



Multiresidue determination and predicted risk assessment of contaminants of emerging concern in marine sediments from the vicinities of submarine sewage outfalls



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ABSTRACT

Submarine sewage outfalls (SSOs) are considered the main input source of contaminants of emerging concern continuously released in coastal areas, with the potential to cause adverse effects for aquatic organisms. This work presents the investigation of nine endocrine disrupting chemicals (EDCs) and 26 pharmaceutically active chemicals (PhACs) in marine sediments within the vicinities of 7 SSOs along the São Paulo State Coast (Brazil). Method optimization for the multi-residue determination by GC-MS/MS and LC-MS/MS using QuEChERS extraction/clean-up are discussed. Results demonstrate the occurrence of EDCs in concentrations ranging from less than method quantification limits (MQL) to 72.5 ng g⁻¹ in sediments. All PhACs were < MQLs. Nonylphenol was the most ubiquitous compound and the diversity of EDCs increased with an increase in populations serviced by SSOs. The predicted environmental risk assessment considering measured environmental concentrations and ecotoxicity endpoints from literature suggest a high-risk potential in some of the investigated SSOs.

1. Introduction

The continuous release of unregulated contaminants of emerging concern (CECs) into aquatic environments has the potential to cause adverse effects on exposed aquatic organisms, even at low environmental concentrations. CECs includes contaminants such as endocrine disrupting chemicals (EDCs), a class of synthetic and endogenous chemicals known as mimic natural hormones, with the potential to modulate normal endocrine system functions, such as growth, energy homeostasis and metabolic pathways, differentiation of tissues and organs, and sexual features (Jugan et al., 2010; Sosa-Ferreira et al., 2013). In the case of sex hormones regulation, EDCs can induce the development of female characteristics in aquatic organisms leading to sexual ratio disturbances or sterility, which can affect the population structure (WHO. World Health Organization, 2012). A number of commonly assessed EDCs include endogenous (17 β -estradiol, estrone and estriol) and synthetic (17 α -ethinylestradiol) steroid hormones, alkylphenols (nonylphenol and octylphenol), chlorophenols (triclosan and methyltriclosan) and bisphenol A, commonly present in industrial, agricultural and urban effluents. Another class of CECs are the

pharmaceutically active chemicals (PhACs), a group of biologically active substances with a broad range of physicochemical properties and used as therapeutic agents in human and veterinary medicine (Bayen et al., 2013; Halm-Lemeille and Gomez, 2016). PhACs are commonly detected in the aquatic environment, which can be related with their widespread use and/or their resistance to wastewater treatments (Coogan et al., 2007; Petrie et al., 2015).

PhACs and EDCs have been detected ubiquitously in all environmental matrices including freshwater, seawater, drinking water, wastewater (Chau et al., 2008; Cerqueira et al., 2008; Gunatilake et al., 2014; Celano et al., 2014), sewage sludge (Cerqueira et al., 2014; Langdon et al., 2011), sediments (Pojana et al., 2007; Berlioz-Barbier et al., 2014), and biota (Gonzalo-Lumbreras et al., 2014). Due to the broad range of physicochemical properties of chemicals classified as PhACs and EDCs they can exhibit variable affinity to solids, although these contaminants are usually investigated within the water column. However, in a constant input scenario coupled with deposition of suspended particulate matter, sediments can become more significant (David et al., 2009; Fernandes et al., 2011). This process can mean sediments are a potential secondary source of contaminants for the

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system, especially where resuspension of the bed sediments occurs (Sosa-Ferreira et al., 2013). In coastal areas CECs can be mainly detected close to submarine outfalls as well as in industrial and illegal sewage discharges on estuarine/marine interface (Cantwell et al., 2010). In comparison with freshwater ecosystems, few studies have been conducted regarding marine environments, once the expected concentrations of CECs are likely to be reduced due to dilution capacity and action and hydrodynamic processes (Arpin-Pont et al., 2016).

