



## A preliminary nationwide survey of the presence of emerging contaminants in drinking and source waters in Brazil



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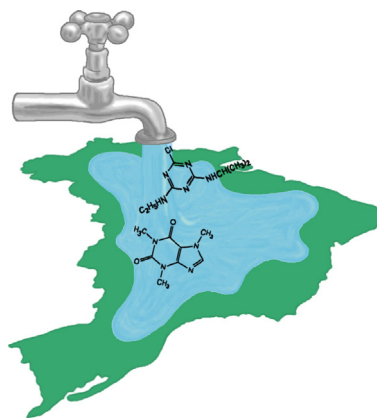
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### HIGHLIGHTS

- First national survey of emerging contaminants in Brazil
- Caffeine detected in 93% of samples
- Strong indication of the presence of domestic sewage in source waters

### GRAPHICAL ABSTRACT



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### ABSTRACT

This is the first nationwide survey of emerging contaminants in Brazilian waters. One hundred drinking water samples were investigated in 22 Brazilian state capitals. In addition, seven source water samples from two of the most populous regions of the country were evaluated. Samples were collected from June to September of 2011 and again during the same period in 2012. The study covered emerging contaminants of different classes, including hormones, plasticizers, herbicides, triclosan and caffeine. The analytical method for the determination of the compounds was based on solid-phase extraction followed by analysis via liquid chromatography electrospray triple-quadrupole mass spectrometry (LC-MS/MS). Caffeine, triclosan, atrazine, phenolphthalein and bisphenol A were found in at least one of the samples collected in the two sampling campaigns. Caffeine and atrazine were the most frequently detected substances in both drinking and source water. Caffeine concentrations in drinking water ranged from 1.8 ng L<sup>-1</sup> to values above 2.0 µg L<sup>-1</sup> while source-water concentrations varied from 40 ng L<sup>-1</sup> to about 19 µg L<sup>-1</sup>. For atrazine, concentrations were found in the range from 2.0 to

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LC-MS/MS  
Tap water  
Raw sewage

6.0 ng L<sup>-1</sup> in drinking water and at concentrations of up to 15 ng L<sup>-1</sup> in source water. The widespread presence of caffeine in samples of treated water is an indication of the presence of domestic sewage in the source water, considering that caffeine is a compound of anthropogenic origin.

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## 1. Introduction

Levels of a growing number of organic substances from both natural and synthetic origins in aquatic environments have been investigated over the past decades. These substances include plasticizers, pesticides, antibacterial compounds, hormones, pharmaceuticals, illicit drugs and personal care products. These pollutants are commonly called emerging contaminants and are being widely detected especially in surface waters such as estuaries, lakes and rivers. They have also been found in drinking water (Leung et al., 2013; Sodr e et al., 2010a; Stewart et al., 2013; Velicu and Suri, 2009; Zuccato et al., 2005).

The presence of emerging contaminants in surface waters has been recurrent because these water bodies receive most of the pollutants released into the environment. Possible sources include atmospheric deposition, leaching of compounds from the soil, storm drainage in rural and urban areas, among others (Sumpter, 2005). However, the discharge of raw and treated sewage has been appointed as the main source of contaminants in surface waters (Ort et al., 2010; Gome z et al., 2006).

Many pollutants are not completely eliminated by the current processes commonly employed in Wastewater Treatment Plants (WWTP) and Drinking Water Treatment Plants (DWTPs). For this reason, even in countries that have adequate sanitation, emerging contaminants are commonly found in rivers, lakes as well as other surface waters and eventually in drinking water (Kasprzyk-Hordern et al., 2008; Ort et al., 2010; Pal et al., 2010; Stackelberg et al., 2007). On the other hand, in developing countries, raw sewage discharge is still an important source of contamination, especially when receiving waters are also used as sources of the population's water supply.

Special attention should be given to the presence of emerging contaminants in surface waters used to produce drinking water, since the latter can be an important route of human exposure to these contaminants. The effects that emerging contaminants can have on wildlife and human health are not fully known, but some studies have showed that they can act as endocrine disruptor chemicals (EDC), causing the feminization of male fish and responsible for changes in the immune systems of wildlife. In humans, possible effects include the increased incidence of breast, testicular and prostate cancer, reduces sperm count, infertility, and endometriosis (Colborn et al., 1993; Gavrilesu et al., 2015; Sumpter and Johnson, 2005; Waring and Harris, 2005).

Therefore, the quantitative investigation of emerging contaminants in source and drinking water represents a key aspect to the search of possible effects of these substances due to their widespread distribution and mobility in aquatic environments as well as to the existing gaps on their relation to possible toxicological effects for the biota and for the human health (Rodil et al., 2012).

One of the first nationwide evaluations of emerging contaminants in natural waters was carried out by Focazio et al. (2008) in the United States. They assessed the presence of 100 substances in 49 surface and drinking water samples serving populations in several American states. Of the 100 compounds tested, 63 were detected, including cholesterol, metolachlor, carbamazepine, and bisphenol A.

In a study conducted in Australia, Watkinson et al. (2009) investigated the presence of 28 antibiotics in several water matrices, among them, six rivers and drinking water of a storage catchment of Queensland. Monensin, erythromycin, sulfamethoxazole and norfloxacin were more frequently detected in surface water, at concentrations ranging from low ng L<sup>-1</sup> to 2.0 µg L<sup>-1</sup>. The authors observed that in the river that does not receive discharges from WWTPs, the total concentration

of the investigated antibiotics was significantly lower than in the other five surface waters, suggesting that WWTP are an important source of antibiotics to the streams.

Meffe and Bustamante (2014) showed that more than 160 emerging contaminants have been identified in Italian surface waters in the past 15 years. The most frequently studied compounds were classified as pharmaceuticals, estrogens, illicit drugs, pesticides and industrial products, whereas the latter two classes were found in higher concentrations.

