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Comparison of 17β-estradiol, bisphenol-A and caffeine concentration levels before and after the water treatment plant

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ABSTRACT

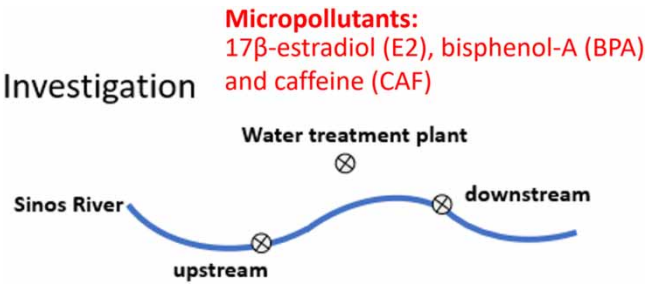
This article compares the concentration levels of 17β-estradiol (E2), bisphenol-A (BPA) and caffeine (CAF) in the Sinos River, Brazil, which is a source of drinking water and the presence of contaminants after the conventional treatment in a municipal water treatment plant (WTP). A total of nine sampling campaigns were carried out, with sample collection in the Sinos River, upstream and downstream of the WTP, in addition to a drinking water sample (DW). The samples were extracted with solid phase extraction (SPE) and the concentration by liquid chromatography coupled to mass spectrometry (LC-MS). The maximum concentration in the Sinos River was 6,127.99 ng·L^{-1} for E2, 3,294.63 ng·L^{-1} for BPA and 1,221.95 ng·L^{-1} for CAF. In drinking water, the concentration range of E2, BPA and CAF was from less than the Detection Limit (DL) up to 437.50 ng·L^{-1}, <DL up to 2,573.34 ng·L^{-1} and <DL up to 832.30 ng·L^{-1}, respectively. In conclusion, the concentrations of these pollutants present in the Sinos River are high, which may represent a negative environmental impact on this water source. Drinking water indicates the need for a new treatment process that could promote the removal of these compounds.

Key words: micropollutants, Sinos River, water supply

HIGHLIGHTS

- The presence of three micropollutants was confirmed in the Sinos River, in southern Brazil.
- 17β-estradiol (E2), Bisphenol-A (BPA) and Caffeine (CAF) have been detected in drinking water.
- Correlations between the sampled locations were found.
- Recommended for continuous monitoring of these substances.

GRAPHICAL ABSTRACT



1. INTRODUCTION

Water is a valuable natural resource, crucial for all living organisms and human domestic, industrial and agricultural activities. Recent studies globally were concerned with the regular occurrence of a variety of compounds, recently identified and named emerging contaminants (ECs), emerging pollutants, micropollutants or microcontaminants (Deblonde *et al.* 2011;

Barbosa *et al.* 2016; Barrios-Estrada *et al.* 2018). Such compounds include endocrine disruptors (ED), pharmaceutical and personal care products, illicit drugs and other substances that are detected in the environment due to anthropic activities. These substances have harmful effects on the environment and living organisms, even at trace levels (Luo *et al.* 2014; Campanha *et al.* 2015; You *et al.* 2015; Gogoi *et al.* 2018; Ahmad & Eskicioglu 2019; Ccanccapa-Cartagena *et al.* 2019; Česen *et al.* 2019; Ravi *et al.* 2020).

A significant concern of the presence of micropollutants is linked to the quality of the drinking water distributed, due to human exposure. Surface and groundwater are the main sources of fresh water, which after treatment reaches the population as drinking water (Machado *et al.* 2016; Bai *et al.* 2019). In addition to the effects on the environment, another important factor is the consequence of these substances on human health. Harmful effects of micropollutants include reduced sperm count in men, increased breast and testicular cancer, obesity (especially in children), reproductive system problems, changes in the immune system and feminization of various species (mainly fish) (Bila & Dezotti 2007; Can *et al.* 2014; Ashfaq *et al.* 2018). Given the adverse effects that these substances can have on human and animal life, it is extremely important to know the concentration and the effects on the organisms (Solano *et al.* 2015).

This work presents an evaluation of the presence of micropollutants 17β-estradiol (E2), bisphenol-A (BPA) and caffeine (CAF) in the Sinos River in southern Brazil, a source of water for treatment and distribution as drinking water. Additionally, it compared the concentration of these contaminants in the Sinos River to that of the drinking water, after treatment at the municipal water treatment plant (WTP).

