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Presence of emerging contaminants in urban water bodies in southern Brazil

Glaucia Ghesti Pivetta and Maria do Carmo Cauduro Gastaldini

ABSTRACT

The presence of pharmaceutical and hormone residues in water bodies is a matter of recent global concern. This study investigated the presence of such contaminants in two urban water bodies located in the city of Santa Maria, in southern Brazil. Two urban catchments, characterized by anthropogenic influences and poor household waste collection and treatment systems, were investigated. The Cancela-Tamandaí catchment covers an area of 2.7 km^2, 50% of which is impervious soil, and is home to 14,300 inhabitants. The João Goulart catchment area covers 5.5 km^2, 40% of which is impervious soil, and houses 11,900 inhabitants. Ten sampling campaigns were conducted in each catchment. Samples were checked for diclofenac, ibuprofen, paracetamol, 17 β-estradiol, estriol, ethisterone, estrone, and megestrol acetate. Four of the hormones (17 β-estradiol, estriol, estrone, and megestrol acetate) were not detected in either catchment. Ethisterone was detected in a single sampling campaign in Cancela-Tamandaí. Ibuprofen and paracetamol were detected in several samples, while diclofenac was absent. The mean concentration of ibuprofen in the João Goulart catchment was 0.51 $\mu g\ L^{-1}$ and in the Cancela-Tamandaí it was 1.26 $\mu g\ L^{-1}$. Mean paracetamol concentrations were 0.4 $\mu g\ L^{-1}$ in the João Goulart catchment and 3.0 $\mu g\ L^{-1}$ in the Cancela-Tamandaí.

Key words | emerging contaminants, hormones, pharmaceuticals, surface water quality, treated wastewater effluent

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INTRODUCTION

Emerging contaminants are chemicals found in drugs, personal hygiene and veterinary products, and pesticides (Sauvé & Desrosiers 2014; Bai *et al.* 2018). The term 'emerging' refers to the fact that their use is on the rise (Sauvé & Desrosiers 2014). As a result, several studies are being carried out to assess the impact of these compounds on the environment and on human health (Rahman *et al.* 2009; Velicu & Suri 2009; Torres *et al.* 2015; Madikizela & Chimuka 2017; Bai *et al.* 2018).

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Among the emerging contaminants mentioned, pharmaceuticals and hormones are of particular concern. Pharmaceuticals refer to a vast and diversified group of chemicals used to prevent and treat diseases, which means that they are used in large quantities throughout the world. The unchecked use of some prescription and non-prescription drugs, such as anti-inflammatories and hormones, could cause serious environmental impacts, and thus, deserves special attention. Hormones are naturally produced by the body, but they can also be synthesized in the form of pharmaceutical drugs. As they interact with the endocrine and reproductive systems of humans and animals, they may cause significant metabolic disorders.

Most drugs are designed to be persistent so that they retain their chemical structure long enough to do their therapeutic work. This characteristic, coupled with their continual input, may cause them to remain in the environment for a significant period of time, which means that they are considered potential environmental pollutants (Jones *et al.* 2002; Torres *et al.* 2015). Exposure to these contaminants may have a harmful effect on human health, such as increased resistance to antibiotics, endocrine disruptions, and cancer (Bai *et al.* 2018).

After a drug is taken, a significant share of it is excreted through urine and feces. According to Mulroy (2001), 50 to 90% of a drug administered to a human or animal may be excreted unmetabolized, and become a persistent environmental contaminant. An additional source of concern is that waste materials may contain partially metabolized pharmaceuticals that can also upset the environmental equilibrium if left untreated.

Emerging contaminants are often found in rivers that receive domestic sewage. These contaminants have been found in studies of rivers in locations around the world, such as Colombia (Botero Coy *et al.* 2018), Portugal (Sousa *et al.* 2019), India (Balakrishna *et al.* 2017; Williams *et al.* 2019), United States (Scott *et al.* 2019), and African countries (Madikizela & Chimuka 2017). In Brazil, although scarce, studies that investigate the occurrence of these substances in water bodies (Campanha *et al.* 2015; Torres *et al.* 2015; Sposito *et al.* 2018) identify the discharge of treated and untreated domestic sewage effluent as the main source of contamination in surface waters. In Brazil, 42.4% of urban areas discharge untreated sewage directly into rivers that are used to supply drinking water, while the average treatment effectiveness for treated sewage is only 44.9% (Brasil 2016). The improper disposal of unused or expired drugs also represents an important source of water contamination (Patrolecco *et al.* 2014).

