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Emerging organic contaminants in coastal waters: Anthropogenic impact, environmental release and ecological risk

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ABSTRACT

This study provides a first estimate of the sources, distribution, and risk presented by emerging organic contaminants (EOCs) in coastal waters off southwestern Taiwan. Ten illicit drugs, seven nonsteroidal anti-inflammatory drugs (NSAIDs), five antibiotics, two blood lipid regulators, two antiepileptic drugs, two UV filters, caffeine, atenolol, and omeprazole were analyzed by solid-phase extraction and liquid chromatography coupled to tandem mass spectrometry (SPE–LC–MS/MS). Thirteen EOCs were detected in coastal waters, including four NSAIDs (acetaminophen, ibuprofen, ketoprofen, and codeine), three antibiotics (ampicillin, erythromycin, and cefalexin), three illicit drugs (ketamine, pseudoephedrine, and MDMA), caffeine, carbamazepine, and gemfibrozil. The median concentrations for the 13 EOCs ranged from 1.47 ng/L to 156 ng/L. Spatial variation in concentration of the 13 EOCs suggests discharge into coastal waters via ocean outfall pipes and rivers. Codeine and ampicillin have significant pollution risk quotients (RQ > 1), indicating potentially high risk to aquatic organisms in coastal waters.

1. Introduction

Organic micropollutants in marine waters represent a threat to the aquatic environment, with effects such as acute and chronic toxicity to aquatic organisms, accumulation in the ecosystem and losses of habitats and biodiversity, as well as threats to human health (Sanchez-Avila et al., 2012). Residues of emerging organic contaminants (EOCs), such as pharmaceuticals, antibiotics, personal care products, and illicit drugs, are widely present in feces, medical waste, sewage treatment plants (STPs), rivers, and groundwater due to their extensive and long-term use in human therapies, illicit drug usage, veterinary medicine, agriculture, and aquaculture (Daughton and Ternes, 1999; Halling-Sorensen et al., 1998; Kasprzyk-Hordern et al., 2008b; Kummerer, 2009; Lapworth et al., 2012; Lopez-Serna et al., 2012; Postigo et al., 2010; Thomas et al., 2012).

The relationship between increased human population density and environmental change caused by human activity in coastal regions is well known. Coastal water is considered the ultimate sink for sewage and other by-products of human activities. Some recent studies show that notable amounts of EOC residues are transported to coastal areas via riverine inputs and STP effluents, except for some residues used in mariculture (Bueno et al., 2012; Comeau et al., 2008; Gulkowska et al., 2007; Hu et al., 2005; Jia et al., 2012; Zheng et al., 2012). Dense populations and intensive industry and agriculture (including animal husbandry and aquaculture) produce large amounts of domestic, industrial, agricultural, and aquacultural waste, which may result in various anthropogenic impacts. Many studies have reported steep gradients of pollutant concentration from rivers or STPs to the sea; nevertheless, despite dilution with seawater, EOCs occur widely in coastal areas, with some EOCs presenting high ecological risk to aquatic organisms. In the Asia–Pacific region, most of the work on EOC contamination in coastal environments comes from Hong Kong and China (Gulkowska et al., 2007; Minh et al., 2009; Richardson et al., 2005; Xu et al., 2007; Yan et al., 2013; Yang et al., 2011; Zhang et al., 2013b, 2012; Zheng et al., 2012; Zou et al., 2011). Le and Munekage (2004) and Managaki et al. (2007) reported monitoring data for antibiotics in Vietnam, and Choong et al. (2006) conducted a preliminary ecotoxicity study of pharmaceuticals in Singapore. To date, in Taiwan, there is only one report (from northern Taiwan) of detectable concentrations of clofibric acid, diclofenac, ibuprofen, and ketoprofen in STP effluents and receiving coastal waters (Fang et al., 2012).