Although widely detected in the environment, most of the emerging contaminants are not included in legislation related to water quality (surface, groundwater or drinking water). Therefore, official monitoring programs that address the determination of these pollutants are scarce. Some groundbreaking actions in this direction have been taken by regulatory agencies such as the U.S. Environmental Protection Agency (U.S. EPA) and the European Union (EU). In 1998, the U.S. EPA announced the first Drinking Water Contaminant Candidate List (CCL1), establishing a list of 50 chemical and 10 microbial contaminant candidates. The substances included in this list were considered priority to regulate the information's collection and decision making regarding the establishment of strategies to minimize the contamination of drinking water and to establish limits for emerging contaminants (USEPA. United States Environmental Protection Agency, 1998). An update of the draft Contaminant Candidate List, the CCL 4, was proposed by the U.S. EPA in 2015 and covered 100 chemicals as well as 12 microbial contaminants (USEPA. United States Environmental Protection Agency, 2015).

Similarly, the EU has been establishing strategies to achieve minimization of water pollution related to the presence of micro-pollutants through the launch of monitoring programs and regulating the presence of them in many countries. Since 2001, there has been a list of various substances considered potentially dangerous to the environment and human health. A final list of updates was published in 2011 and it includes 41 substances, such as atrazine, nonylphenol, octylphenol, among others (EU. European Union, 2008; Padr on et al., 2014).

In Brazil, regulations concerning emerging contaminants in both natural and drinking water require a commitment among researchers and regulatory authorities, since this issue has not been considered as a priority by the government. Pollution of surface water and consequently the quality of drinking water in Brazil is a recurring issue due to the lack of proper public policies designed to solve basic sanitation problems. In a country with about 200 million inhabitants, the percentage of households with access to the sewage treatment system does not exceed 50%, and much of the collected sewage does not receive proper treatment before its release into source waters (IBGE, 2011; SNIS, 2012). Data from the Sanitation's Atlas of 2011, published by the Brazilian Institute of Geography and Statistics (IBGE, 2011) show that around 31% of Brazilian municipalities release untreated sewage into rivers, lakes or ponds, and that same source water are used by people for various purposes among them, irrigation and supply drinking water for population. This is a worrying situation because the inefficiency of sanitation compromises the population's health and causes damage to the environment, especially soil and source waters (Froehner et al., 2010).

Nowadays, the precarious sanitation in some regions coupled with the growth of population in urban agglomerations can be considered as one of the main causes for the degradation of surface waters in Brazil. A recent national report by the Conjunction of Water Resources prepared by the National Water Agency (ANA) showed that the quality of water sources is considered poor or very poor in urban and nearby areas (ANA. National Water Agency, 2013). Because the vast majority

of drinking water produced in Brazilian urban areas originates from surface water treatment, the poor water quality requires advanced treatment for the proper elimination of several unregulated pollutants. On the contrary, most of the DWTP operates with conventional processes such as coagulation, flocculation, sedimentation, filtration and disinfection using chlorine-based products.

The present study was conducted to assess the presence of emerging contaminants in drinking and source waters in more than twenty state capitals and the Federal District in Brazil. The study was carried out in two sampling campaigns during the period from 2011 to 2012. Recognizing the necessity for data at a national scale, this is the first nationwide study conducted in the country which was carried out within the ambit of the National Institute of Advanced Analytical Sciences and Technologies (INCTAA), which established this initiative to evaluate the quality of drinking water served to the Brazilian population as well as from reservoirs used as catchment with respect to the presence of emerging contaminants.

## 2. Material and methods

### 2.1. Chemicals and reagents

The selection of chemicals was made to include substances that were representative of the major classes of contaminants, such as those used in agricultural activities (atrazine), industrial applications (octylphenol, nonylphenol and bisphenol A), personal care (triclosan), pharmaceuticals (17 $\alpha$ -ethinylestradiol) and other anthropogenic needs (caffeine).

The analytical standards were all reagent grade. Estrone (E1), 17 $\beta$ -estradiol (E2), estriol (E3), 17 $\alpha$ -ethinylestradiol (EE2), diethylstilbestrol (DES), levonorgestrel (NGT), mestranol (MEE), progesterone (PROG), testosterone (TTN), bisphenol A (BPA), triclosan (TCS), atrazine (ATZ) and caffeine (CAF) were obtained from Sigma-Aldrich. Octylphenol (OPN) and nonylphenol (NPN) were both obtained from Supelco and phenolphthalein (PhPh) was purchased from Riedel-de-Haen. All solvents were HPLC or pesticide grade. Ultra-pure water (resistivity of 18.2 M $\Omega$  cm) was obtained using a Milli-Q system from Millipore. Stock solutions of 400 mg L<sup>-1</sup> were prepared for each compound individually, in methanol. Standard mixtures with all analytes were prepared in the initial composition of the mobile phase (MeOH:H<sub>2</sub>O 30:70 v:v), at concentrations ranging from 1 to 1000  $\mu$ g L<sup>-1</sup>. These mixtures were used as calibration solutions. Caffeine-d<sub>9</sub> was obtained from CDN Isotopes (Canada).

### 2.2. Sampling sites

Samples were collected during two campaigns, in 2011 and 2012, from July to September. In the first campaign, 45 drinking water samples were collected in 16 Brazilian state capitals whereas in the second campaign 55 samples were collected in 20 capitals. Additionally, seven surface water samples were collected from selected cities. Fig. 1 displays the capitals where the sampling was performed and the number of samples collected.

In order to make a screening of the presence of emerging contaminants in treated water served to the Brazilian population it was important to cover the different regions of the country. Nevertheless, considering the continental dimensions of a country like Brazil and the logistics involved in carrying out sample collections in very distant locations, we decided to collect samples in almost all state capitals in order to cover all five regions.

The number of samples of drinking water collected was defined according to the state capital population. In general, one sample was collected for every 500,000 inhabitants served by local supply systems of treated water. The sampling sites were chosen in order to cover the supply system (or systems) that serve the largest number of inhabitants in each city. Source water points were established based on the results obtained in the first campaign, considering the presence and the concentration of emerging contaminants.

### 2.3. Sample collection and preparation

Drinking water samples were collected from taps that receive treated water directly from the local supply system, avoiding any interference from the contact of the water with the water reservoir of buildings. At each sampling point, 200 mL of drinking water were collected every 2 h, for a period of 10 h, to generate a composite sample of 1000 mL. The samples were collected in amber glass bottles and remained inside a cooler box during the sampling period.

