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Occurrence of pharmaceuticals and cocaine in a Brazilian coastal zone

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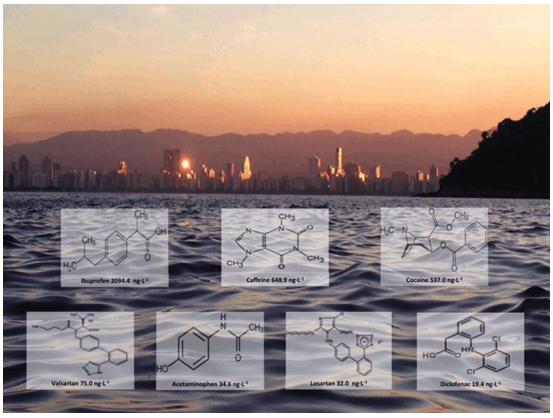
HIGHLIGHTS

- Pharmaceuticals and cocaine were assessed in a subtropical coastal zone
- Acetaminophen, caffeine, diclofenac, ibuprofen, losartan and valsartan were quantified
- Ibuprofen showed highest concentration in order of $\mu g \cdot L^{-1}$
- Cocaine and benzoylecgonine were both quantified in all of the samples

GRAPHICAL ABSTRACT



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ABSTRACT

The present study determined environmental concentrations of pharmaceuticals, cocaine, and the main human metabolite of cocaine in seawater sampled from a subtropical coastal zone (Santos, Brazil). The Santos Bay is located in a metropolitan region and receives over 7367 m^3 of wastewater per day. Five sample points under strong influence of the submarine sewage outfall were chosen. Through quantitative analysis by LC–MS/MS, 33 compounds were investigated. Seven pharmaceuticals (atenolol, acetaminophen, caffeine, losartan, valsartan, diclofenac, and ibuprofen), an illicit drug (cocaine), and its main human metabolite (benzoylecgonine) were detected at least once in seawater sampled from Santos Bay at concentrations that ranged from $ng \cdot L^{-1}$ to $\mu g \cdot L^{-1}$. In light of the possibility of bioaccumulation and harmful effects, the high concentrations of pharmaceuticals and cocaine found in this marine subtropical ecosystem are of environmental concern.

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1. Introduction

As the world's population grows and becomes more concentrated in coastal zones, marine ecosystems become further exposed to both treated and untreated wastewater discharges composed of a mixture of emerging contaminants that includes bioactive compounds.

Drugs consumption is often associated with longevity and stressful lives, particularly in urban areas. Advances in medicine, the significant growth of chemistry and pharmaceutical companies, and changes in social conditions have all led to the more widespread use of pharmaceuticals and psychotropic substances (Borova et al., 2014).

In recent years, pharmaceuticals and personal care products (PPCPs) have been considered emerging contaminants of great concern to environmental protection agencies, such as the USEPA and Environment Canada (USEPA, 2010; Environment Canada, 2011). As reported by Petrie et al. (2015), the presence of PPCPs in the environment is mainly attributed to the discharge of wastewater from WWTPs because conventional processes are not designed to remove such compounds, resulting in their discharge to receiving surface waters including rivers, lakes and coastal waters. There is accumulating evidence that domestic sewage carries PPCPs and illicit drugs into aquatic ecosystems, even after passing through wastewater processing facilities (Zuccato et al., 2008; Terzic et al., 2010; Gilbert, 2011; Baker et al., 2012; Baker and Kasprzyk-Hordern, 2013; Borova et al., 2014; Zenobio et al., 2015).

Most of the efforts to assess PPCPs occurrence and potential impacts on non-target organisms in aquatic environments have been focused in freshwater rivers and streams heavily impacted by wastewater effluent. However, because urban estuarine and marine environments typically receive inputs of complex mixtures of chemical contaminants from a variety of sources, including numerous municipal and industrial wastewater outfalls, characterization of PPCP concentrations in these environments is also important (Klosterhaus et al., 2013). A large number of analytical methodologies are available for their determination in surface waters, and recent trends are focused toward the development and application of generic methods that permit simultaneous analysis of multiclass compounds, including acidic, neutral, and basic pharmaceuticals (Gros et al., 2009).

Previous studies have observed PPCPs, as well as illicit drugs and their metabolites in marine environments (Maranho et al., 2015a; Klosterhaus et al., 2013; Fang et al., 2012; Weigel et al., 2002, 2004). Such compounds have been found at low concentrations in surface waters ($ng \cdot L^{-1}$), but they are continually released into ecosystems. This steady flow contributes to their persistence and potential adverse effects (Andreu et al., 2016; Alygizakis et al., 2016). Concerning specifically illicit drugs and their breakdown products, occurrences in regions of production and use and areas with insufficient wastewater treatment are not well studied (Rosi-Marshall et al., 2015).

