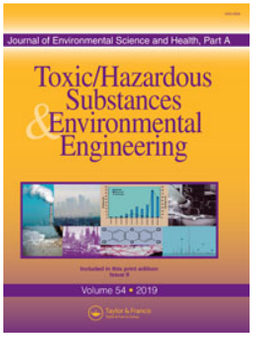

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Assessing the presence of endocrine disruptors and markers of anthropogenic activity in a water supply system in northeastern Brazil

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ABSTRACT

Several chemical substances known as micropollutants are used in daily activities, and they pose risks to both human health and the environment. Some of these substances disrupt the endocrine system in addition to being responsible for major public health issues and for endangering some aquatic species. The aim of this research is to investigate the frequency of endocrine disruptors and anthropogenic activity markers in a Water Supply System (SAA) in Sergipe State, Brazil. Twenty-two water samples were collected from five SAA points from 2016 to 2017. They were prepared through solid phase extraction and analyzed in a gas chromatographer coupled to a mass spectrometer. In total, 13 compounds (diethyl phthalate, dibutyl phthalate, nonylphenol, pentachlorophenol, bisphenol A, androstane, estrone, estradiol, 17 α-ethinyl estradiol, progesterone, coprostanol, cholesterol and caffeine) that are endocrine disruptors and antrophic activity markers were herein assessed – both in raw (underground and surface) and treated water (distribution system and reservoir) samples. Based on our results, 50% of the samples contained caffeine; 45.5%, cholesterol; 31.81%, diethyl phthalate; 31.81%, dibutyl phthalate; 18.18%, bisphenol A; and 4.54%, estradiol. Therefore, it is important to create and implement public policies focused on public health and on assuring the safety of aquatic ecosystems.

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Introduction

Chemical substances are part of humans' daily lives, but many of them – known as micropollutants – are organic and inorganic compounds that pose risks to both human health and the environment, even at low concentrations (μg L^{-1} and ng L^{-1}). These micropollutants comprise a wide variety of chemical compounds such as pharmaceutical and personal care products, hormones, surfactants, and pesticides.[1–3]

According to previous research, several micropollutants can cause changes to the human endocrine system; therefore, they stand out among the largest public health issues. Endocrine disruptors (EDs) are hormone-active compounds capable of disrupting the endocrine systems of humans and animals, even at low concentrations.[1,2,4–7] According to the World Health Organization,[2] approximately 800 chemical substances have impacts or are suspected to have impacts on the endocrine system; however, only a few chemical compounds were already investigated through scientific tests. The results have demonstrated the endocrine effects these compounds have on humans and animals.

Humans are exposed to endocrine disruptors by ingesting contaminated food and water, inhaling gases and particulates and absorbing them through the skin. Pregnant women can transmit these compounds to their fetuses through the placenta and to their newborns through breast milk.[8] Research on the impacts of the exposure to endocrine disruptors conducted in the last few years has highlighted the effects of these substances on the growth, development and reproduction of humans and animals.[9]

Pontelli et al.[10] associated endocrine disruptors with human obesity. The larger number of obesity cases recorded currently is a concern given the potential impact of these cases on health systems. Obesity is the major risk factor for the most common chronic diseases, such as diabetes and cardiovascular issues. According to estimates of the World Health Organization,[2] there are 1.5 billion overweight or obese adults worldwide, and the number of cases of type 2 diabetes has increased from 153 million to 347 million between 1980 and 2008. Costa et al.[7] emphasized that several endocrine disruptors, such as pesticides, bisphenol A (BPA), phthalates, dioxins and phytoestrogens,

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penetrate the female reproductive system and cause endocrine disruption.

The herein assessed substances, which can reach the natural environment due to inefficient or inexistent treatment, can disrupt animal reproduction and development and induce the development of female sexual characteristics in male fish, a result that can cause sterilization or population reduction.[11] Aquatic organisms are particularly important targets of these substances because these organisms are often exposed to compounds found in domestic and industrial waste. Many fish species living downstream of domestic sewage discharge points presented feminization characteristics, such as testes malformation, and some specimens were hermaphroditic.[12]

Micropollutants responsible for endocrine disruption are found in environmental matrices such as sewage, receiving bodies, sediments, biological sludge and even in water collected in supply systems.[13] These findings explain the qualitative and quantitative changes observed in drinking water in Brazil. The improper raw sewage disposal and the technologies used in Water and Sewage Treatment Stations highlight the need for creating public policies focused on improving basic sanitation conditions and on developing and implementing new technologies in order to eliminate particulates that are transferred to drinking water.[5]

Leusch et al.[14] analyzed endocrine disruptors in drinking water, surface water, and treated wastewater collected in six countries. Twenty-three (23) of the 58 chemical substances monitored by these authors recorded rates higher than the Limit of Quantification (LQ) established for water samples. These substances included drugs such as diclofenac, carbamazepine and atenolol – their concentrations in treated wastewater were expressed in micrograms per liter ($\mu g\ L^{-1}$). Triclosan (which is used in personal hygiene), bisphenol A (industrial compound) and diuron (herbicide) concentrations were expressed in nanograms per liter ($ng\ L^{-1}$) – these substances were also detected in surface water. The aforementioned authors detected nine compounds (among them, BPA and caffeine) in drinking water samples – their concentrations were expressed in $ng\ L^{-1}$.

