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

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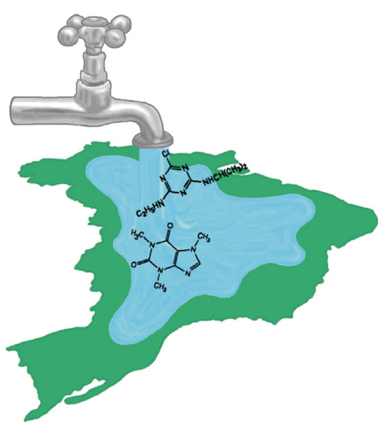
HIGHLIGHTS

- 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^{-1} to values above 2.0 μg L^{-1} while source-water concentrations varied from 40 ng L^{-1} to about 19 μg L^{-1}. 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^{-1} in drinking water and at concentrations of up to 15 ng L^{-1} 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.

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; Sodré 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; Goméz 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; Gavrilescu 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^{-1} to 2.0 μg L^{-1}. 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; Padrón 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 Conjuncture 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