Collection of surface water samples was carried out as close as possible to the water collection points of the local supply system. One liter of water was collected at each sampling point. Samples were collected in a bailer and then transferred to amber bottles and stored under refrigeration until the extraction.

Samples were submitted to solid-phase extraction (SPE) employing Oasis HLB SPE cartridges (Hydrophilic-Lipophilic-Balance) containing 500 mg of sorbent phase material from Waters®. The solid-phase cartridges were conditioned with two aliquots of 3.0 mL methanol

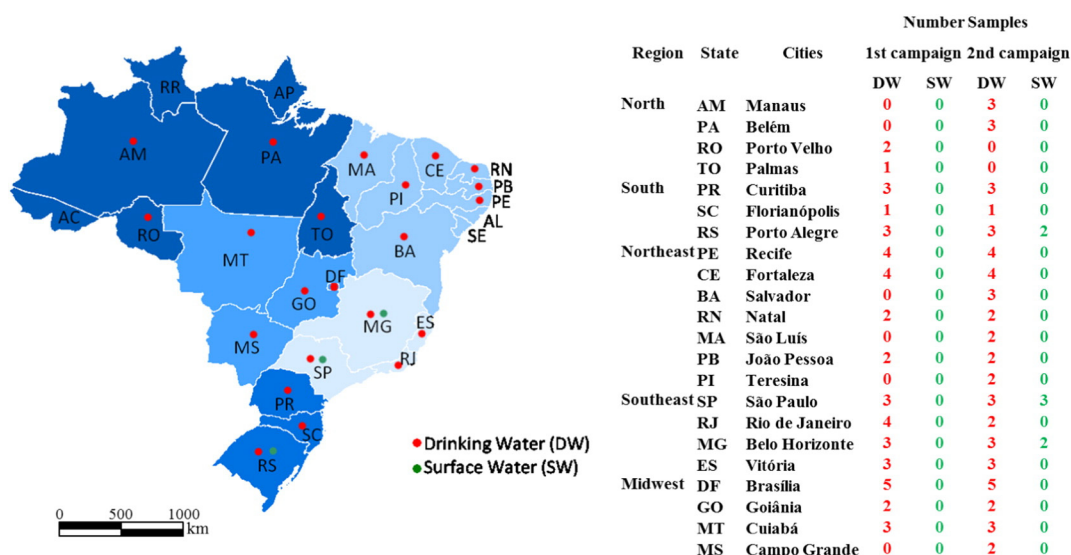


Fig. 1. Regions, state capitals and cities in Brazil where sampling was performed, as well as the number of samples collected in each campaign.

followed by two aliquots of 3.0 mL ultrapure water. The samples were passed through the cartridge at a flow rate of 6.0 mL min<sup>-1</sup> (Raimundo, 2011). For surface water analysis, samples were first filtered through a 0.45- $\mu$ m cellulose acetate membrane (Sartorius, Germany) using a vacuum filtration system holder and then submitted to SPE extraction within 24 h of collection. After the extraction, cartridges were wrapped with aluminum foil, stored under refrigeration (4 °C) and sent by express mail to the INCTAA headquarter at the University of Campinas (UNICAMP). The conditioning and extraction steps were always performed on site to avoid possible losses during transportation across the country. The maximum time between sample collection in the field, the subsequent step and the transport of the cartridges to the INCTAA headquarter was no longer than 5 days (additional details can be assessed in the Supplementary material).

Immediately after receiving the cartridges, the sorbent phase was washed using 3 mL ultrapure water. The analytes were then eluted using two aliquots of 2.5 mL methanol followed by 1 aliquot of 2.0 mL acetonitrile in a 12-port vacuum Manifold system. The eluates were dried completely under a gentle stream of N<sub>2</sub>, and the final extracts were recovered in 0.4 mL MeOH:H<sub>2</sub>O 30:70% v/v solution, then individually diluted when necessary.

#### 2.4. Chromatographic analysis

The chromatographic analyses were carried out on a liquid chromatographic systems (Agilent 1200 Series) coupled to an Agilent 6410 TripleQuad mass spectrometer equipped with an electrospray ionization source (ESI) (Agilent Technologies) operating in both positive and negative modes. The separation was performed using a Zorbax SB-C18 column (2.1 × 30 mm, particle size 3.5  $\mu$ m, Agilent Technologies). The mobile phase was composed of water and methanol, with 0.01% v/v ammonium hydroxide added to enhance ionization. The gradient elution started at 30% of methanol, achieving 70% in 3 min, increased to 90% in 2 min, and this composition was held for 7 min. Initial conditions were reestablished in 5 min, resulting in 17 min of chromatographic analysis. The mobile phase flow rate was 0.3 mL min<sup>-1</sup>, the column temperature was set to 30 °C and the injection volume was 10.0  $\mu$ L. The mass spectrometer acquisition mode was set to multiple reaction monitoring (MRM). This procedure was based on previous studies described in the literature (Sodré et al., 2010b; Raimundo, 2011; Pescara, 2014) (additional details can be assessed in the Supplementary material).

### 3. Results and discussion

#### 3.1. Method performance

The instrumental and analytical parameters for the methods used are shown in Table 1. Method performance was evaluated through verification of linearity, intermediate precision and recovery. The limits of detection (LOD) and of quantification (LOQ) were calculated using the regression parameters from the analytical curve according to equations,  $LOD = \frac{3s}{a}$  and  $LOQ = \frac{10s}{a}$ , where  $a$  is the sensitivity and  $s$  is the regression standard error, then multiplied by sample concentration factor.

The recovery was calculated based on matrix-matched standard using the method described by Buhrman et al. (1996); Matuszewski et al. (2003) and Niessen et al. (2006) (additional details can be assessed in the Supplementary material).

#### 3.2. Emerging contaminants in Brazilian drinking water

The study utilized a total of 100 samples of drinking water from 61 sampling points spread across 22 Brazilian state capitals spread over five Brazilian regions. Fig. 2 shows the results regarding the frequency of occurrence of emerging contaminants in drinking water, presented by region.