Tröger et al.[15] used the multiresidue screening method to simultaneously measure a wide range of micropollutants in drinking water samples in Sweden. Forty-one (41) of the 134 pollutants investigated by them weredetected in at least one sample – their individual concentrations were expressed in $ng\ L^{-1}$.

Twenty-seven (27) of the 84 chemicals monitored by Glassmeyer et al.[16] in the United States were observed in the assessed water source (at least once), and 21 of them were detected in treated drinking water (at least once). According to these authors, the collected data provided information about the dysregulating contaminants found in surface, ground and drinking water.

Machado et al.[17] investigated 100 drinking water samples collected in 22 Brazilian capitals to find emerging contaminants belonging to different classes, including hormones, plasticizers, herbicides, triclosan and caffeine. They found caffeine, triclosan, atrazine, phenolphthalein and bisphenol A in at least one of the samples collected during the two sampling campaigns. Caffeine and atrazine were the most frequently identified substances in drinking water samples and in samples collected in water supply systems.

It is important to investigate the presence of these endocrine disrupting micropollutants in water bodies because they pose different risks to both human health and the environment. The aim of this study was to identify the presence of endocrine disruptors in water samples collected in the Supply System of Rosário do Catete County, Sergipe State, Brazil.

Materials and methods

Study site

The small Water Supply System (SAA) located in the rural area of Rosário do Catete County, Sergipe State, was our study site. Samples were collected between February 2016 and January 2017, throughout the dry and rainy seasons. Five (5) analysis points were determined, and their locations and geographic coordinates are shown in Figure 1 and in Table 1, respectively.

Caldas Source (P1) and Stream (P5) are close to an intermunicipal highway, and the water rising in them is captured by pumps that transfer it to the city reservoir. Cipó well (P2) is 42 meters deep, and its groundwater is also pumped to the reservoir.

The reservoir (P3) is fed by water from points P1 and P2, and its water is distributed to the population after a simple treatment. P4 belongs to the distribution network and provides water for human consumption (Fig. 2).

A DJI drone model MAVIC Pro (Shenzhen, Chine) was used to capture aerial images of areas surrounding the study site and to depict possible anthropic impacts caused by soil use and occupation on the assessed SAA (Fig. 3).

According to the recorded images (Fig. 3), there is a sugarcane crop by the studied water source, a fact that can negatively impact water quality. We also took into account the possible use of agrochemicals in the region given the agricultural activity in the area, not to mention the livestock and mining activities.

Rosário do Catete County lies in the Japaratuba River basin, which crosses twenty Sergipe counties. Only 5 of these counties have their entire territory in the basin area (Capela, Carmópolis, Cumbe, General Maynard and Rosário do Catete), whereas other counties only have part of their territories in it. The soil in this basin has been occupied by livestock farms and sugarcane crops for two centuries.[18]

Based on the aerial images, there is a small ciliary forest remnant protecting both Caldas Source and Cipó Well. These images complied with the literature, which describes this environment as an agricultural area covered with sugarcane crops and livestock farms.

Endocrine disruptor determination through SPE-GC/MS

Water samples were prepared through chromatographic analysis, which was applied to the compounds of interest, based