The concentrations of pharmaceuticals in surface waters vary significantly based on region (Li *et al.* 2016) and on the consumption habits of people in different social classes. Environmental factors, such as climate, rainfall, and use of soil, also affect pharmaceutical transport to the water (Lee *et al.* 2007).

Growing concern over pharmaceutical pollutants in water bodies justifies an investigation of such compounds in the Vacacaí–Vacacaí Mirim catchment, in Brazil, since there are no recent studies on this topic in published literature. It is necessary to understand the status of these compounds in order to provide guidelines to regulate and mitigate their environmental impact. The aim of this study is to assess the presence of selected pharmaceutical and hormone pollutants in two urban water bodies in the city of Santa Maria in southern Brazil.

MATERIALS AND METHODS

Description of the study area

The Vacacaí and Vacacaí Mirim watershed has an area of 11,077.34 km^2 and is located in the center-west part of Rio Grande do Sul in southern Brazil, between 29°35′ and 30°45′ south and 53°04′ and 54°34′ west (SEMA 2019).

The watershed area contains two major water bodies, the Vacacaí Mirim and the Vacacaí rivers, where two monitoring locations were selected to sample the water quality. For the Vacacaí River, the Cancela-Tamandaí catchment was selected, and for the Vacacaí Mirim it was the João Goulart catchment.

The major similarity between the two catchments is the presence of anthropogenic interference, consisting of a high degree of urbanization combined with poor domestic wastewater collection and treatment systems. In the city of Santa Maria, only 49.32% of the population has access to wastewater collection services (Rio Grande do Sul 2015). According to the city environmental service plan (2015), neighborhoods located in the catchment areas of this study have a wastewater and sewage collection rate of 75%. However, one of the major sanitation problems in the city is the lack of connections to the wastewater treatment system, which means that the actual treatment rate is much lower. Wastewater is not collected by the municipality; it is probably discharged into the rainwater network or directly into the nearest water bodies.

This study area was selected because of its importance to the development of the region as a source of water for human and animal consumption, irrigation, and recreation. Figure 1 shows the location of the Cancela-Tamandaí and João Goulart catchment areas.

The Cancela-Tamandaí catchment area is located in the urban area of Santa Maria and covers a total area of 2.7 km^2. Approximately 50% of the area is impervious soil, with 6.5% corresponding to fields and 23.5% to trees (Santos &