The most frequently detected substance in drinking water was caffeine. Considering all the samples collected in this study, the frequency of detection of caffeine corresponds to 93%. This corresponds to a higher frequency than found in similar studies conducted in China (Leung et al., 2013) and Spain (Boleda et al., 2011), in which the frequency of detection did not exceed 88%. The lowest detection frequency for caffeine was observed in the northeast region, where 77% of samples showed positive result for caffeine. In the other regions caffeine was found in all collected samples. Atrazine was the substance with the second highest detection frequency. It was found in 75% of the drinking water samples collected in both campaigns.

Aside from caffeine and atrazine, only two other substances were detected in drinking water samples. Triclosan was detected in a sample collected in the city of Porto Alegre, located in the south of Brazil and phenolphthalein was found in a sample collected in the city of Palmas, at the northern region. Both positive results are related to the samples collected in the first sampling campaign.

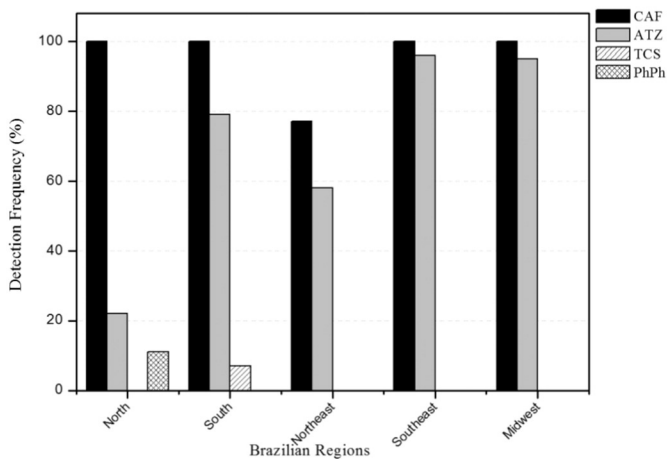
The hormones, pharmaceuticals and industrial products investigated in this study were not detected in the drinking water samples. This

**Table 1**  
Instrumental and analytical method parameters.

Compound	Instrumental			LOD (ng L <sup>-1</sup> )	LOQ (ng L <sup>-1</sup> )	Recovery (%)	SD (N = 3)	RSD (%)
	Linear range ( $\mu$ g L <sup>-1</sup> )	Linearity (r <sup>2</sup> )	Intermediate precision N = 5 (RSD %)					
Atrazine (ATZ)	1–200	0.99	5	1.0	2.0	83	18.0	20
Caffeine (CAF)	5–200	0.99	12	1.0	4.0	91 <sup>a</sup>	1.0	1
Triclosan (TCS)	25–200	0.99	3	3.0	9.0	21	4.0	18
Bisphenol A (BPA)	25–200	0.93	10	17.0	58.0	64	1.0	2
4-n-Octylphenol (OPN)	25–200	0.97	22	4.0	14.0	31	4.0	13
4-n-Nonylphenol (NPN)	25–200	0.97	26	2.0	6.0	17	7.0	43
Estrone (E1)	5–200	0.96	8	5.0	15.0	41	5.0	11
17 $\beta$ -Estradiol (E2)	15–200	0.98	8	3.0	11.0	46	1.0	2
17 $\alpha$ -Ethinylestradiol (EE2)	25–200	0.95	3	8.0	26.0	51	5.0	9
Estriol (E3)	15–200	0.95	5	5.0	17.0	42	8.0	18
Diethylethylbestrol (DES)	1–200	0.98	13	3.0	10.0	25	4.0	14
Levonorgestrel (NGT)	1–200	0.99	6	1.0	5.0	84	6.0	7
Mestranol (MEE)	15–200	0.99	16	2.0	8.0	68	9.0	14
Progesterone (PGN)	1–200	0.99	7	1.0	4.0	82	11.0	12
Testosterone (TTN)	1–200	0.99	5	1.0	4.0	80	20.0	28
Phenolphthalein (PhPh)	1–200	0.99	7	1.0	3.0	67	5.0	7

RSD: relative standard deviation; LOD: limit of detection; LOQ: limit of quantification; SD: standard deviation.

<sup>a</sup> Evaluated as deuterated caffeine CAF-D9.



**Fig. 2.** Detection frequency of emerging contaminants in the five Brazilian regions, considering all of the samples collected in the two sampling campaigns in 2011 and 2012.

implies that levels of these compounds in the samples may be non-existent. Alternatively, these compounds may be present under concentrations below the detection limits of the working method (Rodil et al., 2012; Sodr e et al., 2010a).

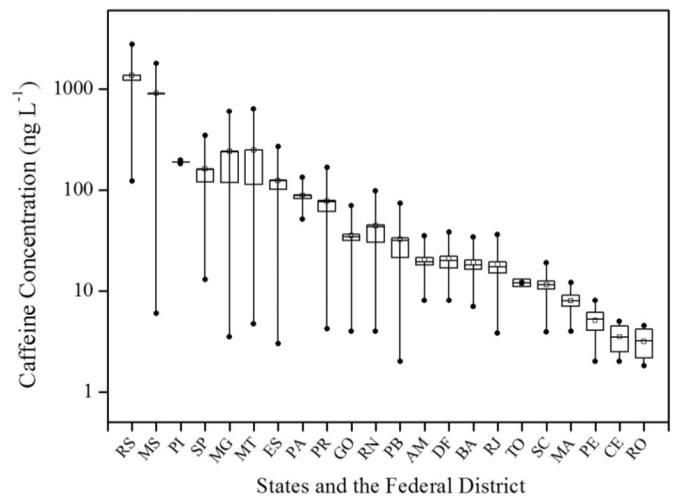
Comparing the results across regions, the frequency of detection for caffeine did not present substantial variation. However, frequency of detection for atrazine varied greatly. The highest detection frequency was observed in the Southeast and Midwest regions, where more than 90% of samples presented positive results for atrazine. In the southern region atrazine was detected in 79% of the samples followed by the Northeast with 58% and the North region with 22% of the samples.