The present study focuses on the southwestern coast of Taiwan, which has a population of approximately 8 million people and includes heavily urbanized and industrialized areas, and activities

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such as intensive animal husbandry and aquaculture. For example, the study area includes two highly urbanized cities, Tainan City and Kaohsiung City, with population densities of 4390 and 9948 persons/km^2, respectively. The Kaohsiung coast receives significant input of wastewater not only from river discharges but also from three ocean outfalls (Zuoying, Jhongjhou, and Dalinpu), which discharge 400,000 m^3 of treated civil wastewater effluent through the Jhongjhou STP outfall, and 150,000 m^3 of industrial wastewater through the Zuoying and Dalinpu outfalls daily (TWEPA, 2012). Additionally, there is input of wastewaters to the southwestern coast from two large animal husbandry areas, via the Erren River, Gaoping River, and Donggang River. Yet, little is known about the presence of EOCs in these discharges. The objectives of this study are to comprehensively survey the occurrence and distribution of 31 target EOCs (pharmaceuticals and personal care products (PPCPs) and illicit drugs) to the coastal environment, considering rivers and STP effluent discharge to the sea through ocean outfalls as pollution sources and seawater as the receptor. Ecological risks to aquatic organisms in the marine environment are assessed using calculated risk quotients (RQs).

2. Materials and methods

2.1. Sample collection

Seawater samples were collected (approximately 0–50 cm below the surface) at 53 stations in coastal southwestern Taiwan using a stainless steel bucket aboard the research vessel ORIII (voyage No. 1495) in October 2010. Each sample was immediately transferred to a 5 L pre-cleaned amber glass bottle. The glass bottle was rinsed with sample water prior to sampling. Following collection, samples were stored at 4 °C and transported to the laboratory. Based on its location, each sampling station was assigned to one the following groups: Tainan coast (T1–T11), Kaohsiung coast (K1–K23), or Pingdong coast (P1–P18) (Fig. 1).

2.2. Chemicals and standards

Methanol and acetonitrile (HPLC grade) were purchased from Merck Co. (Darmstadt, Germany). ACS-grade formic acid and hydrochloric acid were obtained from Fluka (Buchs, Switzerland). ACS-grade ammonium acetate was purchased from Sigma–Aldrich (St. Louis, MO, USA). Analytical-grade disodium ethylenediaminetetraacetate (Na_2EDTA) was obtained from Mallinckrodt Baker (Phillipsburg, PA, USA). Deionized (DI) water was prepared with a Milli-Q water purification system (Millipore, Bedford, MA, USA).

Thirty-one EOCs were selected as target compounds, comprising eight groups: nonsteroidal anti-inflammatory drugs (NSAIDs), antibiotics, lipid regulators, antiepileptic drugs, psychostimulants, ulcer-healing compounds, UV filters, and illicit drugs (Table 1). Most of the target EOCs are commonly used for prescription medication, over-the-counter remedies, human treatment, veterinary medicine, and drugs of abuse in Taiwan. These EOCs are also reported in many other locations, such as Europe, USA, Japan, Korea, and China (Del Rio et al., 2013; Gulkowska et al., 2007; Kasprzyk-Hordern et al., 2008b; Kolpin et al., 2002; Nakada et al., 2007; Thomas et al., 2012; Walraven and Laane, 2009; Yang et al., 2011; Yoon et al., 2010). Acetaminophen (ACE), acetaminophen-d_4, diclofenac (DIC), ibuprofen (IBU), ketoprofen (KET), naproxen (NAP), salicylic acid (SAL), codeine (COE), ampicillin (AMP), gemfibrozil (GEM), carbamazepine (CAB), fluoxetine (FLU), atenolol (ATN), caffeine (CAF), omeprazole (OME), amphetamine (APT), amphetamine-d_{11}, methamphetamine (MAP), methamphetamine-d_{14}, cocaine (COA), heroin (HRO), ketamine (KTM), pseudoephedrine (PED), cannabinol (CAN), flunitrazepam (FTP), 3,4-methylenedioxymethamphetamine (MDMA), MDMA-d_5 and gamma-hydroxybutyric acid (GHB) were obtained from Cerilliant (Round Rock, TX, USA). Sulfamethoxazole (SMX), tetracycline (TET), erythromycin-H_2O (ERY), cefalexin (CFX), and clofibric acid (CFB) were purchased from Sigma–Aldrich (St. Louis, MO, USA). Benzophenone-3 (BP3) and benzophenone-4 (BP4) were obtained from Fluka (Buchs, Switzerland). $^{13}C_3$-caffeine and $^{13}C_6$-ibuprofen (1 mg/mL) were purchased from Cambridge Isotope Laboratories (Andover, MA, USA). Stock standard solutions of 1000 mg/L were prepared in methanol and stored in amber glass bottles at −20 °C for a maximum of 15 days. Working solutions were prepared by diluting the stock standard solution in methanol.