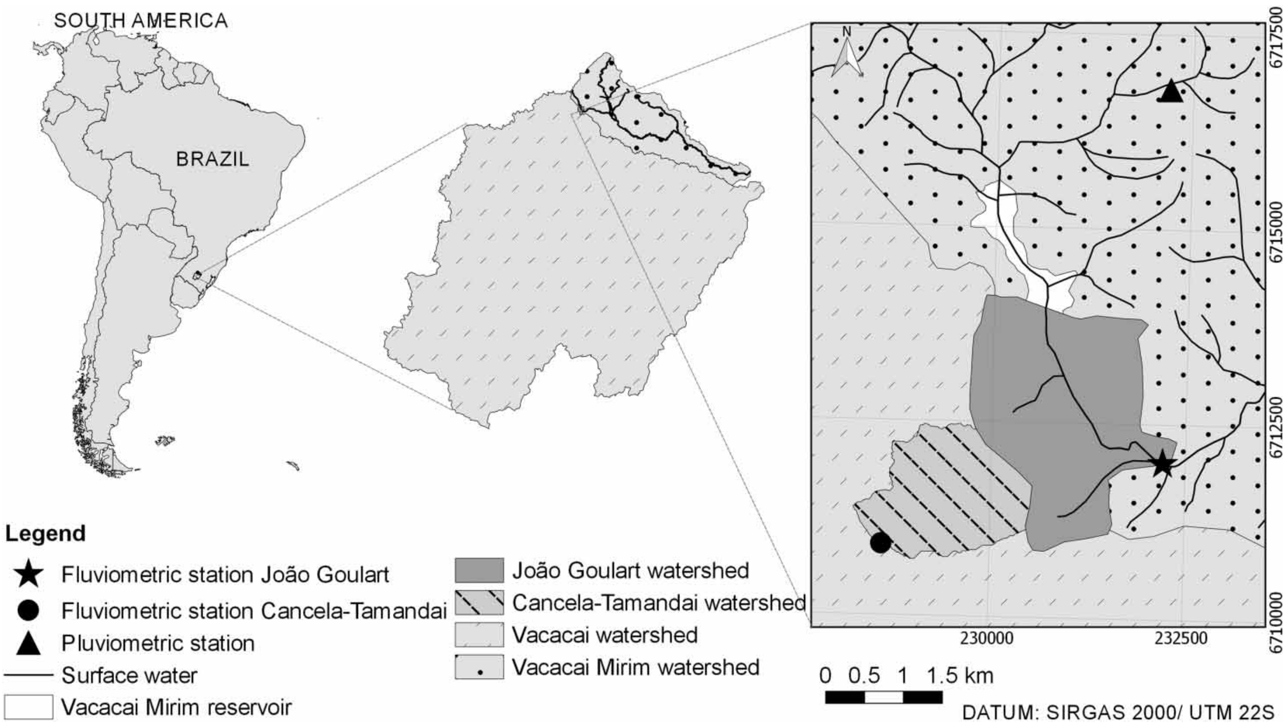

Figure 1 | Location of the catchment areas in the study.

Gastaldini 2016). The catchment is home to 14,300 inhabitants in 6,230 households, according to the most recent Brazilian census (IBGE 2013).

The João Goulart catchment is partly located in an urban area and has a drainage area of 5.5 km^2. Natural vegetation covers 31.5% of this catchment, while 8% of the land is bare soil, and 19.7% is used for agricultural activities. Approximately 40% of the catchment area is impervious soil (Teixeira 2015). The estimated population in this catchment is 11,900 inhabitants in 3,930 households (IBGE 2013).

Water sampling and analysis

The goal was to conduct monthly samplings during one year of monitoring. Collection was precluded by weather conditions during two months of the investigation, since the goal was to make collections only in dry weather. In the end, each catchment area was sampled ten times. Samples were collected by hand in dry weather, at points near the center of each catchment. Water flow during collection was determined by flow profile measurement in the monitoring area using a hydrometric grinder and the mid-section method.

After collection, the presence of pharmaceuticals and hormones in the samples was determined using combined liquid chromatography-mass spectrometry (LC-MS). The compounds analyzed were selected according to the availability of standards for analysis by LC-MS. Table 1 lists the substances analyzed and their respective detection limits. Detection limits modified between the dates due to changes in matrices of method quantification.

Table 1 | Hormones and pharmaceuticals analyzed and detection limits

Substances	Detection limits (μg·L^{-1})
17 *β*-estradiol	0.15; 0.024*
Estriol	0.15; 0.024*
Estrone	0.3; 0.15; 0.012*
Ethisterone	0.02; 0.006*
Megestrol acetate	0.02; 0.006*
Diclofenac	0.06; 0.15*
Ibuprofen	0.06; 0.15*
Paracetamol	0.02; 0.006*

Note: (*) Variable between the dates.

The detected concentrations of hormones and pharmaceuticals in each water body were multiplied by the respective flow of the river. In this way, the loads of the compounds detected in each water body were quantified. The loads were checked for statistically significant differences using analysis of variance (ANOVA) and Kruskal-Wallis non-parametric tests. The R software package was used for statistical analysis.

RESULTS AND DISCUSSION

The impact of the poor management of water resources was clear, particularly in relation to the water quality indicated by samples from September 2015 to November 2016 in the Cancela-Tamandaí and João Goulart catchments. Table 2 shows the concentration data for compounds found in the sampled water bodies. In samples where the concentration was below the detection limit for the compound, the detection limit itself was assigned as the compound's concentration.