2. MATERIALS AND METHODS

2.1. Study area

The Sinos River Basin is located in southern Brazil and occupies 3,694 km^2. There are 30 cities within the basin. It represents about 1.3% of the state's territory and is responsible for generating approximately 21% of its gross domestic product (GDP), this area is home to an estimated population of 1,440,500 inhabitants (ComiteSinos 2022).

The Sinos River is one of the main rivers in the state and it forms, along with seven other rivers, the Guaíba Hydrographic Region. With about 190 km in length, from Caraá (source) to Canoas City (mouth), the Sinos River receives contribution from a drainage network of 3,471 km. The climate of this region is subtropical with annual temperature averages around 20 °C and about 1,600 mm of rain per year, equally distributed in four seasons (ComiteSinos 2022).

The Sinos River is a source of water for the population and industry. The place where the samples were collected is characterized by the release of industrial effluents and sanitary sewage without prior treatment, a fact that has already been evidenced by environmental disasters (Gomes *et al.* 2018). The main physical–chemical characteristics of this water are temperature around 18 °C, pH average of 6.5, turbidity of 57 Nephelometric Turbidity Unit (NTU), chemical oxygen demand of 20.0 $mg{\cdot}L^{-1}$, biochemical oxygen demand of 1.0 $mg{\cdot}L^{-1}$ and dissolved oxygen of 5.5 $mg{\cdot}L^{-1}$, according to ANA (2022).

2.2. Sample collection

The samples were collected in duplicates from February to October 2020, totaling nine sampling campaigns. The sampling period was extended during rainy and dry periods, to evaluate the seasonal effect on the concentrations of the compounds analyzed. The samples were carried in 1 L amber glass bottles, with a polyethylene sampler, both previously rinsed with the sample and transported in a styrofoam box and kept refrigerated at 4 °C until analysis, which did not exceed 30 h. Sampling details are presented in Table 1.

In the Sinos River, the samples were collected upstream and downstream of the WTP. Both points are located in an urban area, with a significant agglomeration of residences and sanitary wastewater disposal points. For drinking water samples, a sample from the tap was collected, representing the quality of the water that leaves the WTP and enters the distribution system, for use by the consumer. The WTP has a capacity to capture 1,500 L s^{-1} of water. It operates with conventional treatment, including a rapid mixing system with a Parshall flume, hydraulic flocculators, conventional decanters, rapid filters, a disinfection system with chlorine (gas) and the addition of flour.

2.3. Sample preparation and extraction

All samples were filtered through 0.47 mm glass filter membranes (Macherey-Nagel). After filtration, they were acidified with a 1% acetic acid solution ($v.v^{-1}$) to adjust the pH to 3.0 ± 0.5.

Table 1 | The sites of water collection

Sampling point	Geographic coordinates	Sampling dates
Surface water (River) –upstream city water capitation	29°44′12.19″S 51° 5′54.75″O	17 fev 13 ago 18 ago 25 ago 14 set 22 set 05 out 14 out 20 out
Surface water (River) –downstream city water capitation	29°45′32.38″S 51° 9′2.03″O	
Drinking water – tap water	29°47′34.96″S 51° 9′10.12″O	

The enrichment of contaminants was performed by solid phase extraction (SPE). The reversed-phase C18 cartridge (Silicycle) was conditioned with 7 mL acetonitrile (ACN), 5 mL methanol (MeOH) and 5 mL water pH 3.0 ± 0.5. Samples (500 mL) were added to the cartridges at a flow rate of 5–10 mL min^{-1}. After sample addition, the cartridges were dried under vacuum for 5 min, followed by washing with water pH 3.0 ± 0.5 and dried again under vacuum for 5 min. Elution was carried out with 8 mL of ACN. The extracts were concentrated under vacuum and reconstituted with 1 mL of MeOH.

2.4. Instrumental analysis

The chromatographic analyses were performed in a liquid chromatography system (Agilent 1260) coupled to a single quadrupole mass spectrum detector (Agilent 6120), with electrospray ionization (ESI) (Agilent Technologies). Separation was performed using a Zorbax XDB-C18 reversed-phase column (150 mm × 5 mm and 0.45 μm particle size).