Although the two sampling campaigns were carried out during similar periods, due to the continental dimensions of the country, the sampling period occurred during the rainy season in some regions, such as the Northeast, while the collection of samples occurred during the dry season in the South and Southeast. This is one of the factors that can partially explain the variations observed for the presence of emerging contaminants in drinking water in the different regions of the country. Once the catchment in most of the country utilizes primarily surface waters directly affected by variations in rainfall, fluctuations in the concentrations of pollutants in these aquatic environments are to be expected.

Similar variations related to the concentration levels of emerging contaminants in surface water have also been observed and reported in other studies. Such changes are usually associated with seasonal variations, whereby increased concentrations of contaminants result from decreased rainfall (Alvarez et al., 2014; Montagner and Jardim, 2011). However, no study has shown evidence related to possible seasonal effects in drinking water samples.

The average concentration of caffeine in drinking water is shown in Fig. 3. Porto Alegre/RS, located in the south region, was the city which presented the highest levels of caffeine considering both the average concentration and the maximum concentration found. The minimum and maximum values determined in samples collected in Porto Alegre were  $122 \text{ ng L}^{-1}$  and  $2769 \text{ ng L}^{-1}$ , respectively (6 samples collected in two sampling campaigns). The second highest average concentration was observed in the drinking water of Campo Grande/MS, where only two samples were collected both during the second campaign. While one sample presented a concentration of  $6.0 \text{ ng L}^{-1}$ , the second sample showed a much higher concentration:  $1793 \text{ ng L}^{-1}$ . A high variation between concentrations of caffeine found in samples from different sampling points could be explained by possible deficiencies on the water treatment systems in this city.

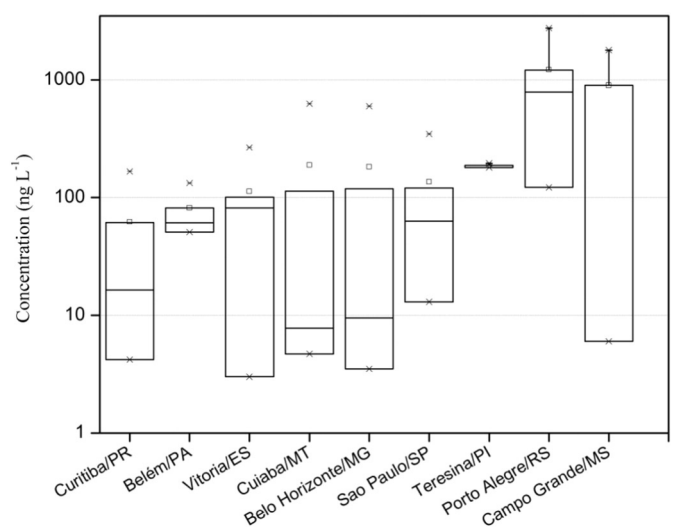
Caffeine was detected in nine of the 22 state capitals evaluated, at concentrations higher than  $100 \text{ ng L}^{-1}$  in at least one of the samples. They are Porto Alegre/RS ( $122$ ;  $139$ ;  $236$ ;  $1342$ ;  $2659$  and  $2769 \text{ ng L}^{-1}$ ), Curitiba/PR ( $157$  and  $167 \text{ ng L}^{-1}$ ), S o Paulo/SP ( $198$



**Fig. 3.** Average concentration of caffeine in the drinking water of 22 Brazilian state capitals. The square indicates the mean and the black circle indicates the maximum and minimum concentration. Adapted from Canela et al. (2014).

and  $348 \text{ ng L}^{-1}$ ), Belo Horizonte/MG ( $599 \text{ ng L}^{-1}$ ), Vit ria/ES ( $157$ ,  $165$  and  $267 \text{ ng L}^{-1}$ ), Cuiab /MT ( $629 \text{ ng L}^{-1}$ ), Bel m/PA ( $133 \text{ ng L}^{-1}$ ), Teresina/PI ( $180$  and  $196 \text{ ng L}^{-1}$ ) and Campo Grande/MS ( $1793 \text{ ng L}^{-1}$ ). However, when we considered the individual caffeine concentrations at all sampling points of the same capital during both sampling campaigns for the average calculated, five state capitals presented average concentrations ranging from  $100$  to  $1000 \text{ ng L}^{-1}$ . Teresina/PI and S o Paulo/SP with the average concentration of  $286 \text{ ng L}^{-1}$  and  $121 \text{ ng L}^{-1}$ , respectively, followed by Belo Horizonte/MG ( $119 \text{ ng L}^{-1}$ ), Cuiab /MT ( $114 \text{ ng L}^{-1}$ ), Campo Grande/MS ( $899 \text{ ng L}^{-1}$ ) and finally Vit ria/ES with  $101 \text{ ng L}^{-1}$ . Fig. 4 shows the distribution of caffeine found in drinking water samples collected at the nine cities with the highest concentrations.

Although S o Paulo/SP is the most populous city in Brazil, with 11.2 million inhabitants (19.9 million in the metropolitan region), and is more likely to suffer the impacts of urbanization, the average concentration of caffeine ( $121 \text{ ng L}^{-1}$ ) was ten times lower when compared to the samples collected in Porto Alegre/RS (average  $1211 \text{ ng L}^{-1}$ ). The results obtained in Porto Alegre may be related to peculiarities related to



**Fig. 4.** Box-plot depicting the distribution of caffeine in nine Brazilian state capitals. The black horizontal line inside the box represents the median and the black square indicates the mean.

cultural habits as well as the water source that supplies the water supply system. First, in Porto Alegre, as well as in the whole Rio Grande do Sul State, people cultivate the habit of taking a hot drink made of yerba mate, which has caffeine as a major component. As the consumption of this product happens on a daily basis, and the quantities consumed are high, this is one aspect that could justify the higher caffeine concentrations found in the treated drinking water. Second, the main water source that supplies Porto Alegre comes from the Guaíba Lake, which is located in the middle of the urban region. As a consequence, the reservoir is highly impacted by its location in an industrialized and populous region that concentrates nearly 3.9 million people, which corresponds to approximately 70% of the Rio Grande do Sul population. In addition, the lake receives treated as well as untreated wastewater of the whole metropolitan region (Nicolodi and Farina, 2010).