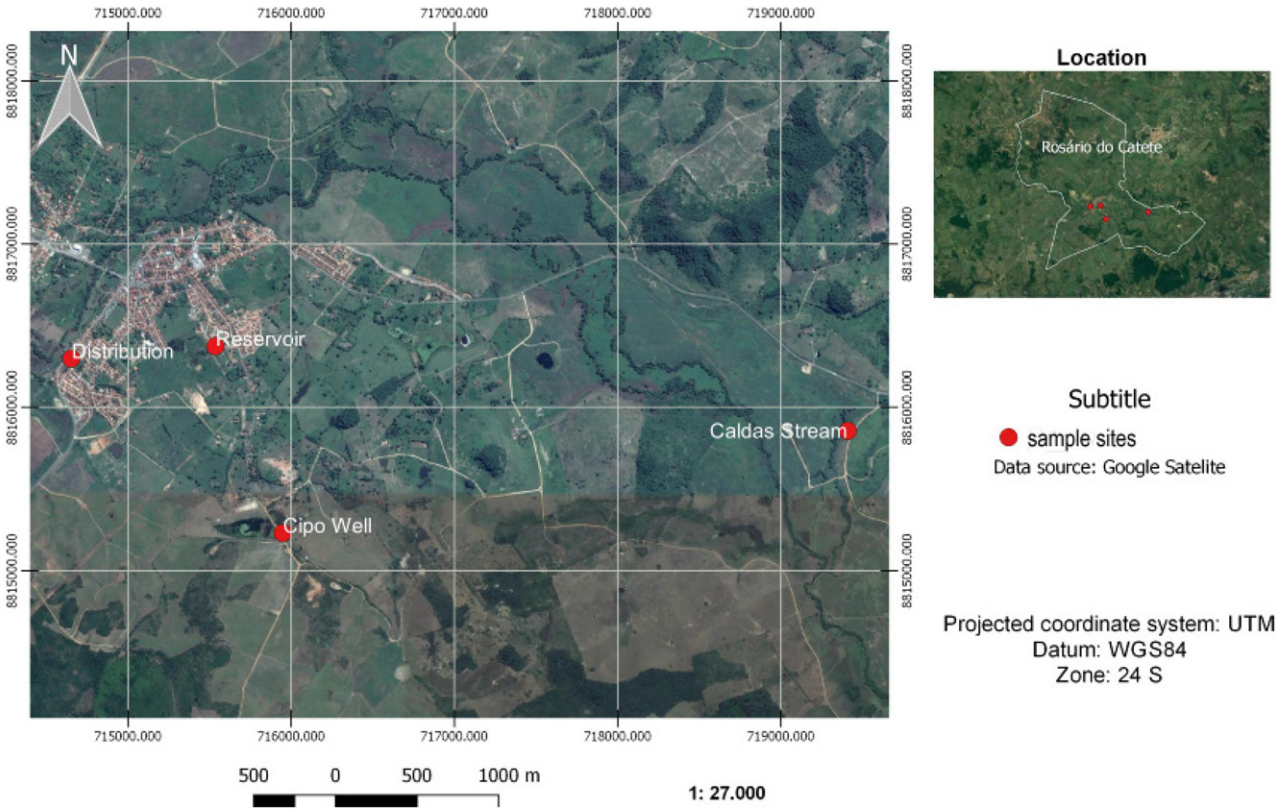

Figure 1. Geospatial location of the water collection points. Source: Google Earth, 2018.

Table 1. Geographical coordinates of the collection points of the assessed water supply system.

Point	Description	Geographic coordinates WSG 84
P1	Caldas source (raw water, groundwater)	10°42′ 20.21″ S/36°59′ 38.03″ O
P2	Cipó well (raw water, groundwater)	10°42′ 41.30″ S/37°01′ 31.84″ O
P3	Reservoir (drinking water)	10°42′ 04.23″ S/37°01′ 45.63″ O
P4	Distribution (drinking water)	10°42′ 06.89″ S/37°02′ 14.67″ O
P5	Caldas stream (raw water, superficial)	10°42′ 20.21″ S/36°59′ 38.03″ O

on Otomo,[19,20] Souza[21] and Oliveira.[22] Samples were filtered in a vacuum filtration system by using 0.45-μm membranes to retain the suspended solids. Samples were then acidified with dilute hydrochloric acid solution to pH 3 (after filtration), so they could be used for further solid phase extraction. The cartridges used in the extraction (C18) were conditioned in 5 mL of methanol (MeOH), which was followed by 5 mL of ultrahigh MeOH/H_2O at pH 3 (1:9 v/v). One liter (1 L) of the previously filtered and acidified samples was percolated into the cartridge at an approximate flow rate of 6 mL min^{-1}. The cartridges were washed in 5 mL of ultrapure MeOH/H_2O (1:9 v/v) – after percolation was complete – in order to remove possible matrix interferants. The cartridges were centrifuged for 20 minutes at 2500 rpm (revolutions per minute) to remove all water from them.

The elution step was run twice, in sequence, by using 5 mL of dichloromethane (DCM) and MeOH (6:4 v/v). A pipette was used to transfer the resulting solution to a vial (2 mLvolume), so it could evaporate through gentle N_2 flow (<30 ml min^{-1}). The aliquot of 100 μL of derivatizing agent (N,O-Bis(trimethylsilyl)trifluoroacetamide – BSTFA with trimethylchlorosilane – TMCS) was added to the dry residue in the vial, which was oven-heated at 100 °C for 30 minutes and then cooled and diluted to 1 mL in DCM. The chromatographic analyses were conducted on the same day the analytes were derivatized.