In both catchments, the concentrations of 17 β-estradiol, estriol, estrone, and megestrol acetate never exceeded the detection limits of the method used. However, this does not mean that these substances were not present in these water bodies. What can be said is that, if present, they were at concentrations below their detection limits. In most cases, these substances are found in trace amounts, which means that the analytic methods used need to be highly sensitive with very low detection limits. In a study of surface waters located in Chester County, Pennsylvania, Velicu & Suri (2009) detected the hormone estrone in 90% of the samples tested, and estriol was found in 80% of the samples, with maximum concentrations of 2.6 and 19 ng L^{-1}, respectively.

Diclofenac, an anti-inflammatory drug, was not detected in any samples in either catchment, possibly due to its high detection limit for the analysis method or the quick decomposition of this substance. Buser *et al.* (1998) investigated the concentration of diclofenac in the inlet and outlet of Lake Greifensee, in Switzerland, and estimated that over 90% of the concentration of diclofenac

Table 2 | Hormone and pharmaceutical concentrations in the Cancela-Tamandaí and João Goulart catchments

Watershed	Sample	Date	17 β-estradiol (μg L^{-1})	Estriol (μg L^{-1})	Estrone (μg L^{-1})	Ethisterone (μg L^{-1})	Megestrol acetate (μg L^{-1})	Diclofenac (μg L^{-1})	Ibuprofen (μg L^{-1})	Paracetamol (μg L^{-1})
Cancela-Tamandaí	1	23 Oct 2015	0.15*	0.15*	0.3*	0.02*	0.02*	0.06*	0.61	0.12
	2	20 Jan 2016	0.15*	0.15*	0.15*	0.02*	0.02*	0.06*	0.60	9.90
	3	24 Feb 2016	0.15*	0.15*	0.15*	0.02*	0.02*	0.06*	0.93	0.52
	4	15 Mar 2016	0.15*	0.15*	0.15*	0.02*	0.02*	0.06*	0.83	0.32
	5	04 May 2016	0.024*	0.024*	0.012*	0.006*	0.006*	0.06*	2.71	0.85
	6	20 June 2016	0.024*	0.024*	0.012*	0.006*	0.006*	0.06*	2.21	3.58
	7	03 Aug 2016	0.024*	0.024*	0.012*	0.053	0.006*	0.06*	1.66	7.75
	8	08 Sep 2016	0.024*	0.024*	0.012*	0.006*	0.006*	0.06*	0.95	0.006*
	9	29 Sep 2016	0.024*	0.024*	0.012*	0.006*	0.006*	0.06*	1.22	6.16
	10	24 Nov 2016	0.024*	0.024*	0.012*	0.006*	0.006*	0.06*	0.94	0.54
	Mean		0.074	0.074	0.082	0.017	0.012	0.060	1.266	2.975
João Goulart	1	09 Sep 2015	0.15*	0.3*	0.15*	0.03*	0.02*	0.15*	0.15*	0.02*
	2	20 Jan 2016	0.15*	0.15*	0.15*	0.02*	0.02*	0.06*	0.20	0.20
	3	24 Feb 2016	0.15*	0.15*	0.15*	0.02*	0.02*	0.06*	0.38	1.29
	4	15 Mar 2016	0.15*	0.15*	0.15*	0.02*	0.02*	0.06*	0.30	0.37
	5	04 May 2016	0.024*	0.024*	0.012*	0.006*	0.006*	0.06*	0.50	0.99
	6	20 June 2016	0.024*	0.024*	0.012*	0.006*	0.006*	0.06*	1.75	0.88
	7	03 Aug 2016	0.024*	0.024*	0.012*	0.006*	0.006*	0.06*	0.98	0.006*
	8	08 Sep 2016	0.024*	0.024*	0.012*	0.006*	0.006*	0.06*	0.006*	0.14
	9	29 Sep 2016	0.024*	0.024*	0.012*	0.006*	0.006*	0.06*	0.55	0.19
	10	24 Nov 2016	0.024*	0.024*	0.012*	0.006*	0.006*	0.06*	0.33	0.17
	Mean		0.074	0.089	0.067	0.013	0.012	0.069	0.515	0.426

Note: (*) Detection limit value.

was eliminated in the lake by means of photolytic degradation.

Ethisterone was detected in a single sample in the Cancela-Tamandaí catchment. The concentration detected was 0.053 μg L^{-1} in the sample collected on 03 August 2016. In the João Goulart catchment, the concentration of ethisterone was below the detection limit.