The mobile phase was composed of a mixture of ultrapure water, 0.01% ammonium hydroxide ($v.v^{-1}$) and 100% methanol. The mobile phase gradient started with 10% methanol, reaching 30% in 3 min and 90% in 5 min and this composition was maintained for 14 min, resulting in the end of the chromatographic analysis. The mobile phase flow rate was 0.3 mL min^{-1} and the injection volume was 10.0 μL.

Due to the diversity of the analyzed compounds, it was necessary to carry out the ionization in the positive and negative modes, adopting the following parameters in the mass spectrometry: carrier gas (nitrogen) temperature of 335 °C, flow rate of 10 L min^{-1}, nebulizer gas pressure at 40 psi and capillary voltage at 4,500 V (positive and negative).

Ionization was performed in positive and negative modes, with the capillary voltage optimized at 3,000 V for positive mode and 2,500 V for negative mode; the nebulizer gas flow rate was 20 L h^{-1} while the desolvation gas flow rate was 750 L h^{-1}. The temperatures used were 500 °C for the nebulizer gas and 150 °C for the source block temperature. The target compounds were first identified using the scanning mode (SCAN) (50–500 mz^{-1}) and then, the ions that characterize the compounds are monitored individually, through the SIM (Single Ion Monitoring) mode.

2.5. Quality control

The analytical curves were obtained by the internal standardization method, with a concentration range from 0.05 to 50,000 ng L^{-1}. In this case, individual solutions were prepared for each interest analyte, in High-Performance Liquid Chromatography (HPLC) grade (Honeywell) methanol. All standards have high purity analytical grade. The Detection Limit (DL) and Quantification Limit (QL) values were calculated based on analytical curve parameters. Precision was evaluated in the form of repeatability, at three fortification levels (0.05, 500 and 50,000 ng L^{-1}) (Table 2).

2.6. Data analysis

The data were processed in the SPSS software, version 22 and in Microsoft Excel. It was executed by the Kolmorogov–Smirnov and Shapiro–Wilk normality tests. These tests showed significant results ($p = 0.000$) for all the samples and different evaluated groups, that means it suggests the non-normality of the data. Thus, it used Kruskal–Wallis, Mann–Whitney and Kolmogorov–Smirnov non-parametric tests ($p < 0.05$) for the statistical study of the results. For these data analyses, however, the Kolmogorov–Smirnov test was chosen for two reasons: (1) for its applicability to compare two different groups and (2) for its higher capacity for sample sizes lower than 25 per group.

Table 2 | Parameters including linearity, limits of detection and quantification (DL and QL)

Compound	Linearity (r^2)	DL (ng L^{-1})	QL (ng L^{-1})	Precision %DSW
E2	1.0000	19.73	59.81	7.17%[a] 2.42%[b] 0.61%[c]
BPA	0.9872	37.76	114.44	0.86%[a] 1.71%[b] 0.23%[c]
CAF	1.0000	34.24	103.77	0.94%[a] 1.14%[b] 0.74%[c]

[a]Considering a spike of analytes at a concentration of 50,000 ng L^{-1} in triplicate.
[b]Considering a spike of analytes at a concentration of 0.05 ng L^{-1} in triplicate.
[c]Considering a spike of analytes at a concentration of 500 ng L^{-1} in triplicate. DL, limit of detection; QL, limit of quantification.

3. RESULTS AND DISCUSSION

3.1. Occurrence of E2, BPA and CAF in the Sinos River

The occurrence of E2, BPA and CAF in the Sinos River is summarized in Table 3.

Table 1 shows the impact on the water quality of the Sinos River in relation to the presence of the micropollutants studied. In general, concentrations in upstream were lower than in downstream. In this study, the maximum concentrations found for E2 were 1,885.8 and 6,128.0 ng·L^{-1}, for upstream and downstream, respectively. These values were similar to those reported by Bai *et al.* (2019), who analyzed a total of 311 samples, in the South Platte River, in the USA, finding a maximum concentration of 1,960 ng·L^{-1} for E2. This may be associated with mechanisms of biotransformation, degradation and lipophilicity of E2 (Barreiros *et al.* 2016) since the downstream also has a large concentration of an urban population close to the river, receiving loads of sanitary wastewater.

Torres *et al.* (2015) report that when hormones, such as E2 and estriol, are detected in surface water, there is an indication of contamination by wastewater as these are the main hormones produced and excreted by the human body.