The parameters adopted for the GC analysis were also based on Otomo,[19,20] Souza[13,21] and Oliveira:[22] injector and interface temperature = 300 °C, source-ion flow temperature = 230 °C and column ramp temperature from 80 °C to 300 °C. The chromatographic analysis lasted 21 minutes, in total, at a column flow rate of 1.9 mL min^{-1}, total flow of 28 mL min^{-1} and total pressure of 123.9 kPa. A RTX5MS chromatographic column was used (Restek crossbond 5% diphenyl/95% dimethyl polysiloxane, 30 cm length × 0.25 mm diameter × 0.25 μm film thickness). Helium (99.99% purity) was the carrier gas. MS data were collected through the SIM mode (Single Ion Monitoring) by using 3 to 4 mass fragments of each compound (Table 2).

Linearity

Table 3 shows the action ranges of each compound and their determination coefficients. The coefficients were found through line equations of different calibration curves, based on the study matrix.

The accuracy (result dispersions between independent trials) of our study was found by estimating the relative standard deviation (DPR), also known as coefficient of variation (CV). All the measurements showed coefficients of variation

Figure 2. Points established for water collection.

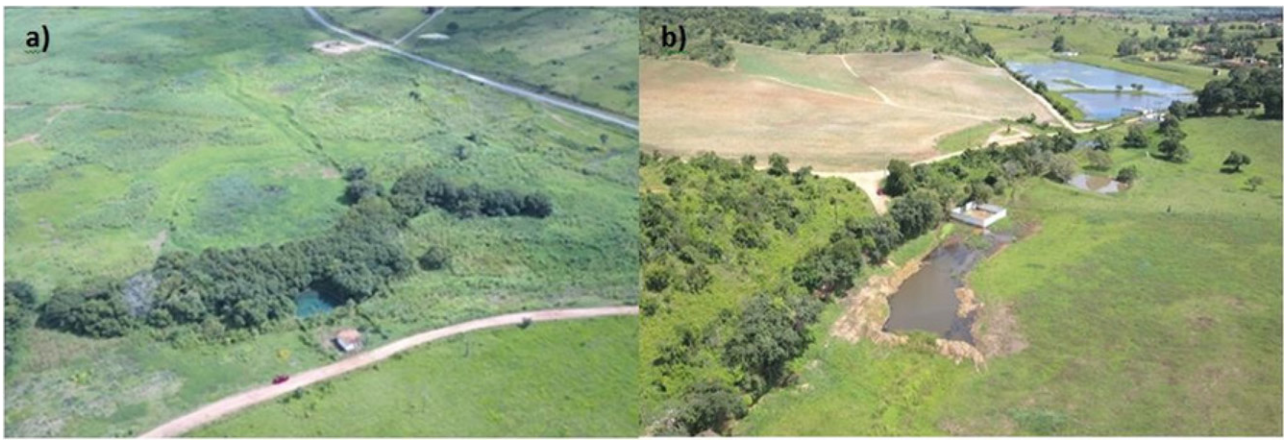

Figure 3. Drone images: (a) Caldas Source – riparian forest remnant close to the water source and (b) Cipó well – wetlands, crops, pasture and dams in its surroundings.

Table 2. Mass/load ratios (m/z) of the 13 assessed compounds and their respective monitoring intervals.

Compound	Time interval (minutes)	Ch1 (m/z)	Ch2 (m/z)	Ch3 (m/z)	Ch4 (m/z)
Diethyl phthalate	5.00 to 8.75	149*	176	177	
Nonylphenol	8.75 to 10.00	207*	221	235	
Caffeine	10.00 to 10.48	193*	194		
Pentachlorophenol	10.48 to 10.75	321	323	325*	
Dibutyl phthalate	10.75 to 11.48	104	149*	150	
Androstano	11.48 to 12.00	135*	203	245	
Bisphenol A	12.00 to 13.00	357*	358	372	
Estrone	13.00 to 15.35	218	257	342*	285
Estradiol	13.00 to 15.35	218	257	342*	285
17α-Ethinylestradiol	15.35 to 15.75	105	135	285	286
Progesterone	15.75 to 17.00	124	147*	314	
Coprostanol	17.00 to 18.80	215	355	370	
Cholesterol	18.80 to 19.80	107	129*	215	

*Mean major fragments.

Table 3. Action ranges and determination coefficients of the assessed compounds based on the surface water matrix of the used calibration curves.

