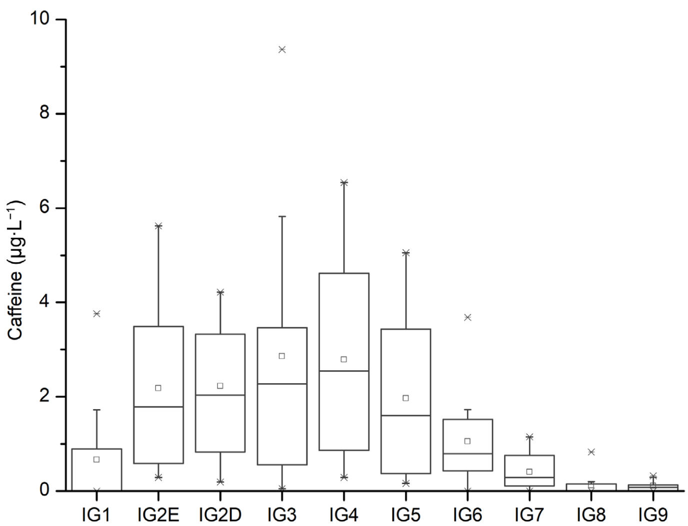


Figure 7. Caffeine concentration (μg·L^{-1}) along with monitoring points in the Iguaçu River, upper and middle Iguaçu sub-basins.

A positive correlation (**Figure 8**) between concentrations of ammoniacal nitrogen and caffeine was observed at the sampling campaigns C2 (R = 0.7371), C5 (R = 0.9190), C6 (R = 0.5901), C7 (R = 0.7959), C8 (R = 0.6784), C9 (R = 0.5465) and C10 (0.8653), confirming the influence of domestic wastewater. A rise in the concentration of caffeine was observed from sampling sites IG2E to IG5, subsequently, concentrations diminish, indicating a state of rehabilitation of the river.

A negative correlation between the concentrations of caffeine and DO was observed (R = −0.56190, confirming the flow of domestic wastewaters into the river. According to [29] caffeine concentrations on the Atuba and Belem rivers were expressive, 22 $\mu g \cdot L^{-1}$, and 59.81 $\mu g \cdot L^{-1}$, respectively, in November of the year 2012.

The estrogens which were detected most frequently during the sampling campaigns over the Iguaçu River were estradiol and ethinylestradiol (illustrated in **Figure 9**). This high frequency for the detection of such compounds may be related to the facts that these are produced by the human organism, both are frequently synthesized by pharmaceutical factories, and are main ingredients for the manufacturing process of hormone replacement medication. According to [43] approximately 700 kilograms of ethynylestradiol are discharged into environmental compartments.

