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Baseline

Antibiotics in the coastal environment of the Hailing Bay region, South China Sea: Spatial distribution, source analysis and ecological risks

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ABSTRACT

In this study, the occurrence and spatial distribution of 38 antibiotics in surface water and sediment samples of the Hailing Bay region, South China Sea, were investigated. Twenty-one, 16 and 15 of 38 antibiotics were detected with the concentrations ranging from <0.08 (clarithromycin) to 15,163 ng/L (oxytetracycline), 2.12 (methacycline) to 1318 ng/L (erythromycin–H₂O), <1.95 (ciprofloxacin) to 184 ng/g (chlortetracycline) in the seawater, discharged effluent and sediment samples, respectively. The concentrations of antibiotics in the water phase were correlated positively with chemical oxygen demand and nitrate. The source analysis indicated that untreated domestic sewage was the primary source of antibiotics in the study region. Fluoroquinolones showed strong sorption capacity onto sediments due to their high pseudo-partitioning coefficients. Risk assessment indicated that oxytetracycline, norfloxacin and erythromycin–H₂O posed high risks to aquatic organisms.

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As a class of pharmaceuticals, antibiotics are used extensively for several decades to prevent and treat human and animal diseases, as well as being growth promoters in livestock and aquaculture (Shi et al., 2014). In China, the annual production of antibiotics has been estimated to 210,000 tons, with 180,000 tons applied in medicine and agriculture (Luo et al., 2010). After administration, a significant fraction has been released into different environmental compartments in the parent, active metabolite or conjugate forms (Zhou et al., 2013a). Due to limited removal efficiencies (for example, sulfonamides (–62.5% to 94.8%), tetracyclines (–88.1% to 100%), macrolides (7.94–93.4%), trimethoprim (57–76.5%)) (Zhou et al., 2013a,b) in sewage treatment plants (STPs) or direct discharge, varieties of antibiotics have been found in surface water (Murata et al., 2011), groundwater (Mutiyar and Mittal, 2014), sediments (Na et al., 2013), soil (Hansen et al., 2009) and animal manure (Zhou et al., 2013b), which are still intrinsically bioavailable and bioactive, resulting in undesirable effects on non-target organisms (Leung et al., 2012).

Oceanic water bodies can act as a major receptacle of antibiotic residues (Zhang et al., 2013a,b). Large amounts of antibiotics are

transported from the land into coastal waters via riverine inputs (Zheng et al., 2012; Mutiyar and Mittal, 2014) and effluents of sewage treatment plants (Xu et al., 2007, 2009). These residues have caused various levels of antibiotic contamination in seawater in the USA, Germany, Greece, Turkey, Italy (Noedler et al., 2014), Belgium (Wille et al., 2010), and China (Minh et al., 2009; Jia et al., 2011; Zhang et al., 2012; Zhang et al., 2013a,b). Four antibiotics including clarithromycin, erythromycin, roxithromycin, and sulfamethoxazole were detected in 153 seawater samples collected from the shorelines of the Baltic Sea, Northern Adriatic Sea, Aegean Sea, Dardanelles, San Francisco Bay, Pacific Ocean, Mediterranean Sea, and Balearic Sea (Noedler et al., 2014). Sulfamethoxazole was most frequently detected antibiotics in San Francisco Bay with concentrations ranging from 13 to 61 ng/L (Noedler et al., 2014). Two antibiotics sulfamethoxazole and trimethoprim were detected in the range of not detected (ND)–96 ng/L in seawater of Belgian harbours (Wille et al., 2010). Compared with other countries, antibiotics detected in seawater in China were much higher (Minh et al., 2009; Jia et al., 2011; Zhang et al., 2012, 2013a,b). For example, the maximum concentrations of erythromycin, trimethoprim, sulfamethoxazole and roxithromycin were up to 1730, 330, 77, 630 ng/L in Victoria Harbour of Hong Kong, Laizhou Bay, Liaodong Bay and Bohai Bay,

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respectively (Minh et al., 2009; Jia et al., 2011; Zhang et al., 2012; Zhang et al., 2013a,b). However, most studies mainly focused on the presence of antibiotics in marine environment coming from terrestrial discharge, knowledge on the pollution levels of antibiotics in the aquaculture zones and their surrounding coastal areas was very limited. In addition, most studies have only targeted one group or a narrow range of antibiotics and their metabolites (Minh et al., 2009; Jia et al., 2011; Zhang et al., 2012), making it hard to understand the pollution levels of antibiotics which are widespread used, especially in aquaculture industry of China.