	Action range (μg mL^{-1})		r^2	
Compound	Minimum	Maximum	1st collection	2nd collection
Diethyl phthalate	0.002	0.045	0.988	0.998
Nonylphenol	0.002	0.080	0.996	0.999
Caffeine	0.003	0.104	0.997	0.998
Pentachlorophenol	0.025	0.500	0.986	0.999
Dibutyl phthalate	0.002	0.042	0.990	0.998
Androstano	0.009	0.180	0.994	0.994
Bisphenol A	0.001	0.050	0.997	0.999
Estrone	0.005	0.250	0.997	0.993
Estradiol	0.005	0.250	0.996	0.994
17α-Ethinylestradiol	0.006	0.300	0.997	0.993
Progesterone	0.056	1.120	0.996	0.999
Coprostanol	0.006	0.300	0.994	0.991
Cholesterol	0.011	0.550	0.996	0.997

below 20% DPR in the trace or impurity analysis – which is an acceptable result.[23]

Results and discussion

Determination of endocrine disruptors

We assessed the time distributions of 13 compounds (diethyl phthalate, dibutyl phthalate, nonylphenol, pentachlorophenol, bisphenol A (BPA), androstane, estrone, estradiol, 17 17α-ethinyl estradiol, progesterone, coprostanol, cholesterol and caffeine) found in samples of all the water treatment processes. Seven (7) of the 13 evaluated compounds recorded numbers above the acceptable quantification limit: diethyl phthalate, dibutyl phthalate, bisphenol A, androstane, estradiol, cholesterol and caffeine. Tables 4 and 5 present the determination results of the compounds of interest as well as the measurement uncertainties of 22 raw and treated water samples recorded during the experimental period (2016–2017).

There was androstane in 9.09% of the samples collected in the distribution network (P4) ($0.027 \pm 0.003\ \mu g\ L^{-1}$) and in the reservoir (P3) ($0.018 \pm 0.002\ \mu g\ L^{-1}$) in August 2016.

There was bisphenol A in 18.18% of the samples. The highest bisphenol A value recorded in Caldas Source (P1) was $0.043 \pm 0.005\ \mu g\ L^{-1}$ (January 2017), and the lowest one was $0.006 \pm 0.001\ \mu g\ L^{-1}$ (July 2017). Leusch et al.[14] conducted a similar study in Germany, Australia, France, South Africa, Holland and Spain and detected BPA (at concentration $0.165\ \mu g\ L^{-1}$) in four surface water samples. Kuch and Ballschmiter[24] found BPA (at concentrations ranging from 0.0003 to $0.002\ \mu g\ L^{-1}$) in treated water collected in Southern Germany. Valcárcel et al.[25] found bisphenol A (BPA) (at concentration $0.051\ \mu g\ L^{-1}$) in a sample of treated water collected in Madrid, Spain.

There was caffeine in 50% of the collected samples. Its highest value was $0.45 \pm 0.04\ \mu g\ L^{-1}$, which was in samples collected in Caldas Stream (P5) (July 2017), and its lowest value was $0.004 \pm 0.001\ \mu g\ L^{-1}$, which was in samples from Caldas Stream (P5) (February 2016). Four treated water samples also presented caffeine: in the distribution network, P4, $0.14 \pm 0.01\ \mu g\ L^{-1}$ (August 2016) and 0.008 ± 0.001 (January 2017), and in the reservoir, P3, $0.014 \pm 0.001\ \mu g\ L^{-1}$ (August 2016) and 0.19 ± 0.02 (July 2017).

Machado et al.[17] found caffeine in drinking water samples at concentrations ranging from $0.0018\ \mu g\ L^{-1}$ to values higher than $2.0\ \mu g\ L^{-1}$. Caffeine concentrations in the water source ranged from $0.04\ \mu g\ L^{-1}$ to $19\ \mu g\ L^{-1}$ in their study. The amount of caffeine in treated water samples indicated the presence of domestic sewage in water, since caffeine is an anthropogenic compound.

There was cholesterol in 45.45% of the collected samples. The highest cholesterol value was $0.09 \pm 0.01\ \mu g\ L^{-1}$ in samples collected in Caldas Stream (P5) in July 2017, and its lowest value, $0.005 \pm 0.001\ \mu g\ L^{-1}$, was in samples collected in the reservoir (P3) in January 2016.

There was diethyl phthalate in 31.81% of the samples. The highest value was $0.024 \pm 0.001\ \mu g\ L^{-1}$ in samples collected in Caldas Source in August 2016, and its lowest value

Table 4. Endocrine disruptors in treated-water samples collected between February 2016 and July 2017.