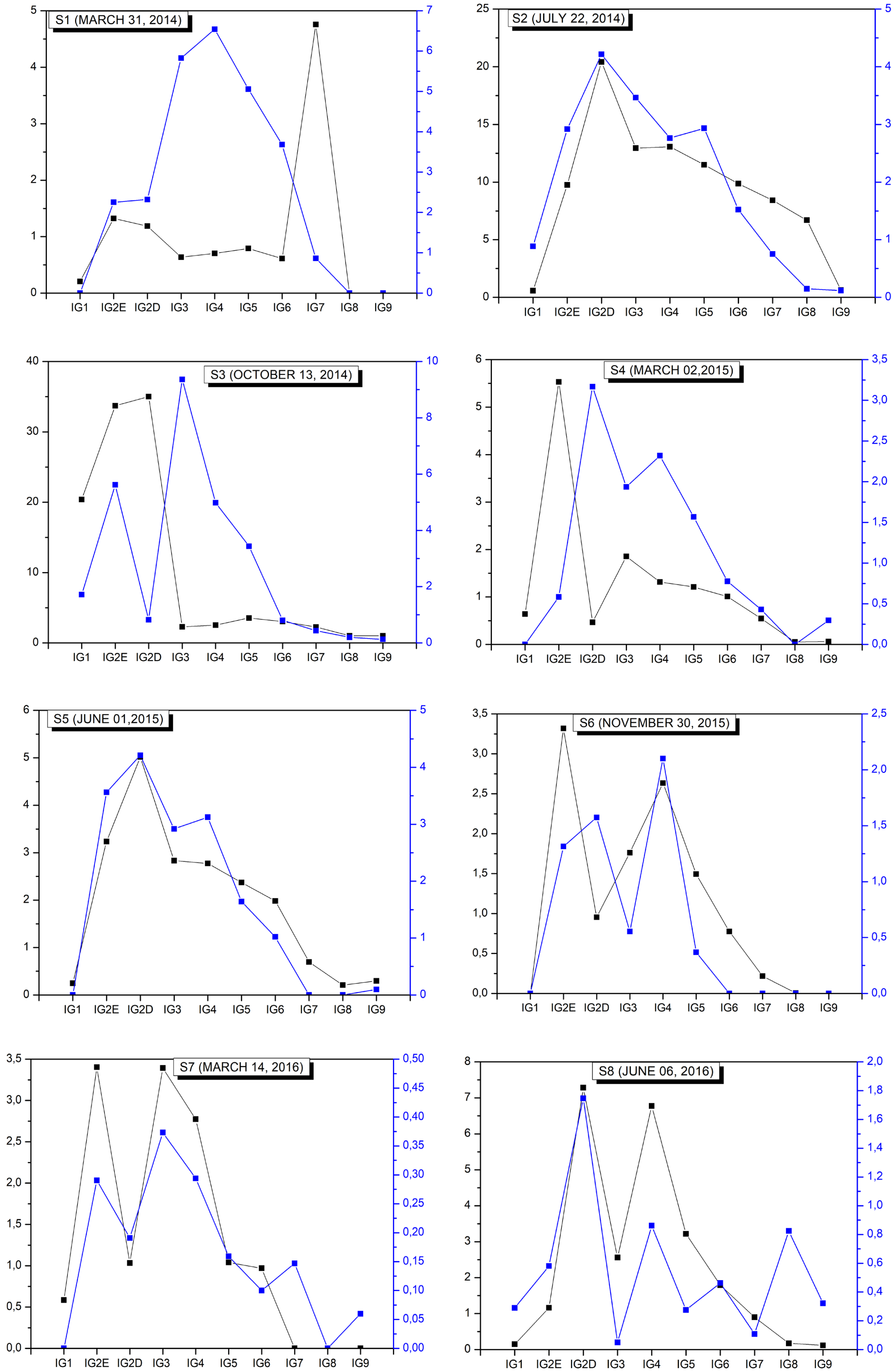
The high concentration of ethynylestradiol measured on IG2D site, in 2016, may be associated to the discharge of the WWTP Atuba, upstream of the Atuba river, which flows to the Iguaçu river over the IG2 sampling sites. Yet, the concentrations found for the prior and subsequent years measured lower values. This is due to the variance of concentration for this compound, which may be affected by seasonality, wastewater treatment efficiency, and the socioeconomical picture, as higher concentrations are usually measured within highly urbanized regions [44] apud [45].

5. Discussion

According to studies performed by [29] on the Atuba and Belem rivers, DO concentrations were low, falling below 5.83 $mg \cdot L^{-1}$ and 5.15 $mg \cdot L^{-1}$, respectively. These rivers are located near the IG2D (Atuba) and IG3 (Belem) sampling sites, which could be related to the DO concentrations obtained (5.45 $mg \cdot L^{-1}$ and 5.38 $mg \cdot L^{-1}$, respectively).