Ibuprofen was detected in most samples collected in both catchments. In the João Goulart catchment, ibuprofen was below detection limit in only two samples, on 09 September 2015 with a concentration below 0.15 μg L^{-1} and on 08 September 2016, with a concentration below 0.006 μg L^{-1}. The highest concentration of this substance was 1.75 μg L^{-1} in a sample collected on 20 June 2016. The mean concentration of ibuprofen in the João Goulart catchment was 0.51 μg L^{-1}.

Samples from the Cancela-Tamandaí catchment showed the highest concentrations of ibuprofen in this study, with a mean value of 1.26 μg L^{-1} and a maximum concentration of 2.71 μg L^{-1}, recorded in the sample collected on 04 May 2015. Ibuprofen was detected in all samples in the Cancela-Tamandaí catchment.

Ibuprofen was the most commonly detected pharmaceutical in other surface water assessment studies (Matongo *et al.* 2015; Madikizela & Chimuka 2017). This is probably due to the discharge of treatment effluents into the water bodies and the high consumption of this drug in most countries (Madikizela & Chimuka 2017). In a study of the Umgeni River in South Africa, the highest concentration of ibuprofen in surface waters was 62 μg L^{-1}, which was attributed to the availability of this substance as a non-prescription drug (Matongo *et al.* 2015).

For paracetamol, the Cancela-Tamandaí catchment had the highest concentrations. It was detected in all samples except the one collected on 08 September 2016, which showed a concentration below 0.006 μg L^{-1}. The highest concentration of paracetamol was 9.9 μg L^{-1}, recorded on 20 January 2016, and its mean concentration was approximately 3.0 μg L^{-1}.

In the João Goulart catchment, paracetamol was detected in all but two samples. On 09 September 2015, the concentration was below the detection limit of 0.02 μg L^{-1}, and on 03 August 2016, the concentration was below 0.006 μg L^{-1}. The highest concentration recorded was 1.3 μg L^{-1}, and its mean concentration was 0.4 μg L^{-1}.

Figures 2 and 3 show the patterns of the concentrations of ibuprofen and paracetamol in the samples in relation to the flow rates in the catchments.

The Cancela-Tamandaí catchment shows the highest concentrations of both compounds, but the Vacacaí river

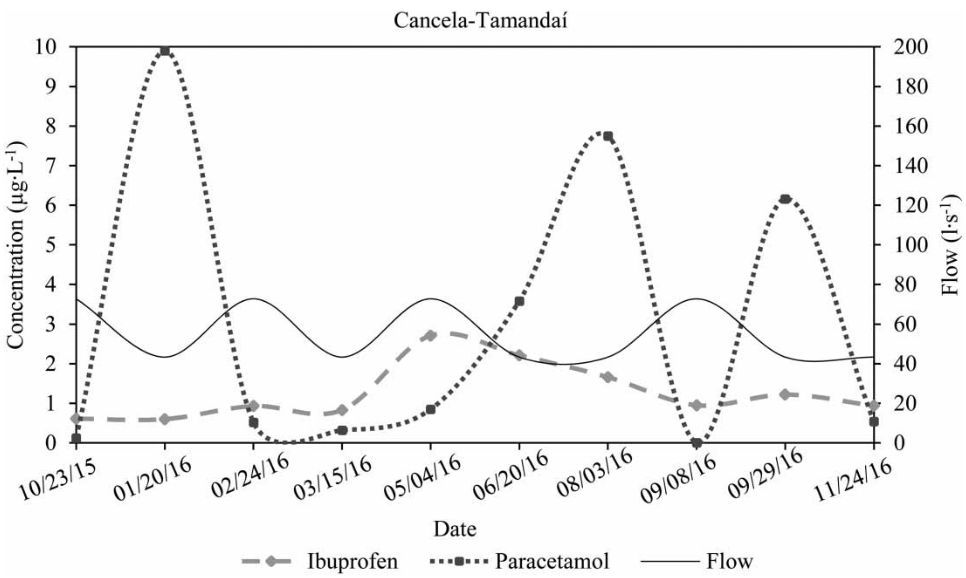

Figure 2 | Flow rates and concentrations of ibuprofen and paracetamol in the Cancela-Tamandaí catchment, river Vacacaí.