Hailing Bay region, including Hailing Bay and Hailing Island, is located in the southwest of Guangdong province. The Hailing Bay includes two parts, the inner bay being a semi-enclosed sea and the outer bay being an open sea. Hailing Island is a nationally well-known major aquaculture zone, with aquatic product output of 18.06 million tons and the output value of ¥1.7 billion in 2012 (Seafood Information of Hailing Island, 2012). The Hailing Bay region, which serves as a sink of various terrestrial pollutants, receives terrestrial waste from municipal sewage, agricultural waste and industrial wastewater. According to field investigation, there are no STPs in this region, and wastewater is directly discharged into the marine environment without any treatment. Furthermore, in China, including Hailing Bay, most aquaculture farms are hydrologically connected with the external aquatic environment. Thus the antibiotic residues in wastewater from these aquaculture farms may be discharged into external water bodies, posing potentially ecological risks on aquatic environment, including those aquatic organisms (Rico et al., 2013). A previous study reported the contamination of fluoroquinolone residues in different samples from Hailing Island (He et al., 2012), with high level of norfloxacin (255 ng/g) detected in liver tissue of *Siganus fuscescens*. In our previous investigation, 14 and 3 antibiotics have been detected in seawater (<0.7–15,163 ng/L) and sediment (0.8–4.8 ng/g) samples in aquaculture farms on Hailing Island, respectively (Chen et al., 2015). Despite of these two studies, investigation on the occurrence and source of antibiotics in Hailing Bay region has been limited. Meanwhile the fate and potential adverse impacts of these pollutants on ecosystems surrounding the region are largely unknown yet. Therefore, the objectives of this study were to (1) investigate the occurrence of 38 antibiotics in the water and sediment phases in the Hailing Bay region, (2) evaluate the spatial distribution and the sources of the antibiotics based on the correlations between environment variables and antibiotic concentrations, (3) determine the partitioning behavior of antibiotics between water and sediment phases, (4) assess the ecologic risk of the antibiotics to the aquatic organisms according to the calculated risk quotients (RQs).

Thirty-eight target antibiotics belong to six different antibacterial classes: (1) sulfonamides (SAs), including sulfameter (SM), sulfapyridine (SPD), sulfadiazine (SDZ), sulfamethazine (SMZ), sulfathiazole (STZ), sulfisoxazole (SX), sulfadimethoxine (SDM), sulfamethoxazole (SMX), sulfadoxine (SDO), sulfamonomethoxine (SMM), sulfaquinoxaline (SQX), trimethoprim (TMP). TMP is grouped with the sulfonamides due to its similar properties to other sulfonamides; (2) tetracyclines (TCs), including chlortetracycline (CTC), doxycycline (DC), oxytetracycline (OTC), tetracycline (TC), methacycline (MT); (3) fluoroquinolones (FQs), including ciprofloxacin (CFX), danofloxacin (DAN), difloxacin (DIF), enrofloxacin (EFX), fleroxacin (FL), lomefloxacin (LFX), norfloxacin (NFX), ofloxacin (OFX), marbofloxacin (MAR), pefloxacin (PEF); (4) macrolides (MLs), including clarithromycin (CTM), leucomycin (LCM), oleandomycin (ODM), erythromycin (ETM), roxithromycin (RTM) and tylosin (TYL). (5) Ionophores (IPs), including salinomycin (SAL) and narasin (NAR). (6) Others, including monensin (MON), lincomycin (LIN) and novobiocin (NOV). All these targets were purchased from US Pharmacopoeia (Rockville,