In Brazil, several studies on the occurrence of E2 in surface waters were done. Pivetta & Gastaldini (2019) analyzed 10 samples from the Cancela-Tamanda Basin and João Goulart Basin, located in the city of Santa Maria-RS and detected concentrations in the range from 24 to 150 ng·L^{-1} of E2. In Curitiba-PR, Ide *et al.* (2017) found a maximum concentration of 940 and 740 ng·L^{-1}, in the Iguaçu River and the Barigui River, respectively. In the State of São Paulo, Campanha *et al.* (2015) reported a concentration range from <0.04 up to 5.36 ng·L^{-1} in the Monjolinho River. In the Piracicaba River, Torres

Table 3 | E2, BPA and CAF in the Sinos River (ng·L^{-1})

	Upstream			Downstream		
Number of sampling events	E2	BPA	CAF	E2	BPA	CAF
1	1,885.8 ± 18.6	<DL	608.8 ± 21.8	6,128.0 ± 128.3	49.4 ± 3.8	701.9 ± 19. 7
2	20.2 ± 2.5	<DL	76.5 ± 2.1	21.18 ± 1.12	<DL	88.6 ± 1.3
3	<DL	44.2 ± 2.7	103.7 ± 8.4	<DL	100.0 ± 4.4	121.4 ± 121.8
4	<DL	56.1 ± 15.1	193.0 ± 4.2	<DL	<DL	185.4 ± 33.7
5	<DL	<DL	<DL	<DL	<DL	<DL
6	<DL	3,294.6 ± 227.9	220.7 ± 1.8	<DL	260.7 ± 33.4	512.4 ± 14.3
7	<DL	44.2 ± 0.3	232.9 ± 20.6	<DL	37.0 ± 0.7	152.1 ± 7.9
8	<DL	186.3 ± 13.4	512.3 ± 141.9	<DL	70.1 ± 5.5	541.4 ± 29.4
9	<DL	144.7 ± 2.3	905.0 ± 62.1	23.15 ± 0.48	196.9 ± 5.6	1,222.0 ± 127.6
%	22	67	89	33	67	88

E2, 17β-estradiol; BPA, bisphenol-A; CAF, caffeine; DL, limit of detection.

et al. (2015) identified a concentration in the range from 90 up to 137 ng·L^{-1}; and the Atibaia River (Montagner & Jardim 2011) obtained an average concentration of 2,516.5 ng·L^{-1}.

Results of 10 years of analysis of E2, BPA, CAF and other contaminants in the State of São Paulo were presented by Montagner *et al.* (2019). For surface water, the average concentration was 969, 513 and 4,823 ng·L^{-1} for E2, BPA and CAF, respectively. Zhang *et al.* (2007) analyzed the presence of 56 micropollutants in the Mississippi River, in the United States and the concentrations obtained were 0 up to 4.5, 0 up to 147.2 and 0 up to 38.0 ng·L^{-1}, for E2, BPA and CAF, respectively.

In most of the reported studies, the concentrations were below that found in this research. It is noteworthy that Brazil is a country with a large area and different socioeconomic and environmental scenarios. Therefore, it is to be expected that the regional characteristics of each state influence the concentration of contaminants.

Results obtained for E2 in this study are high as studies show that the predicted no-effect concentration (PNEC) for E2 is around 1 up to 2 ng·L^{-1} (Caldwell *et al.* 2012; Sodré *et al.* 2018a, 2018b) and that exposure of fish to concentrations of around 10 ng·L^{-1} of E2 leads to feminization of male fish and inhibition of sexual organ development (Imai *et al.* 2005; Woods & Kumar 2011; Andaluri *et al.* 2012; Sun *et al.* 2019).

Regarding BPA, the concentrations obtained during the nine campaigns were quite varied. For upstream, it ranged from <DL up to 3,294.6 ng·L^{-1} and for downstream from <DL up to 260.68 ng·L^{-1}. Peteffi *et al.* (2019) also analyzed the Sinos River, but in the portion located in the municipality of Novo Hamburgo, in southern Brazil. The authors collected 12 samples upstream of WTP from Novo Hamburgo and BPA in the range of 3.7 to 517 ng·L^{-1} and in the range of 328.5 to 5,503.4 ng·L^{-1} for CAF.