Compounds	QL $\mu g\ L^{-1}$	Distribution Feb/16	Distribution Jul/16	Distribution Aug/16	Distribution Jan/17	Distribution Jul/17	Reservoir Feb/16	Reservoir Jul/16	Reservoir Aug/16	Reservoir Jan/17	Reservoir Jul/17
Androstano ($\mu g\ L^{-1}$)	0.005	<QL	<QL	0.027 ± 0.003	<QL	<QL	<QL	<QL	0.018 ± 0.002	<QL	<QL
Bisphenol A ($\mu g\ L^{-1}$)	0.001	<QL	<QL	<QL	0.013 ± 0.004	<QL	<QL	<QL	<QL	0.043 ± 0.005	<QL
Caffeine ($\mu g\ L^{-1}$)	0.003	<QL	<QL	0.14 ± 0.01	0.008 ± 0.001	<QL	<QL	<QL	0.014 ± 0.001	<QL	0.19 ± 0.02
Cholesterol ($\mu g\ L^{-1}$)	0.002	<QL	0.005 ± 0.002	0.053 ± 0.003	0.04 ± 0.01	<QL	0.005 ± 0.001	0.043 ± 0.002	0.014 ± 0.002	0.007 ± 0.002	<QL
Coprostanol ($\mu g\ L^{-1}$)	0.004	<QL	<QL	<QL	<QL	<QL	<QL	<QL	<QL	<QL	<QL
Dibutyl phthalate ($\mu g\ L^{-1}$)	0.002	<QL	<QL	0.034 ± 0.003	0.0020 ± 0.0003	<QL	<QL	<QL	<QL	<QL	<QL
Diethyl phthalate ($\mu g\ L^{-1}$)	0.002	<QL	<QL	0.019 ± 0.001	<QL	<QL	<QL	<QL	<QL	<QL	<QL
Estrone ($\mu g\ L^{-1}$)	0.001	<QL	<QL	<QL	<QL	<QL	<QL	<QL	<QL	<QL	<QL
Estradiol ($\mu g\ L^{-1}$)	0.001	<QL	<QL	<QL	<QL	<QL	<QL	<QL	<QL	<QL	<QL
Ethinylestradiol ($\mu g\ L^{-1}$)	0.001	<QL	<QL	<QL	<QL	<QL	<QL	<QL	<QL	<QL	<QL
Nonylphenol ($\mu g\ L^{-1}$)	0.002	<QL	<QL	<QL	<QL	<QL	<QL	<QL	<QL	<QL	<QL
Pentachlorophenol ($\mu g\ L^{-1}$)	0.002	<QL	<QL	<QL	<QL	<QL	<QL	<QL	<QL	<QL	<QL
Progesterone ($\mu g\ L^{-1}$)	0.011	<QL	<QL	<QL	<QL	<QL	<QL	<QL	<QL	<QL	<QL

*Quantification of Limit.

Table 5. Endocrine disruptors in raw-water samples collected between February 2016 and July 2017.

Compounds	QL*	Caldas stream Feb/16	Caldas stream Aug/16	Caldas stream Jan/17	Caldas stream Jul/17	Caldas source Jul/16	Caldas sources Aug/16	Caldas sources Jan/17	Caldas sources Jul/17	Cipó well Jul/16	Cipó well Aug/16	Cipó well Jan/17	Cipó well Jul/17
Androstano (μg L^{-1})	0.005	<QL	<QL	<QL	<QL	<QL	<QL	<QL	<QL	<QL	<QL	<QL	<QL
Bisphenol A (μg L^{-1})	0.001	<QL	<QL	<QL	<QL	<QL	<QL	<QL	0.006 ± 0.001	<QL	<QL	0.010 ± 0.001	<QL
Caffeine(μg L^{-1})	0.003	0.004 ± 0.001	0.036 ± 0.003	<QL	0.45 ± 0.04	<QL	0.19 ± 0.01	<QL	0.14 ± 0.02	<QL	0.029 ± 0.002	0.076 ± 0.004	<QL
Cholesterol(μg L^{-1})	0.002	<QL	<QL	0.005 ± 0.002	0.09 ± 0.01	<QL	<QL	<QL	<QL	<QL	<QL	0.014 ± 0.002	<QL
Coprostanol (μg L^{-1})	0.004	<QL	<QL	<QL	<QL	<QL	<QL	<QL	<QL	<QL	<QL	<QL	<QL
Dibutyl phthalate(μg L^{-1})	0.002	<QL	0.006 ± 0.001	<QL	<QL	<QL	0.068 ± 0.003	0.0024 ± 0.0002	<QL	<QL	0.0065 ± 0.0005	0.0091 ± 0.0005	<QL
Diethyl phthalate(μg L^{-1})	0.002	0.0024 ± 0.0002	0.0054 ± 0.0005	0.0024 ± 0.0002	<QL	<QL	0.024 ± 0.001	0.0026 ± 0.0004	<QL	<QL	0.017 ± 0.001	<QL	<QL
Estrone(μg L^{-1})	0.001	<QL	<QL	<QL	<QL	<QL	<QL	<QL	<QL	<QL	<QL	<QL	<QL
Estradiol (μg L^{-1})	0.001	<QL	<QL	<QL	<QL	<QL	<QL	<QL	0.014 ± 0.003	<QL	<QL	<QL	<QL
Ethinylestradiol (μg L^{-1})	0.001	<QL	<QL	<QL	<QL	<QL	<QL	<QL	<QL	<QL	<QL	<QL	<QL
Nonylphenol(μg L^{-1})	0.002	<QL	<QL	<QL	<QL	<QL	<QL	<QL	<QL	<QL	<QL	<QL	<QL
Pentachlorophenol (μg L^{-1})	0.002	<QL	<QL	<QL	<QL	<QL	<QL	<QL	<QL	<QL	<QL	<QL	<QL
Progesterone (μg L^{-1})	0.011	<QL	<QL	<QL	<QL	<QL	< QL	<QL	<QL	<QL	<QL	<QL	<QL