In many cities along the Brazilian Coast the discharge of domestic effluents via submarine sewage outfalls (SSOs) is the main solution for sewage discharge due to its relatively low costs (Abessa et al., 2012). For example, São Paulo is the most populated state in Brazil and its coastal zone is covered by a number of different sewage outfalls with total maximum flows of $> 13.8 \text{ m}^3 \text{ s}^{-1}$ (CETESB. CETESB. Companhia Ambiental do Estado de São Paulo, n.d.). Prior to submarine discharges, treatment of sewage usually only consists of screening, settling of solids and chlorination (CETESB. CETESB. Companhia Ambiental do Estado de São Paulo, n.d.; Abessa et al., 2005). As a result, the incomplete removal of contaminants can be observed in sewage from these SSOs, released in the coastal areas that can also receive contaminants from wastewater inputs via coastal rivers, diffuse sources and urban runoff. The coastal sites attended by SSOs have high ecological and economic relevance through activities including tourism, fishing and boating and the population of these regions can increase substantially during summer (December–February), and the volume of effluents discharged may surpass the and treatment capacity of sewage treatment facilities (CETESB. Companhia Ambiental do Estado de São Paulo. São Paulo Environmental Agency, 2013).

This study assessed a number of EDCs and PhACs in sediments sampled close to SSOs from São Paulo State Coast. Due to the trace levels ($\text{ng mL}^{-1}/\text{ng g}^{-1}$ or less) of EDCs and PhACs, the detection and quantification of microcontaminants in complex environmental matrices such as sediments can represent a challenge (Sosa-Ferreira et al., 2013; Arditoglou and Voutsas, 2011). The strong interaction between analytes and environmental matrices can increase detection and quantification limits, without significant inputs of, often laborious, pre-analytical clean extraction and clean-up (Nuñez et al., 2015). Both the physicochemical properties of contaminants, as well matrix complexity, are important to determine the ideal extraction and analysis conditions (Halm-Lemeille and Gomez, 2016). The quick, easy, cheap, effective, rugged and safe (QuEChERS) represents a simplified extraction and clean-up technique involving the determination of these compounds that has been widely used. The procedure involves a single extraction followed by a salting out partitioning step using different salts (NaCl, MgSO_4) and the increasing recovery of analytes in the organic phase followed by a dispersive SPE (d-SPE) (Cerqueira et al., 2008; Gonzalo-Lumbreras et al., 2014). In this sense, a multiresidue method using GC–MS/MS and LC–MS/MS were optimized and applied to the extracted samples. An ecological risk assessment of the concentrations found was performed at the risk characterization level in order to estimate the impact of these compounds on non-target organisms in coastal systems.

2. Experimental

2.1. Reagents

Standards: triclosan (TCS), methyltriclosan (MeTCS), bisphenol A (BPA), 17- α ethynylestradiol (EE2), 17- β estradiol (E2), estrone (E1), estriol (E3), 4-nonylphenol (4NP), 4-t-octylphenol (4-t-OP), triclosan d3 (TCSd3), bisphenol A d16 (BPAd16), phenyl nonylphenol ^{13}C (PnP ^{13}C), 17- β estradiol $^{13}\text{C}_2$ (E2 $^{13}\text{C}_2$) and estrone $^{13}\text{C}_2$ (E1 $^{13}\text{C}_2$) and all pharmaceuticals (SM-4) were purchased from Sigma Aldrich (NSW, Australia), 17 α -ethynylestradiol $^{13}\text{C}_2$ (EE2 $^{13}\text{C}_2$) was purchased from ScyVac Pty Ltd. (NSW, Australia). Acetonitrile, methanol and acetic acid were purchased from Thermo Fisher Scientific (Vic, Australia). PSA and C18 dispersive salts, Florisil, Pyridine, BSTFA + TMCS were

purchased from Sigma Aldrich (NSW, Australia).