Similar results of this study were observed by Wilkinson *et al.* (2017), at the Hogsmill River, London, where they reported mean concentrations of BPA between 22.7 and 137 ng·L^{-1}. Bai *et al.* (2019) reported the presence of BPA in the South Platte River, in the United States, at a mean concentration of 150 ng·L^{-1}.

In Malaysia, the Langat River is also a source of potable water for some cities and BPA was detected at several points in it with a mean concentration of 3.83 ng·L^{-1} (Wee *et al.* 2019). In water samples from the Atibaia River, in the city of Campinas-SP, Montagner & Jardim (2011) reported BPA concentrations in the range of 204 up to 13,016 ng·L^{-1}.

According to the study by You *et al.* (2015), the PNEC for BPA is around 60 ng·L^{-1}. The BPA in this study exceeded this PNEC more than once during the nine sampling campaigns. Due to its wide use and properties of bioaccumulation and persistence, it is believed that there is increasing contamination of BPA in water resources, the main sources being the release of industrial effluents and sanitary sewage (Wee *et al.* 2019).

CAF was the contaminant with the highest frequency of quantification (89%) at the points analyzed in the Sinos River. Ng *et al.* (2021) reported a similar frequency of CAF in the Biscayne Bay, located in South Florida. The authors also detected a maximum concentration of E2 of 178.5 ng·L^{-1}, a value lower than that found in this study.

In that study, CAF was detected in a range of <DL up to 905.04 ng·L^{-1} at the upstream site and <DL up to 1,221.95 ng·L^{-1} at the downstream site. Similar values were detected in other regions of Brazil. In Paraná, the Barigui River had a variation in CAF concentration of 90 up to 1,590 ng·L^{-1}, while in the Iguaçu River, the average concentration was 27,000 ng·L^{-1} (Ide *et al.* 2017) and in the Belém River, the variation range was 70 up to 23,080 ng·L^{-1} (Mizukawa *et al.* 2019). In Brasília, on Lake Paranoá, the CAF variation was 2 up to 288 ng·L^{-1} (Sodré *et al.* 2018a, 2018b) and, in São Paulo, on the Monjolinho River, the average CAF was 14,955 ng·L^{-1} (Campanha *et al.* 2015).

The concentration of CAF was higher at the upstream sampling point than the downstream sampling point at the fourth and seventh sampling events when compared to the point downstream, indicating a possible dilution and degradation of the compound along the Sinos River. A similar result was observed in the study by Sodré *et al.* (2018a, 2018b), suggesting that the occurrence of CAF in upstream locations may be a consequence of buildings not connected to the wastewater pipelines. The influence of fixed or diffuse sources of pollution was also suggested by Wilkinson *et al.* (2017).

Several authors confirm that the presence of CAF in surface waters can be correlated with the release of wastewater since this substance is highly consumed by humans through coffee, tea, soft drinks, tobacco and drugs and can be used as an indicator of anthropic activities (Montagner *et al.* 2017; De Sousa *et al.* 2018; Sodré *et al.* 2018a, 2018b; Caldas *et al.* 2019; Česen *et al.* 2019; Ng *et al.* 2021). Kumar *et al.* (2018) report that in countries such as Brazil, Denmark and Finland, the average intake of CAF is 300 mg day^{-1}.

Furthermore, the fact that CAF is a very water-soluble, biodegradable compound with a relatively short half-life (about 3.5–5.2 days), but very resistant to direct photolysis from sunlight, reinforces the importance of this compound as a recent sanitary sewer release marker (Froehner *et al.* 2011; Starling *et al.* 2019; Ng *et al.* 2021).

Based on the results obtained in this study, it was observed that BPA has a contaminating profile of industrial and pesticide origin, while the other contaminants, E2 and CAF, are more directly related to domestic wastewater input.

Finally, trying to evaluate the uniformity of contamination by the micropollutants studied in this work, comparing the upstream and downstream points evaluated, the Kolmogorov–Smirnov test was performed ($p < 0.05$). The results showed that there are no significant differences for E2 ($p = 0.387$), BPA ($p = 0.987$) and CAF ($p = 0.878$), comparing the concentrations of the Upstream and Downstream points. Therefore, the concentrations of these contaminants in the Sinos River are not significantly different at these two points.

3.2. Occurrence of E2, BPA and CAF in drinking water

The results of the occurrence of E2, BPA and CAF in drinking water are summarized in Table 4.