The ordinance n˚ 357 from the Brazilian National Environmental Council (CONAMA) legally regulates the limitations of some parameters, for the definition of the frame of reference of water resources quality. DO concentrations of 5 $mg \cdot L^{-1}$, 4 $mg \cdot L^{-1}$, and 2 $mg \cdot L^{-1}$ determine the limits of the 2, 3, and 4 classes, respectively. According to this definition, the IG1, IG7, IG8 and IG9 sampling sites are defined as being a part of Class 2, as of the other points, they are of Classes 3 or 4, depending on the time of the sampling.

Reference [17] and [20] studied the ammoniacal nitrogen concentration on IG1 and IG2 sampling sites. Concentrations ranged from 0.44 to 5.34 $mg \cdot L^{-1}$ on


S1 (MARCH 31, 2014)
S2 (JULY 22, 2014)
S3 (OCTOBER 13, 2014)
S4 (MARCH 02,2015)
S5 (JUNE 01,2015)
S6 (NOVEMBER 30, 2015)
S7 (MARCH 14, 2016)
S8 (JUNE 06, 2016)
IG1 IG2E IG2D IG3 IG4 IG5 IG6 IG7 IG8 IG9

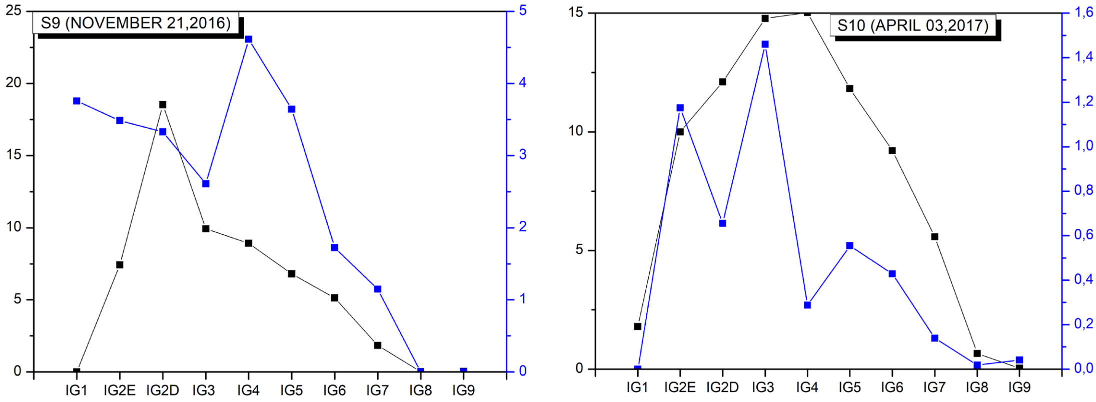
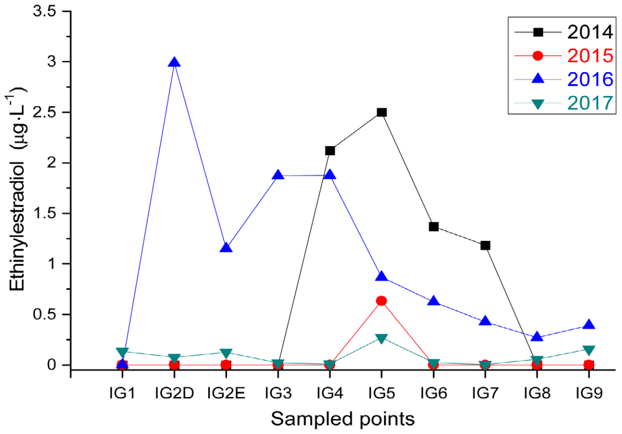
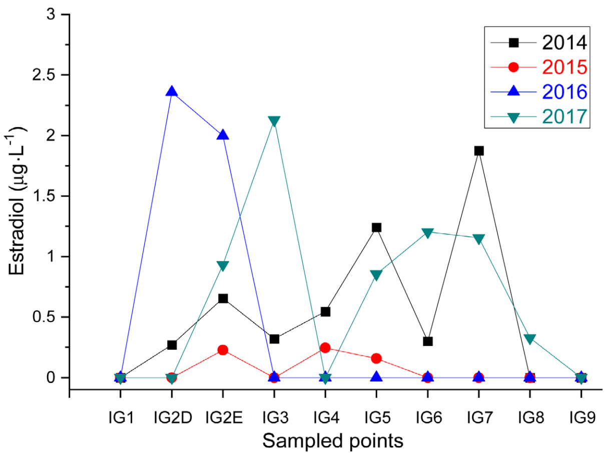