Maryland), Sigma–Aldrich (St. Louis, MO, USA), Dr. Ehrenstorfer GmbH (Germany). Five isotope-labeled internal standards, ciprofloxacin-D₈ (CFX-D₈), erythromycin-¹³C-D₃ (ETM-¹³C-D₃), lincomycin-D₃ (LIN-D₃), thiabendazole-D₄ (TBD-D₄) and trimethoprim-D₃ (TMP-D₃) were purchased from Toronto Research Chemicals (North York, ON, Canada). Other three internal standard, meclocycline (MC), sulfamerazine-D₄ (SMR-D₄) and sulfamethazine-¹³C₆ (SMZ-¹³C₆) were purchased from Dr. Ehrenstorfer GmbH (Germany), Sigma–Aldrich (St. Louis, MO, USA), Cambridge Isotope Laboratories (Andover, MA, USA), respectively. HPLC-grade methanol and acetonitrile were obtained from Merck (Darmstadt, Germany). Oxalic acid and ammonium acetate were obtained from Sigma–Aldrich (St. Louis, MO, USA), formic acid was purchased from Tedia Company (Fairfield, OH, USA). Other chemicals, disodium edetate (Na₂EDTA), citric acid and sodium citrate were analytical grade and purchased from Yaohua Chemical Reagent Factory (Tianjin, China). Strong anion exchange (SAX) cartridges (6 mL, 500 mg) were obtained from Varian (Lake Forest, CA, USA), and Oasis HLB cartridges (6 mL, 200 mg or 6 mL, 500 mg) were purchased from Waters (Milford, MA, USA). Glass fiber filters (GF/F, pore size 0.7 μm) were purchased from Whatman (Maidstone, England).

The locations of study areas and sampling sites are illustrated in Fig. 1. During September 23–29, 2013 at the low tide, a total of 39 samples of surface seawater, 1 discharge site wastewater and 24 sediment samples were collected from the Hailing Bay region. Detail information on the sampling sites is given in Table S2. Water samples were collected using a hydrophore and transferred to 5 L pre-cleaned bottles immediately. Two parallel samples were sampled at each sampling point. Then about 5% (v/v) of methanol was added to each water sample to suppress microbial activity. The pH value of each sample was adjusted to 3 by using 4 M H₂SO₄ and kept at 4 °C. All water samples were processed within 48 h. Surface sediment samples (0–30 cm) were collected in polyethylene bags by Peterson grab sampler and kept in an ice box. After returning to the laboratory, the surface sediment samples were freeze-dried immediately, then crushed and homogenized. More background information for water and sediment samples were provided in Tables S2, S4 and S5.

The target antibiotic compounds were analyzed according to the previous method (Zhou et al., 2012). The LC–MS/MS system consisted of an RRLC–MS/MS (Agilent Liquid Chromatography 1200 series RRLC system) and a Triple Quadrupole detector (Agilent 6460) with an electrospray ionization (ESI+) source (Agilent, Palo Alto, CA, USA). The analyses were operated in the positive mode and multiple-reaction monitoring (MRM) mode. Separation of the compounds were carried out by an Agilent 1200 series (Agilent, Palo Alto, USA) on an Agilent Zorbax Eclipse Plus-C18 column (100 mm × 2.1 mm, 1.8 μm) with a guard column.

The mobile phases were 0.2% (v/v) formic acid aqueous solution with 2 mM ammonium acetate (mobile phase A) and acetonitrile (mobile phase B). The mobile phase gradient was ramped at a flow rate of 0.3 mL/min from 10% to 15% B in 5 min and 15–20% B in 2 min, then ramped from 20% to 40% B in 4 min and 40–60% B in 4 min, finally ramped to 95% B in 1 min and kept for 9 min. The column temperature was 40 °C. The injection volume was 5 μL. The mass spectrometric operating conditions were optimized: The gas temperature and gas flow were 325 °C and 6 mL/min, respectively. The nebulizer pressure was 45 psi and sheath gas flow was set to 11 L/min. The sheath gas temperature was 350 °C. The nozzle voltage and capillary voltage were 0 V and 3500 V, respectively. More detailed method information is described in Tables S1.

All chemical analyses of antibiotics were subject to strict quality assurance and quality control procedures. Quantitative analysis of antibiotics was performed using liquid chromatography-tandem

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