The values obtained in this study for E2 and CAF were higher than others reported in the literature. Regarding E2, the average for drinking water in Brazil was 6.8 ng·L^{-1} (Lopes *et al.* 2010), whereas, in Germany, the value was 0.10 ng·L^{-1} (Kuch & Ballschmiter 2001). Regarding CAF, in Brazil the average concentration was 8.6 ng·L^{-1} (Sodré *et al.* 2018a, 2018b) and in Portugal, the range of 2.7 up to 46 ng·L^{-1} (Gaffney *et al.* 2015). The concern of these contaminants in water is because human exposure to high concentrations of estrogen, such as E2, can cause several health disorders, such as gynecomastia (breast growth in men), decreased sperm count, increased breast and prostate and ovarian cancer (Cotrim *et al.* 2016).

Montagner *et al.* (2019) presented a dataset for 39 micropollutants of different classes, analyzed in 289 samples of drinking water, from 2007 to 2015, in the State of São Paulo. The E2, BPA and CAF average were 25, 23 and 548 ng·L^{-1}, respectively. In Campinas, Sodré *et al.* (2010) investigated the presence of 11 micropollutants in a sample of drinking water and observed averages of 110, 160 and 220 ng·L^{-1} for E2, BPA and CAF, respectively, very similar to those obtained in this study.

Machado *et al.* (2016) surveyed the presence of micropollutants in drinking water samples in 22 Brazilian capitals. Porto Alegre was the city that presented the highest levels of CAF for drinking water, ranging from 122 up to 2,769 ng·L^{-1}. The authors associated the high CAF results in drinking water in Porto Alegre, with cultural habits and to the water source supply.

In this study, the maximum concentration of CAF was 832.3 ng·L^{-1}, a value lower than that reported in Porto Alegre. But the presence of CAF in samples of drinking water is a great indication of the presence of wastewater in the water source since CAF is a compound of anthropogenic origin (Machado *et al.* 2016).

BPA was the compound with the highest concentrations detected in drinking water for this study, levels ranged from <DL to 2,573.3 ng·L^{-1}, indicating high variability between samples. BPA concentrations reported in drinking water vary between countries: 10.5 up to 53 ng·L^{-1} in France (Loos *et al.* 2007), an average of 220 ng·L^{-1} in the United States (Stackelberg *et al.* 2007), from <DL up to 6 ng·L^{-1} in Italy (Valbonesi *et al.* 2021) and 0.02 ng·L^{-1} in Germany (Kuch & Ballschmiter 2001).

According to the Drinking Water Directive of the Council of the European Union, the upper limit for BPA in drinking water is 2, 500 ng·L^{-1} (EU 2020). In the present study, the maximum BPA concentration was 2,573.34 ng·L^{-1}, a value above the European Union Regulation limit (EU 2020).

Table 4 | Parameters obtained in drinking water (ng·L^{-1})

Number of sampling events	E2	BPA	CAF
1	437.5 ± 9.0	1,784.4 ± 164.5	832.3 ± 5.9
2	<DL	<DL	<DL
3	<DL	<DL	<DL
4	<DL	48.8 ± 4.2	<DL
5	<DL	508.3 ± 104.3	<DL
6	112.3 ± 7.4	157.9 ± 7.2	<DL
7	<DL	2,573.3 ± 411.9	31.5 ± 3.5
8	74.0 ± 0.8	2,377.7 ± 57.9	31.4 ± 18.5
9	<DL	<DL	<DL
%	33	66	33

E2, 17β-estradiol; BPA, bisphenol-A; CAF, caffeine; DL, limit of detection.

BPA exposure in humans has been linked to endocrine effects, heart disease, diabetes, premature birth, low birth mass, polycystic ovary syndrome, breast and prostate cancer, as well as reduced sperm concentration (Li *et al.* 2011; Tse *et al.* 2017; Gounden *et al.* 2019; Starling *et al.* 2019).

Due to the high concentrations in drinking water obtained for the three compounds, an overview of the average concentrations of the three micropollutants identified in the two points of Sinos River and drinking water is presented in Figure 1. For the calculation of the average, in the campaigns in which the concentration was below the DL, considering the worst hypothesis, the DL value of the compound.