In Belo Horizonte/MG, located in southeastern Brazil, the mean caffeine concentration was  $118.9 \text{ ng L}^{-1}$ . One of the samples reached a caffeine concentration of  $599 \text{ ng L}^{-1}$ , which contributed to an increase in the average, placing it among the cities with the highest average levels of caffeine in drinking water. However, it is noteworthy that the drinking water sample was collected in an area that receives water taken from a river that is under the impact of a greatly urbanized region, suggesting that caffeine concentration in this sample can be directly related to the contamination of the water supply by domestic sewage. Belo Horizonte has 2.4 million inhabitants in the municipality, with almost 5.5 million living inside the metropolitan region and represents the sixth most populous city in Brazil.

Cuiabá/MT exhibited an average caffeine concentration of  $113.6 \text{ ng L}^{-1}$ . The higher individual concentration was of  $629 \text{ ng L}^{-1}$  in one sample. This sample was collected at a sampling point that received water from a pickup point located downstream from the city center, which would explain the presence of higher levels of caffeine. In both cities these high levels of caffeine were only observed in the second campaign. Cuiabá is located in the Midwest region and boasts a population of 550 thousand people.

In Vitória, capital of the Espírito Santo State, six samples were collected in two sampling campaigns and as in Belo Horizonte and Cuiabá, caffeine concentrations in drinking water were higher in the second campaign than in the first. The three samples collected in Vitória during the second campaign showed caffeine concentrations above  $100 \text{ ng L}^{-1}$  (267; 157 and  $165 \text{ ng L}^{-1}$ ). During the first campaign, in contrast, the maximum concentration did not exceed  $10 \text{ ng L}^{-1}$ . Vitória is a medium size city with 330 thousand inhabitants, with 1.7 million people living in the metropolitan region.

In four state capitals, the average caffeine concentration in drinking water varied from 30 to  $100 \text{ ng L}^{-1}$ , as is shown in Fig. 4. The city of Belém/PA, which is located in the northern region, with a population of 1.4 million and a metropolitan region that has about 2.1 million people, exhibited an average caffeine concentration of  $82 \text{ ng L}^{-1}$ . Following that there were Curitiba/PR ( $61 \text{ ng L}^{-1}$ ), Goiânia/GO ( $31 \text{ ng L}^{-1}$ ) and Natal/RN ( $30 \text{ ng L}^{-1}$ ). In all these cities, higher levels were determined during the second campaign. The other state capitals showed average concentrations of caffeine less than  $21 \text{ ng L}^{-1}$  with lower concentrations were determined in São Luís/MA  $8.0 \text{ ng L}^{-1}$ , Recife/PE  $5.0 \text{ ng L}^{-1}$ , Fortaleza/CE  $4.0 \text{ ng L}^{-1}$  and Porto Velho/RO  $3.0 \text{ ng L}^{-1}$ .

In summary, in 63% of the analyzed samples, caffeine concentrations did not exceed  $20 \text{ ng L}^{-1}$ . Nevertheless, in 16%, the caffeine levels reached 100 to  $1000 \text{ ng L}^{-1}$ . In about 4%, the caffeine levels exceeded  $1000 \text{ ng L}^{-1}$ .

In general, higher concentrations of caffeine were measured in the state capitals located inland as compared to those cities situated on the coast. Among the ten state capitals with the highest concentrations of caffeine in drinking water, nine are located in the continent. With the exception of Vitória/ES, all of the coastal state capitals investigated in this study showed average caffeine concentrations lower than  $30 \text{ ng L}^{-1}$ . This trend may be related to the fact that in coastal cities very often domestic sewage is released into the ocean as opposed to

cities located in the mainland in which treated or untreated sewage discharges reach receiving surface waters that many times are used as source for the water supply systems (Sodré et al., 2010a).

Atrazine was detected in 75% of all drinking water samples collected during the two campaigns, although the detection tendency observed for this substance was quite different from that observed for caffeine. Fig. 5 shows the average concentration of atrazine in Brazilian state capitals water samples.

Atrazine was detected in 16 capitals of the 22 that were evaluated and its presence was not observed in three state capitals of the northern region (Manaus/AM, Belém/PA and Palmas/TO) and other three located in the Northeast region (Salvador/BA, Natal/RN and São Luís/MA). Nonetheless, atrazine was detected in one or more samples from all capitals from the South, Southeast and Midwest regions, considering both the 2011 and 2012 sampling campaigns. These results may be related to the fact that these three are the main agricultural regions of Brazil being all together responsible for the consumption of more than 80% of the total amount of this herbicide which is consumed in the country (IBAMA, 2015).

The average concentration of atrazine did not exceed  $20 \text{ ng L}^{-1}$  in any of the samples from either sampling campaign. There were not observed large variations in the levels of atrazine in general, neither in the average values (ranging from 2.0 to  $15 \text{ ng L}^{-1}$ ) nor in the differences among the minimum and maximum values determined in the same city or even in different regions (ranging from not detected up to  $24 \text{ ng L}^{-1}$ ).

The highest concentration of atrazine was observed in one sample collected in Belo Horizonte in the second campaign ( $24 \text{ ng L}^{-1}$ ). In contrast, five samples showed a concentration of  $2 \text{ ng L}^{-1}$ , the lowest value determined for atrazine in drinking water in this study. All five samples were from southern Brazil, three of them were collected in Porto Alegre/RS and two in Curitiba/PR, all of them in the first sampling campaign.

Atrazine was detected (at a concentration of at least  $15 \text{ ng L}^{-1}$ ) in samples collected from Florianópolis/SC, Fortaleza/CE, João Pessoa/PB, Teresina/PI, São Paulo/SP, Vitória/ES, Cuiabá/MT and Campo Grande/MS. In general, its average concentration in drinking water was higher in the second campaign when compared to the values showed in the first campaign.