In light of the lack of data on the occurrence of pharmaceuticals and illicit drugs in tropical coastal zones, the main objective of this study was to measure the presence of 33 emerging contaminants, including pharmaceuticals, cocaine, and its main metabolite benzoylecgonine in water samples from the Santos Bay (São Paulo, Brazil).

2. Material and Methods

2.1. Sampling sites

The sampling area selected in this study was Santos Bay (São Paulo, Brazil), which receives over 7367 m^3 of sewage per day. The main pollution sources of this coastal zone include wastewater discharges without appropriate treatment (Abessa et al., 2005).

The local wastewater treatment plant (WWTP) receives discharges from the cities of Santos and São Vicente, a dense urban area with 766,421 inhabitants (IBGE, 2015). This population size increases by 18.8% in Santos and 15.8% in São Vicente during the summer holidays, and can reach a total of 897,063 inhabitants (SPDR, 2011). It is important to note that this WWTP performs only a mechanical treatment (railing and screening for the removal of solids) that is followed by chlorination. Subsequently, sewage has been sent through pipes into the Santos Bay, in a 10 meter-deep area located 4.5 km away from the beach. The result is the release of wastewater without sufficient treatment into a semi-closed and low energy coastal system (Hortellani et al., 2005; Martins et al., 2008).

In light of the fact that seasonal dynamics that occur during related cultural events can influence the presence of pharmaceuticals and illicit drugs in the environment (Rosi-Marshall et al., 2015), water column sampling was conducted one day after the Carnival holiday (March, 6th, 2014) at 5 stations (surface — S and bottom — B) surrounding submarine sewage outfall in Santos Bay (Fig. 1). Sampling stations were pre-determined after a consideration of the possibilities for effluent plume dispersion and according to the monitoring stations of the São Paulo Environmental Agency (CETESB, 2014).

At each sampling station, three liters of surface water (1 m) and bottom water (8 m) were sampled only once using a Van Dorn bottle. Next, the samples were packaged into amber glass bottles that had previously been cleaned with HNO_3, methanol and distilled water. The samples were then transported to the laboratory in an insulated box with ice (<6 °C) and placed in a freezer at −20 °C until processing.

2.2. Sample preparation

The extraction technique was adapted from Wille et al. (2010). Prior to extraction, the pH of each seawater sample was adjusted to 7 ± 0.5 using an HCl solution (1 M). Next, 1-L samples were filtered through Whatman filter paper (GF/C diameter 47 mm, particle retention 1.2 μm, Merck, Darmstadt, Germany) to avoid the clogging of the sorbent. The filters were washed with 2 mL of methanol (Sigma-Aldrich) to prevent the loss of the compounds of interest. Methanol extract was collected and added to the filtered sample. Subsequently, solid-phase extraction (SPE) was performed using Chromabond HR-X cartridges (3 mL, 200 mg, Macherey-Nagel, Düren, Germany), as described by Wille et al. (2010) and Ghoshdastidar et al. (2015). The cartridges were pre-conditioned with 5 mL of methanol and 5 mL of Milli-Q water. After they had been loaded with 1 L of the filtered sample pooled with the methanol from the filter washing, the cartridges were rinsed twice with 5 mL of Milli-Q water. The cartridges were then dried under a vacuum for 30 min. Elution was performed using 5 mL of acetone and 2 × 5 mL of methanol.

After the SPE procedure, the samples were dried under nitrogen flow (at 50 °C) and then resuspended in 1 mL with a solution of water/acetonitrile (95:5, v/v) prior to LC–MS/MS analysis. Before the LC–MS/MS analysis, the samples were filtered in a 0.45 μM filter (Millipore).

2.3. LC–MS/MS analysis

An aliquot (10 μL) of each sample was analyzed by an HPLC Agilent 1260 (Agilent Technologies, CA, USA) combined with a 3200 QTRAP hybrid triple quadrupole/LIT (linear ion trap) mass spectrometer ABSciex, Ontario (Canada).

The conditions used for the LC separation were as follows: An injection volume of 10 μL of each sample was analyzed by an Agilent Eclipse XDB-C18 4.6 × 50 mm, 1.8 μm column at 25 °C. The eluent flow rate was 0.7 $ml \cdot min^{-1}$, and the mobile phase for positive mode analysis was 0.1% formic acid (Sigma-Aldrich LC–MS Grade) in water (solvent A) and acetonitrile (J.T. Baker LC–MS Grade) (solvent B). For negative mode analysis, the mobile phase was a 5 mM ammonium acetate buffer (Sigma-Aldrich) with a pH of 4.6 (solvent A) and acetonitrile (solvent B).

For both modes of ionization (positive and negative), a linear gradient of 0.7 $ml \cdot min^{-1}$ was used, starting with a mixture of 95% solvent A and 5% solvent B. The solvent A percentage was decreased linearly from