*Quantification of Limit.

was 0.0024 ± 0.0002 μg L^{-1} in samples collected in Caldas Stream in February 2016 and in January 2017. The distribution network sample (P4) also showed diethyl phthalate at 0.019 ± 0.001 μg L^{-1} concentration.

There was dibutyl phthalate in 31.81% of the samples. The highest value was 0.068 ± 0.003 μg L^{-1} in samples collected in Caldas Source in August 2016, and its lowest value was 0.0020 ± 0.0003 μg L^{-1}, which was in samples collected in the distribution network in January 2017. Leusch et al.[14] detected this plasticizer in five of the six drinking water samples analyzed in their study.

There was estradiol at 0.014 ± 0.003 μg L^{-1} concentration in samples collected in Caldas Source in July 2017. Results by Leusch et al.[14] recorded for drinking water indicated 17α-estrone, 17β-estradiol and the contraceptive 17α-ethinylestradiol at maximum concentrations of 0.0003 to 0.0021 μg L^{-1} from samples collected at different sampling points in Germany.[24] The analysis of estrogenic compounds was also performed in surface water collected in the Langat River, Malaysia,[26] where natural estrone was not detected at any sampling point. However, 17β-estradiol was detected in samples collected at two sampling points, and its concentration ranged from 0 to 0.000004 μg L^{-1}; estriol was observed in three points (0 to 0.000002 μg L^{-1}) and synthetic 17α-ethynylestradiol in four sampling points (0 to 0.00002 μg L^{-1}).

P4 (distribution) provided the treated-water sample presenting the highest rate of DEs in samples collected in August 2016 – the sum of compounds was equal to 0.273 μg L^{-1}. Phthalates (dibutyl phthalate and diethyl phthalate) was found in water collected at this sampling point; it is derived from plastic materials used in the supply network itself (pipes and taps, for example). There was caffeine – an anthropic activity marker – as well as androstane and cholesterol strains in this sample. Such a finding indicates that the applied simplified water treatment was not efficient in protecting water from these substances (Fig. 4).

Raw water samples from Caldas Stream (P5) stood out among the other samples – caffeine (Fig. 5) recorded the highest concentration, 0.45 ± 0.04 μg L^{-1}, in these samples. A cholesterol concentration of 0.09 ± 0.01 μg L^{-1} was also observed in this sample.

Our results evidence values lower than some results in the literature. Otomo[20] observed 14 organic compounds in Guarapiranga dam, São Paulo State. He recorded maximum concentrations of 1.06 μg L^{-1} and 12.9 μg L^{-1} for bisphenol A and dibutyl phthalate, respectively. DEs recorded cholestanol and cholesterol at 0.11 μg L^{-1} and 12.81 μg L^{-1}, respectively, based on the human-activity tracer class.

Conclusions

The compounds assessed in this study are not controlled by national legislation. A gas chromatographer coupled to a mass spectrometer was used to detect them, based on the number of parts per trillion (ppt). This methodology was efficient for finding endocrine disruptors and anthropic activity markers in samples collected in the Water Supply System of Rosário do Catete County.