Although the results showed a low concentration, it should be noted that atrazine is an EDC. A long term and low dose exposure of atrazine caused insulin resistance in adults rats (Lim et al., 2009) an increase in male production of *Daphnia* spp. (Dodson et al., 1999), reproductive

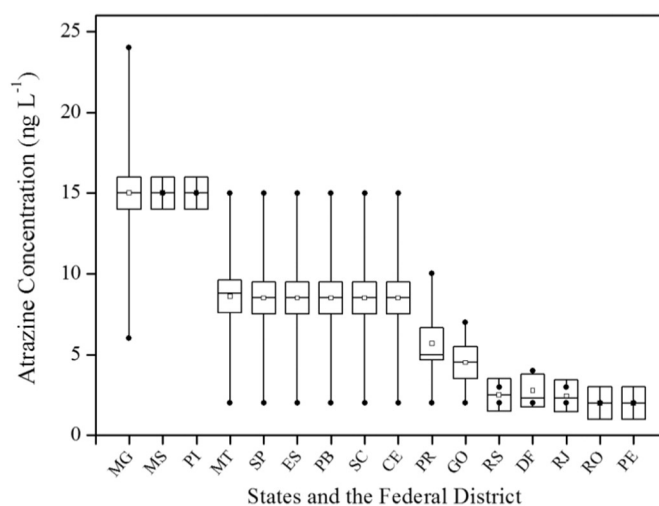


Fig. 5. Average concentration of atrazine in drinking water of 16 Brazilian state capitals. The square indicates the mean and the black circle indicates the maximum and minimum concentration.

effects in female rats (Foradori et al., 2013) and other endocrine related effects (Bergman et al., 2012).

### 3.3. Emerging contaminants in source waters

At the first sampling campaign in 2011, only drinking water samples were collected. However, in view of the results obtained and the wide detection of caffeine and atrazine in this first campaign as well as the relatively high levels of caffeine detected, samples from a source water catchment were also collected during the second sampling campaign.

Seven surface water samples from sources of drinking water were collected in Porto Alegre/RS, São Paulo/SP and Belo Horizonte/MG. These cities were the municipalities with the highest caffeine concentrations in drinking water during the first sampling campaign. In São Paulo, samples were collected from three water sources: the Guarapiranga reservoir (the Guarapiranga system, which supplies 3.8 million inhabitants of Sao Paulo and the metropolitan area with drinking water), the Billings's reservoir (connected to the Rio Grande system, which serves 1.6 million people with treated water), and the Cantareira system (the largest and main source, which provides water to about 8.1 million inhabitants) (ANA, 2013).

In Belo Horizonte/MG one sample was collected in the Rio das Velhas, which is the water source of the Rio das Velhas's system which supplies water to approximately 2.4 million inhabitants. A second sample was collected from the Vargem das Flores reservoir, which is the water source for the Paraopeba system, which provides drinking water to 1.4 million people (ANA, 2010).

Two other water source samples were collected in the city of Porto Alegre/RS. Both samples were collected from the Guaíba Lake, main source of drinking water for the population of the municipality as well as the metropolitan region. Sampling occurred close to two water catchment points on Guaíba Lake, one of them linked to the Menino Deus system (which serves roughly 40% of the population) and the other providing water to the Moinhos de Vento and São João systems, which together account for approximately 44% of the population (ANA, 2010).

Caffeine and atrazine were detected in all seven samples, while bisphenol A was detected in three samples, all of them from the three different reservoirs located in São Paulo/SP. Fig. 6 shows the concentrations, expressed in log scale, of these three substances in all samples of source water.

Caffeine was detected at a concentration of 18,828 ng L<sup>-1</sup> at the Billings reservoir. This was the highest concentration of caffeine detected among all source water samples collected. In the other two samples

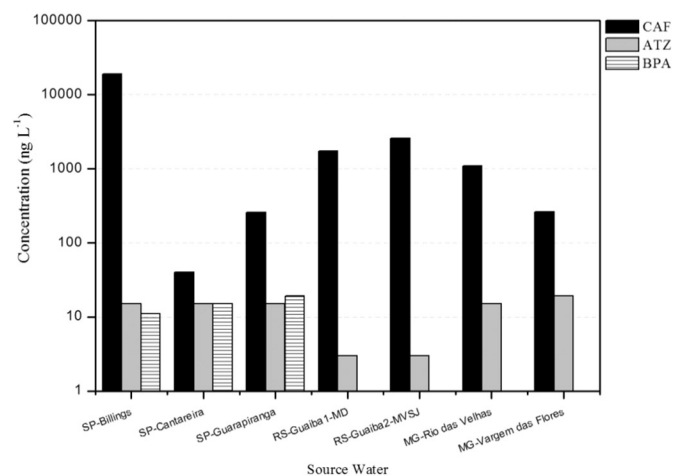


Fig. 6. Caffeine, atrazine and bisphenol A (ng L<sup>-1</sup>) in the water sources that supply drinking water to the cities of São Paulo/SP, Porto Alegre/RS and Belo Horizonte/MG. Samples were collected between July and September of 2012, the dry season.

collected in São Paulo caffeine as determined at 255 ng L<sup>-1</sup> and 40 ng L<sup>-1</sup> in the samples from the reservoir of Guarapiranga and Cantareira, respectively. Atrazine and bisphenol A were also detected in samples collected at the reservoirs in São Paulo. Atrazine was detected at 15 ng L<sup>-1</sup> in the three samples. As it is shown in Fig. 6, bisphenol A was determined at the concentrations of 11 ng L<sup>-1</sup>, 15 ng L<sup>-1</sup>, and 19 ng L<sup>-1</sup> for Billings, Cantareira and Guarapiranga, respectively.

The second highest concentration (ranging from 1733 to 2572 ng L<sup>-1</sup>) of caffeine was measured in samples collected at Guaíba Lake in Porto Alegre. In Porto Alegre, atrazine was detected at concentrations of 3 ng L<sup>-1</sup>. The lowest concentrations were detected in source-water samples.

In Belo Horizonte the caffeine concentrations in source water reached 262 ng L<sup>-1</sup> in the sample from Vargem das Flores reservoir and 1086 ng L<sup>-1</sup> in the one from Rio das Velhas. For atrazine, the highest concentration detected in source water was 19 ng L<sup>-1</sup> (Vargem das Flores).

### 3.4. Source to drinking water

An overview of the emerging contaminants identified in samples of drinking and source water in the two campaigns is presented in Table 2. The average concentration, maximum concentration and frequency of detection are presented as well.

On average, samples collected during the second year exhibited caffeine and atrazine concentrations higher than those collected during the first year of the study.