2.3. Extraction and analytical procedure

EOCs were extracted from the water samples by solid-phase extraction (SPE) using an Oasis HLB cartridge (500 mg, 6 mL; Waters Corporation, Milford, MA, USA). The extraction protocol is modified for use with EOCs, as described previously (Jiang et al., 2013; Kasprzyk-Hordern et al., 2008a; Nebot et al., 2007). In summary, a 5 L seawater sample was filtered through 0.7 μm glass fiber filters (GF/F, Whatman, Maidstone, England), then adjusted to pH 6 (with 0.1 M HCl), followed by addition of 0.2 g Na_2EDTA. Before the samples were extracted, 300 ng of acetaminophen-d_4, amphetamine-d_{11}, methamphetamine-d_{14}, MDMA-d_5, $^{13}C_6$-ibuprofen, and $^{13}C_3$-caffeine were spiked to each sample as isotopically labeled surrogates to quantify procedural recovery. An Oasis HLB cartridge was conditioned sequentially with 6 mL of methanol and 6 mL of DI water. The water samples were then loaded onto the cartridge and eluted at a rate of approximately 10 mL min^{-1}. The cartridge was then washed with 6 mL DI water. Finally, the target fraction was eluted with 6 mL methanol. The volume of elute was reduced under a gentle stream of nitrogen, then dissolved in 50% aqueous methanol to a final volume of 1 mL, then transferred into an amber autosampler vial for chemical analysis.

Concentrations of EOCs were analyzed using high-performance liquid chromatography-electrospray ionization tandem mass spectrometry (HPLC–ESI-MS/MS) with multiple-reaction monitoring (MRM). Two different methods were applied for separation of analytes (method 1 for PPCPs and method 2 for illicit drugs), and both were performed using an Agilent 1200 series chromatograph (Agilent, Palo Alto, USA) interfaced with an API 4000 triple quadrupole mass spectrometer (Applied Biosystems, Foster City, CA) operated in positive and negative modes. The injection volumes for method 1 and method 2 were 50 μL and 10 μL respectively, and the autosampler was operated at 25 °C. Separation in method 1 was performed on a 150 mm × 4.6 mm ZORBAX Eclipse XDB-C18 column with 5 μm particle size (Agilent, Palo Alto, CA, USA) and a mobile phase consisting of 0.1% formic acid (v/v) and 5 mM ammonium acetate in DI water (mobile phase A) and 0.1% formic acid (v/v) in methanol (mobile phase B) gradient. The flow rate was maintained at a constant 1.0 mL/min. The gradient was initiated with 0% mobile phase B for 0.5 min, increased to 40% from 0.5–3.0 min, to 70% from 3.0–7.5 min, to 95% from 7.5–9.0 min, kept constant at 95% until 11 min, decreased to 0% from 11 min to 12 min, and kept at 0% thereafter. Separation in method 2 was performed using a Kinetex PFP column (Phenomenex, Torrance, CA, USA; 100 mm × 2.1 mm, 2.6 μm). Flow rate through the column was 300 μL/min, with gradient elution conditions initiating at 10% mobile phase B, increasing to 95% at 6 min, before reverting to the original conditions at 10 min. Compositions of the mobile phases were as follows: (A) deionized water/0.1% formic acid; (B) acetonitrile/0.1% formic acid.

Ions were acquired in MRM mode with a dwell time of 200 ms and unit mass resolution on both mass analyzers. Two MRM pairs were used to identify the target compounds (Table 1). Conditions

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