Figure 8. Ratio of ammonia-N and caffeine concentrations over monitored points at each collection in the Iguaçu River, Paraná. Left axis, black, ammonia-N concentrations (mg·L^{-1}), the right axis, blue, Caffeine (μg·L^{-1}).



(a)



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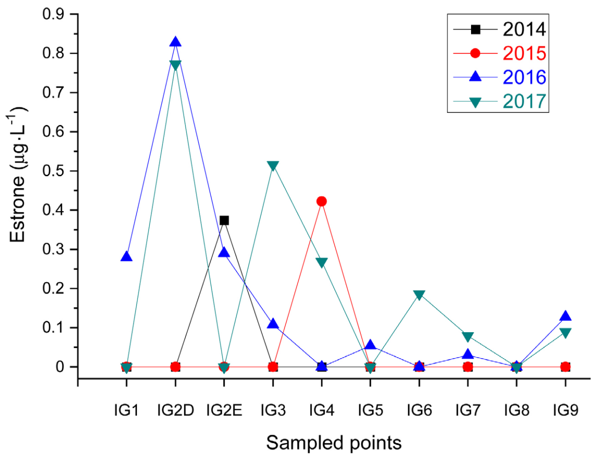

(c)

Figure 9. Concentration of ethinylestradiol (a), estradiol (b) and estrone (c).

IG1 and from 1.18 to 17.85 mg·L^{-1} on IG2, from 2009 until 2011. In 2011, the average concentration, between both points, was 13.39 mg·L^{-1}. In this paper, on the years of 2014 and 2015, values ranged from 0.15 mg·L^{-1} to 39.76 mg·L^{-1} (with the maximum concentration found during the dry period, on the tenth sampling campaign). This indicates that the water quality of the Iguaçu River has been deteriorating over the years.

Caffeine concentrations detected in rivers have as source the discharges of WWTP for the treatment of domestic sewage. They also report a relationship between ammoniacal nitrogen and caffeine, as where the concentration of the former rises, a growth in the concentration of the latter is observed [46].

Several studies have found that situations in which the concentration for ethinylestradiol are higher than 0.001 $\mu g \cdot L^{-1}$ may lead to adverse or even toxic effects to aquatic organisms [47] [48] [49] [50] [51]. For both estradiol and estrone, the lower limit for the chance of deleterious effects is 0.01 $\mu g \cdot L^{-1}$ [52]. For these latter compounds, the concentrations have also surpassed this limit, their behavior illustrated in **Figure 9**.

6. Conclusions

Anthropic influence over the Iguaçu River, from the MRC, is clear and corroborated by the results analyzed. In general, there is a similar behavior between the concentrations of nutrients and caffeine, in respect to the densely urbanized region (from point IG2D to IG5) that presented the highest concentrations for these compounds. Such urbanization is reflected in the increased concentrations of ammoniacal nitrogen, orthophosphate, and caffeine, which originated in domestic wastewaters.

Towering human pressure exerted on the aquatic environment, by the MRC, is confirmed by the presence of caffeine in 82% of the analyzed samples.

Three indicators tended to have lower concentrations in less urbanized areas, from point IG6 to IG9, which could be due to heftier flow which would allow for increasing dilution of the compounds.

This quali-quantitative approach, utilizing pollution indicators, makes for an important tool for water quality monitoring, especially the quantification of caffeine as a tracer for anthropic influence.

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Conflicts of Interest

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

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