At certain sampling locations, variations of up to two orders of magnitude were observed for caffeine (for example, from 5.3 ng L<sup>-1</sup> to 629 ng L<sup>-1</sup> in a sample collected in Cuiabá). Variation in atrazine levels was smaller, with values remaining in the same order of magnitude, which corresponds to a range of a few nanograms per liter.

In both drinking and source waters, caffeine reached concentration values from a few ng L<sup>-1</sup> to µg L<sup>-1</sup>. The detection frequency of caffeine in drinking water found in this study is higher than values reported in the literature. Besides that, the average and maximum concentrations found in countries such as China (Leung et al., 2013), Spain, and in some cases France (Boleda et al., 2011) are much smaller than those found in Brazil.

Previous studies conducted in more restricted areas in Brazil have reported the presence of caffeine and other emerging contaminants in

Table 2

Overview of substances detected in drinking (100 samples) and source water (7 samples) collected from 21 state capitals and the federal district in 2011 and 2012.

Substance	No. positives		Frequency (%)		C average (ng L <sup>-1</sup> )		C max (ng L <sup>-1</sup> )	
	DW	SW	DW	SW	DW	SW	DW	SW
Atrazine (ATZ)	75	7	75	100	6.5	12.1	24.0	19.0
Caffeine (CAF)	93	7	93	100	146	3540	2769	18,828
Triclosan (TCS)	1	0	1	0	n.a.	n.d.	n.d.	n.d.
Bisphenol A (BPA)	0	3	0	42	n.d.	n.a.	n.d.	n.d.
4-n-Octylphenol (OPN)	0	0	0	0	n.d.	n.d.	n.d.	n.d.
4-n-Nonylphenol (NPN)	0	0	0	0	n.d.	n.d.	n.d.	n.d.
Estrone (E1)	0	0	0	0	n.d.	n.d.	n.d.	n.d.
17β-Estradiol (E2)	0	0	0	0	n.d.	n.d.	n.d.	n.d.
17α-Ethinylestradiol (EE2)	0	0	0	0	n.d.	n.d.	n.d.	n.d.
Estriol (E3)	0	0	0	0	n.d.	n.d.	n.d.	n.d.
Diethylethylbestrol (DES)	0	0	0	0	n.d.	n.d.	n.d.	n.d.
Levonorgestrel (NGT)	0	0	0	0	n.d.	n.d.	n.d.	n.d.
Mestranol (MEE)	0	0	0	0	n.d.	n.d.	n.d.	n.d.
Progesterone (PGN)	0	0	0	0	n.d.	n.d.	n.d.	n.d.
Testosterone (TTN)	0	0	0	0	n.d.	n.d.	n.d.	n.d.
Phenolphthalein (PhPh)	1	0	1	0	n.a.	n.d.	n.d.	n.d.

n.a.: not applicable. DW: drinking water. SW: surface water. n.d.: not detected (see Table 1 for LOD values).

both drinking and surface waters (Caldas et al., 2013; Montagner and Jardim, 2011; Sodr e et al., 2007, 2010a; Sousa et al., 2014). The wide detection of caffeine in drinking water is directly related to the input of untreated sewage in the source water supply. Caffeine, like other organic compounds of anthropogenic origin that exhibit greater residence time in the environment and are less susceptible to degradation or are degraded more slowly, has been proposed as an indicator of contamination by sewage (Daneshvar et al., 2012).

Several studies have also indicated the presence of caffeine in surface waters in other countries (Bueno et al., 2012; Knee et al., 2010; Lima Gomes et al., 2013). In countries where the services of collection and sewage treatment are more effective, caffeine is used as a marker to indicate the occurrence of leaks in the sewer system (Conley et al., 2008; Stackelberg et al., 2007).

In Brazil, the presence of caffeine in surface waters and even in treated water is expected due to the low rates of collection and treatment of domestic sewage because the release of untreated wastewater into water bodies can be considered as the main source of this substance. It is important to note that moderate caffeine consumption is not harmful for human health, and the concentrations of caffeine found in drinking water samples and even source water are considerably lower than the concentration of caffeine in a cup of coffee, for example. However, its presence in aquatic environments and in drinking water can provide important information about contamination levels of other substances of greater toxicity, as evidenced in a study published by Montagner et al. (2014), which showed that surface water samples that contained caffeine also contained compounds with estrogenic activity. The positive response of a sample in estrogenic tests indicates the presence of substances that are able to interfere with the hormones and endocrine systems of living organisms, which results in adverse effects.

The frequency of atrazine detection in both treated and source waters requires emphasis that it is the only substance among the 16 investigated in this study that is under regulation. Atrazine is regulated by the Brazilian legislation, which allowed its presence in both drinking and surface water of up to 2.0  $\mu\text{g L}^{-1}$  (CONAMA, 2015; MS. Ministry of Health, 2011).

The levels of atrazine found in this study are between two and three orders of magnitude below the maximum limit established by the Brazilian regulations. However, it is important to point out that the establishment of such limits is based on toxicological and neurotoxicological trials, not taking into account possible estrogenic effects that this contaminant can cause when human and wildlife are being exposed chronically to low concentrations. In addition, the intensive use of atrazine as well as its physicochemical properties have classified this herbicide as persistent and unsafe for the biota as well as to human health (Mnif et al., 2011).

#### 4. Conclusions

The results of this study, conducted in a network encompassed by INCTAA to assess the presence of emerging contaminants in source and treated drinking water for the Brazilian population, revealed the presence of emerging contaminants in samples collected in different Brazilian state capitals.

Among the substances investigated, caffeine and atrazine were observed with greater frequency. These results show that the presence of emerging contaminants in treated water is a reality in Brazil and reveal deficiencies in sanitation and water treatment employed in the Water Treatment Process (WTP) to remove these contaminants.

The widespread presence of caffeine in samples of treated water is an indication of the contamination of source water mainly by domestic sewage, because this substance is a compound of anthropogenic origin. Although caffeine and most of the substances investigated are not legislated, knowledge about their concentrations in treated and source water is important because safe levels of intake for many of these compounds are not yet known.

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#### Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.scitotenv.2016.07.210>.

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