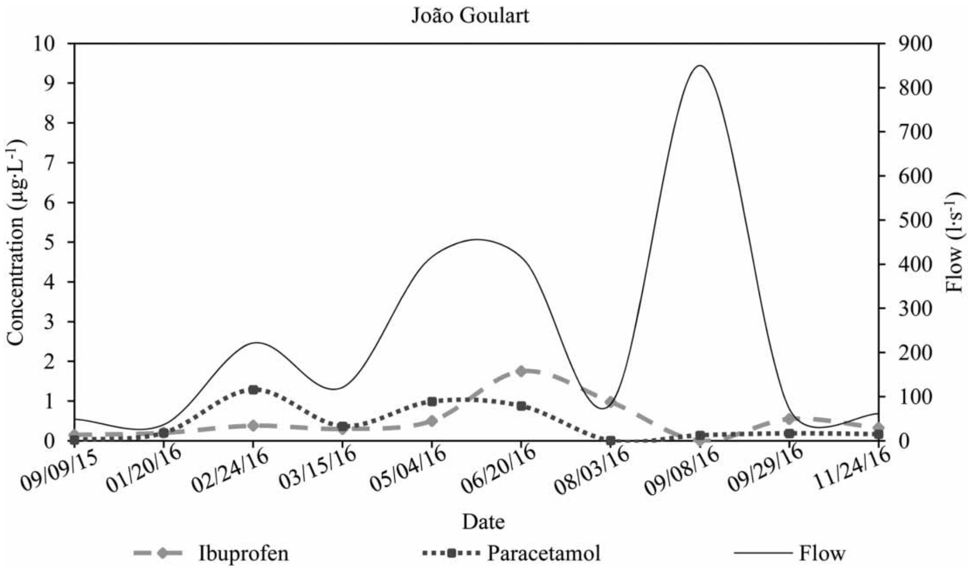

Figure 3 | Flow rates and concentrations of ibuprofen and paracetamol in the João Goulart catchment, river Vacacaí-Mirim.

has a lower flow rate than the Vacacaí Mirim river in the João Goulart catchment. The sample results also show that the highest concentrations of these compounds, in both catchments, were recorded during lower flow periods. This finding is in agreement with a study carried out by Campanha *et al.* (2015) in the southeast of Brazil, where the concentrations of emerging contaminants were higher during the dry season because of the lower water levels in the Monjolinho River.

The loads of the hormone ethisterone and pharmaceuticals ibuprofen and paracetamol, discharged daily to each of the water bodies in the two catchments studied, were calculated, and results are shown in Table 3. Only those that were detected in their collection data were calculated as loads of the compounds.

The highest contaminant loads were recorded in the João Goulart catchment as its water body has higher flows than the water body in the Cancela-Tamandaí catchment, even though lower concentrations of the contaminants were observed in João Goulart. The hydrodynamic difference between the two water bodies studied, such as the flow rate, was the main factor responsible for the difference in the contaminant loads in the rivers. The variability in the loads found between the two catchments may be associated with the different patterns of pharmaceuticals use by the inhabitants, the availability of wastewater treatment services, and the different dynamics of each catchment (Torres *et al.* 2015).

In the Cancela-Tamandaí catchment, the sample collected on 04 May 2016 stands out, as it shows that approximately 17 g of ibuprofen were discharged into the water body. The highest loads of paracetamol were observed in the same catchment, with 37 g on 20 January 2016, 29 g on 03 August 2016, and 23 g on 29 September 2016.

In the João Goulart catchment, a discharge of approximately 63 g of ibuprofen was recorded on 20 June 2016. On the same day, the release of paracetamol was approximately 32 g.

Analysis of variance

One-way ANOVA was used to compare the spatial difference between pharmaceutical loads in water ($p < 0.05$). ANOVA is used to test if the averages of more than two independent groups are different from each other (Bilgin & Konanç 2016).