According to Figure 1, it is possible to verify the presence of all these contaminants in the two matrices studied. The Kolmogorov–Smirnov test ($p < 0.05$), comparing the concentrations of micropollutants in drinking water and from the Sinos River, showed that there are no significant differences for E2 ($p = 0.467$). As for BPA and CAF, the test showed that there are significant differences between BPA ($p = 0.021$) and CAF ($p = 0.000$).

For BPA, concentrations are higher in drinking water than in the Sinos River. As for CAF, concentrations in the Sinos River are higher than those in drinking water. Some authors have reported that BPA in drinking water may come from epoxy and polyester resins used as coatings for pipes and accessories used in water supply systems. Factors such as the age of the pipes, temperature and water quality also influence BPA leaching into the water (Lintelmann *et al.* 2003; Moura *et al.* 2020).

These results may be associated with the low efficiency of conventional WTP in removing these contaminants since they were not designed to remove these compounds. This situation is aggravated by population growth, deterioration of water resources and lack of sanitation (Machado *et al.* 2016; Teodosiu *et al.* 2018; Lintelmann *et al.* 2003).

Couto *et al.* (2019) reported that conventional WTP, which consists of coagulation, flocculation, filtration and disinfection treatments, such as chlorination, have low removal efficiencies, especially in the coagulation, flocculation and sand filtration steps. Therefore, to remove ECs, municipal WTPs need to adopt advanced treatment technologies, such as ozonation, adsorption with activated carbon, reverse osmosis, oxidative processes or membrane filtration (Rodriguez-Narvaez *et al.* 2017; Couto *et al.* 2019).

Finally, Valbonesi *et al.* (2021) reinforced that the quality of drinking water in relation to micropollutants is a concern as the risks posed to human health and the environment are not yet fully understood.

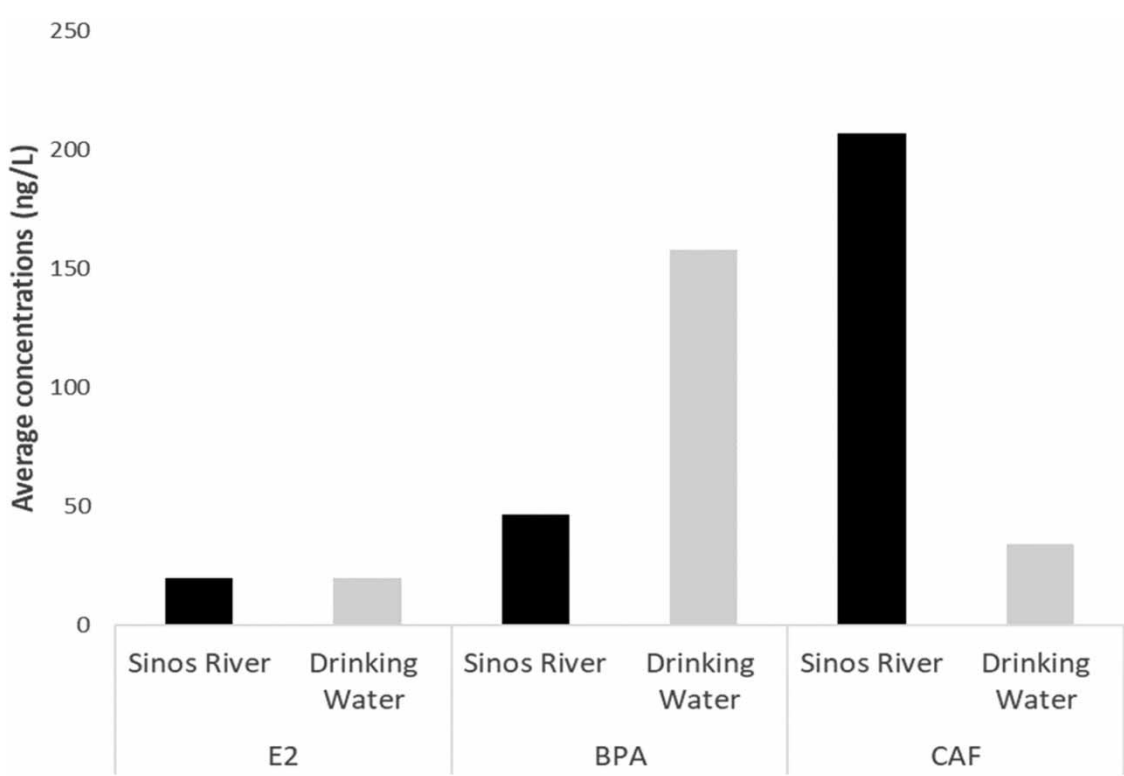


Figure 1 | Average concentration of contaminants in Sinos River and drinking water.