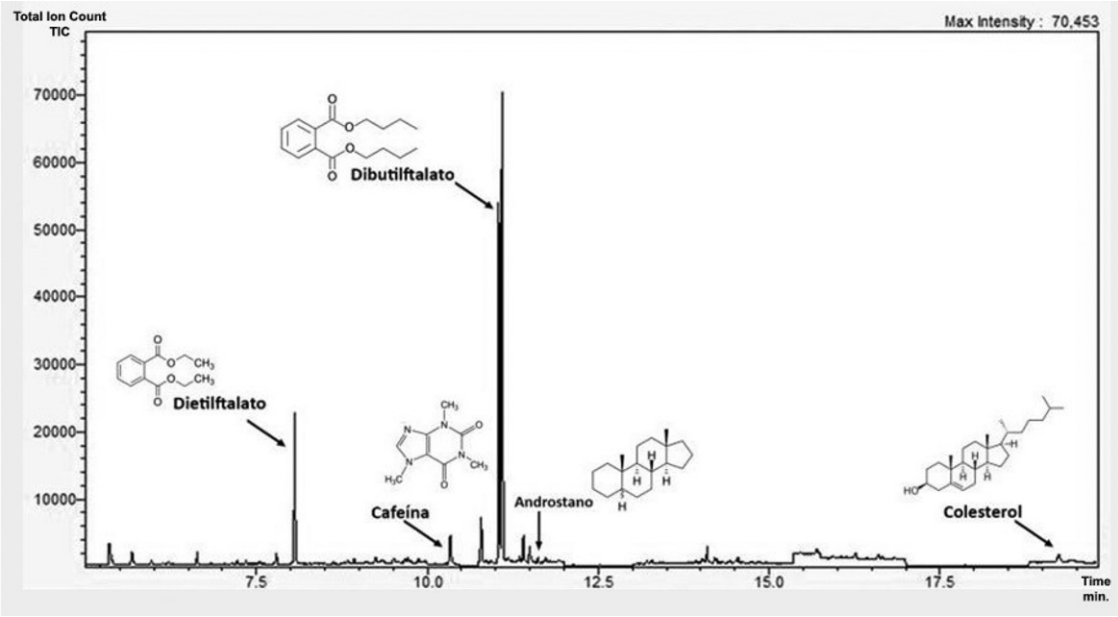

Figure 4. Chromatogram of the total ion count (TIC) applied to the treated-water sample (Distribution, P4, August 2016).

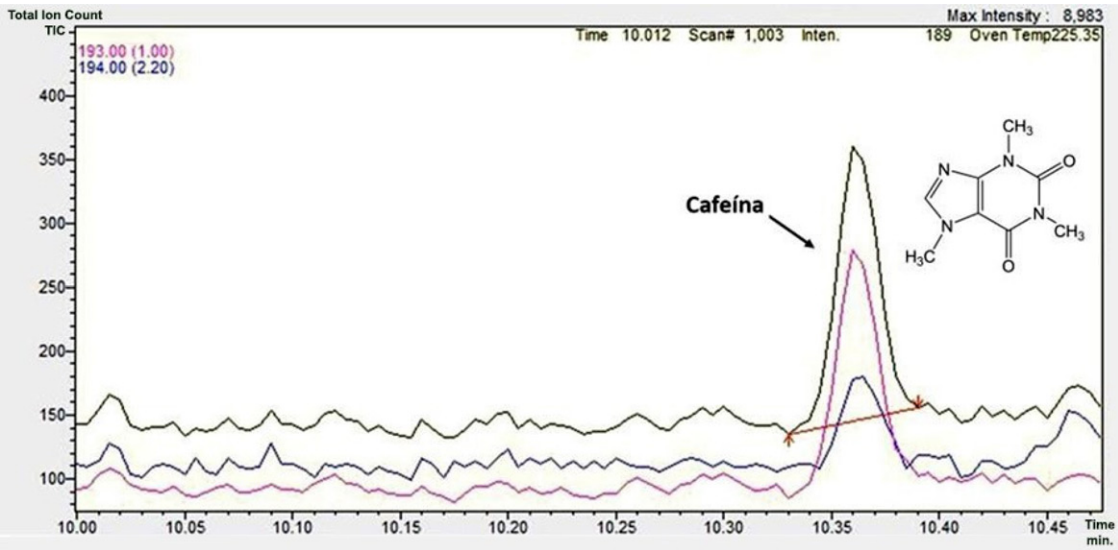

Figure 5. Chromatogram in SIM mode (Single Ion Monitoring) to monitor specific fragments in samples of raw water (Caldas Creek, P5, July 2017).

The origin of phthalates (diethyl phthalate and dibutyl phthalates), caffeine and cholesterol found in the underground water source, which is an abstract source for public supply, must be further investigated, as well as the presence of five DEs (diethyl phthalate, dibutyl phthalate, caffeine, androstane and cholesterol) at a distribution point (treated water).

Technologies that are available to identify and quantify endocrine disrupting compounds in different matrices highlight the relevance of including the compounds in national control and urging their inclusion, with maximum permissible limits, in legislation to assure the supply of high-quality water, given the risks they pose to human health and to the environment.

This research pointed towards the vulnerability of water sources and water supply systems to endocrine disruptors as well as towards risks resulting from human exposure to these substances, even at low concentrations.

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