Stock solutions were prepared in methanol from commercial standards in a concentration of $1 \mu\text{g mL}^{-1}$. The labeled standards: TCSd₃, BPAd₁₆, PnP ^{13}C , E2 $^{13}\text{C}_2$, E1 $^{13}\text{C}_2$ and EE2 $^{13}\text{C}_2$ were prepared at a concentration of $0.3 \mu\text{g mL}^{-1}$ where 0.4 mL was added to each sample 12 h before extraction procedure (final concentration of 50 ng g^{-1}). All solutions were stored at -20°C in the dark and used for a period of 6 months. Florisil was activated for 24 h at 80°C before use.

2.2. Sample collection

For method optimization, sediments were sampled in Santos Bay, São Paulo State Coast, Brazil ($24^\circ00.436\text{S } 46^\circ21.341\text{ W}$) in triplicate, in December 2012. Sediment was sampled using a Van Veen grab sampler and stored in aluminium containers. Redox potential (mV) was measured in the top 2 cm of each sediment sample and bottom water was also sampled for measurements of pH and salinity (PSU). In the laboratory, composite sediments were homogenized, freeze dried and stored at -4°C until analysis. The sediment characteristics were as follows: total carbon (3.9%); organic carbon (3.4%); total nitrogen (0.35%); CaCO_3 (4.5%); clay (32.7%); silt (29.6%); sand (16.7%); total fines (62.3%). Sediments for CECs assessment from seven submarine outfalls from São Paulo State Coast (Fig. 1) were sampled on December 17–18, 2012 (before the tourist season peak) and February 14–15, 2013 (following carnival festival and the end of tourist season peak). Sites included Tupi (T), Forte (F), Guarujá (G), Santos (S), Araçá (A), Ilhabela (I) and Cigarras (C), which underwent the same preparation procedures in the laboratory. Information about sampling points environmental conditions and sediments properties are described on SM-1.

2.3. Method optimization

For QuEChERS method using d-SPE, sediment (1 g) was extracted with acetonitrile and 0.1% acetic acid (10 mL) and Milli-Q water (5 mL) and vortexed in 40 mL glass vials. Then MgSO_4 (1 g) and NaCl (1 g) was added to the vials which were vortexed again and centrifuged for 10 min at 1500 rpm. After extraction, 5 mL of supernatant was removed and placed into vials containing the d-SPE salts (C18 and PSA), vortexed and centrifuged following the previous conditions. From this extract, 4 mL was placed in another test tube, concentrated to 1 mL under a N_2 stream and transferred to a chromatography vial. On the day of GC–MS/MS analysis, extracts were dried and resuspended with 1 mL of the derivatization (silylation) reagents, pyridine and BSTFA + TMCS (4:1) added to a thermal block at 60°C for 30 min and immediately injected for analysis. For pharmaceuticals, collected QuEChERS were injected directly into an LC–MS/MS.

2.4. Apparatus

2.4.1. GC–MS/MS

The system used for EDCs determination was a gas chromatograph (Agilent Technologies SA) tandem mass spectrometry (GC–MS/MS) triple quadrupole (QQQ) operating in MRM (multiple reaction monitoring) mode. The column used was HP-5MS Agilent 19091S-433 ($30 \text{ m} \times 250 \mu\text{m} \times 0.24 \mu\text{m}$ film thickness) using He (1 mL min^{-1}) as carrier gas. The injector temperature was set at 250°C in splitless mode with an injection volume of 1 μL . The oven program used was: 130°C (0.5 min) then $40^\circ\text{C min}^{-1}$ until 240°C and 5°C min^{-1} until 280°C (3.75 min) with a total running time of 15 min. Chromatographic properties of each analyte investigated are present in SM-2 and the typical chromatogram as well as quantifier ion in SM-3. For quantification, chromatograms were processed using Agilent MassHunter Worskstation Software Version B0502, 2008.

2.4.2. LC–MS/MS

For PhACs, extracts were determined by LC–MS/MS (Thermo

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