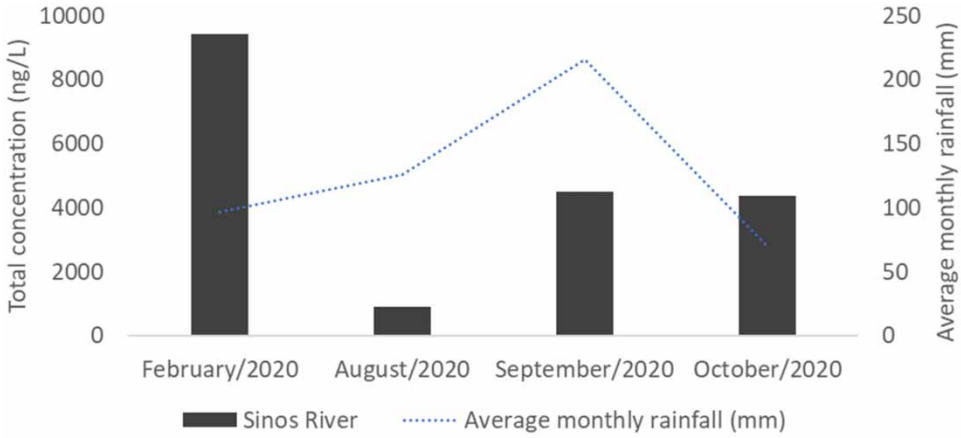


Figure 2 | Total concentration of compounds detected at the Sinos River points and average precipitation during the sampling months.

3.3. Influence of precipitation on concentrations of emerging contaminants

Due to the difficulties in determining the concentration of ECs in the environment, many studies are seeking to correlate EC concentrations and other variables. Ide *et al.* (2013), Ide *et al.* (2017) and Mizukawa *et al.* (2019) analyzed the correlation of some ECs with physicochemical parameters in surface waters. On the other hand, Bai *et al.* (2019), Benotti & Brownawell *et al.* (2007), De Sousa *et al.* (2018), Peteffi *et al.* (2019) and You *et al.* (2015) analyzed the effect of precipitation and temperature, based on the seasons, on EC concentration.

Considering the Sinos River, an assessment was made of meteorological conditions, specifically precipitation and its influence on the presence of BPA, E2 and CAF. Figure 2 shows the relationship between compound concentrations and average precipitation during the sampling period. The concentrations shown are relative to the sum of the concentrations of the compounds, at points upstream and downstream of the Sinos River. When there was a concentration <DL, the worst situation was considered.

The highest concentrations of the compounds were detected during February, September and October. These were drier months, which coincided with the dry period in the Sinos River Basin. The lowest concentration was during the rainiest months. This lower concentration may reflect the dilution of these compounds, which occurs due to the increase in the flow of water resources, due to rainier periods. De Sousa *et al.* (2018) also found higher EC concentrations in dry months and lower concentrations in rainy months.

4. CONCLUSIONS

The evaluation of micropollutants in the Sinos River identified concentrations in the range of <DL up to 6,128.0 ng·L^{-1}, <DL up to 3,294.6 ng·L^{-1} and <DL up to 1,222.0 ng·L^{-1}, for E2, BPA and CAF, respectively. With this, it is possible to conclude that these concentrations are high and may represent a negative environmental impact on this water. Additionally, it is important to mention that the Sinos River is used as a source of water by the municipal WTP, which makes the need for continuous monitoring of these substances, even more important aiming at the protection of aquatic life and of human health.

This situation is aggravated since the investigation of these compounds in drinking water showed the presence of the studied micropollutants in concentrations ranging from <DL to 437.5 ng·L^{-1} for E2, <DL to 2,573.3 ng·L^{-1} for BPA and <DL to 832.3 ng·L^{-1} for CAF. These results indicate the need for new treatment processes that promote the removal of these compounds.

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DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

CONFLICT OF INTEREST

The authors declare there is no conflict.

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