ANOVA is commonly used in surface water assessment studies based on physical, chemical, and biological water quality variables such as dissolved oxygen, total dissolved solids, biological oxygen demand, and

Table 3 | Hormone and pharmaceutical loads in the Cancela-Tamandaí and João Goulart catchments

Catchment	Samples	Date	Ethisterone (g day^{-1})	Ibuprofen (g day^{-1})	Paracetamol (g day^{-1})
Cancela-Tamandaí	1	23 Oct 2015	–	3.835	0.754
	2	20 Jan 2016	–	2.247	37.068
	3	24 Feb 2016	–	5.846	3.269
	4	15 Mar 2016	–	3.108	1.198
	5	04 May 2016	–	17.036	5.343
	6	20 June 2016	–	8.275	13.404
	7	03 Aug 2016	0.198	6.215	29.018
	8	08 Sep 2016	–	5.972	–
	9	29 Sep 2016	–	4.568	23.064
	10	24 Nov 2016	–	3.520	2.022
	Mean			6.062	12.793
João Goulart	1	09 Sep 2015	–	–	–
	2	20 Jan 2016	–	0.634	0.634
	3	24 Feb 2016	–	7.271	24.682
	4	15 Mar 2016	–	3.135	3.866
	5	04 May 2016	–	17.985	35.609
	6	20 June 2016	–	62.946	31.653
	7	03 Aug 2016	–	6.990	–
	8	08 Sep 2016	–	–	10.281
	9	29 Sep 2016	–	3.456	1.194
	10	24 Nov 2016	–	1.744	0.898
	Mean			13.020	13.602

Note: (–): below the detection limit.

Table 4 | ANOVA for the pharmaceutical loads in the Cancela-Tamandaí and Joao Goulart catchments

	Parameters	
Catchment	Ibuprofen	Paracetamol
João Goulart	3.30a	2.53a
Cancela-Tamandaí	5.20a	4.31a

Note: Medians followed by the same letter indicate no statistically significant differences using Kruskal-Wallis with probability = 0.05 (a-a: catchments do not differ statistically).

Escherichia coli (Bilgin & Konanç 2016; Achieng' *et al.* 2017). However, to date, few studies have made use of ANOVA for the assessment of hormones and pharmaceuticals in surface waters.

The analysis of pharmaceutical loads showed no statistically significant differences for ibuprofen and paracetamol between the two catchments ($p < 0.05$), as indicated in Table 4.

Singh *et al.* (2014) investigated the presence of pharmaceuticals in two urban water bodies in India. They used the Kruskal-Wallis test and observed the heterogeneous spatial distribution of the concentration of these substances in the two areas, with statistically significant differences for diclofenac, naproxen, carbamazepine, and trimethoprim. However, no statistical differences were found for ibuprofen and ketoprofen.

CONCLUSION

The study analyzed the presence of pollutants, in the form of pharmaceutical and hormonal compounds, in two water bodies in the city of Santa Maria, in southern Brazil. The concentrations of 17 β-estradiol, estriol, estrone, and megestrol acetate never exceeded the detection limit of the analytical method used. Diclofenac was not detected in any of the samples collected in the two catchments. The high detection limits of the method may have contributed to the non-detection of these compounds.

Ethisterone, a hormone, was detected in one sample in the Cancela-Tamandaí catchment, with a concentration of 0.053 μg L^{-1}. In the João Goulart catchment, ethisterone concentrations in all samples were below the detection limit.

Two anti-inflammatory drugs, ibuprofen and paracetamol, were detected in several samples collected in both catchments in this study. The recurring presence of these substances is a sign of the level of water quality degradation in these bodies.

One-way ANOVA did not show any statistically significant differences between the two water bodies for ibuprofen and paracetamol.

Precarious public and sustainability policies aimed at encouraging the correct disposal of medicines and inadequate collection and treatment of sanitary effluents contributed to the degradation of water quality in the Cancela-Tamandaí and João Goulart catchments. In addition to public agencies, private pharmaceutical companies should conduct awareness campaigns regarding the correct use and disposal of pharmaceuticals.

This study may contribute to the diagnosis of surface water contamination by emerging contaminants, and may also encourage further studies in these and other water bodies. More work is also needed on sediments, and the breakdown and movement of these contaminants in the environment. Other emerging compounds should be analyzed in water bodies for a more comprehensive understanding of the impacts of these compounds on aquatic fauna and flora, beyond the risks to human health.

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