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Antibiotics in riverine runoff of the Pearl River Delta and Pearl River Estuary, China: Concentrations, mass loading and ecological risks

Weihai Xu [a,*], Wen Yan [a], Xiangdong Li [b], Yongde Zou [c], Xiaoxiang Chen [c], Weixia Huang [a], Li Miao [a], Ruijie Zhang [d], Gan Zhang [d], Shichun Zou [e]

[a] *CAS Key Laboratory of Marginal Sea Geology, South China Sea Institute of Oceanology, Chinese Academy of Sciences, Guangzhou 510301, China*
[b] *Department of Civil and Structural Engineering, The Hong Kong Polytechnic University, Kowloon, Hong Kong*
[c] *Nanhai Entry-Exit Inspection and Quarantine, Foshan 528200, China*
[d] *State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China*
[e] *School of Marine Sciences, Sun Yat-sen University, Guangzhou 510275, China*

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ABSTRACT

Ten antibiotics belonging to three groups (macrolides, fluoroquinolones and sulfonamides) were investigated in riverine runoff of the Pearl River Delta (PRD) and Pearl River Estuary (PRE), South China for assessing the importance of riverine runoff in the transportation of contaminants from terrestrial sources to the open ocean. All antibiotics were detected in the eight outlets with concentrations ranging from 0.7 to 127 ng L^{-1}. The annual mass loadings of antibiotics from the PRD to the PRE and coast were 193 tons with 102 tons from the fluoroquinolone group. It showed that antibiotics decreased from the riverine outlets to the PRE and open ocean. Risk assessment showed that most of these antibiotics showed various ecological risks to the relevant aquatic organisms, in which ofloxacin (OFL), erythromycin (ETM) and ciprofloxacin (CIP) posed high ecological risks to the studied aquatic environments.

1. Introduction

In recent years, the occurrence and fate of antibiotics in the aquatic environment has been recognized as one of the emerging and important issues in environmental pollution. The presence of antibiotics in the environment generally results from human and veterinary excretion of metabolized or unmetabolized drug passing into sewage systems (Lindberg et al., 2007; Miao et al., 2002; Nödler et al., 2011; Ternes, 1998; Xu et al., 2007b). Antibiotics are considered as a class of ubiquitous contaminants in aquatic environment due to the fact that most of them are water soluble and resist degradation or transformation (Kolpin et al., 2002; Nödler et al., 2012). Therefore, these compounds have received great attention in aquatic environment from the general public and scientific community owing to their potentially negative impacts on human and animals, such as potential ecological risk, and spreading of antibiotic resistance and antibiotic resistance genes (ARGs), etc (Heddini et al., 2009; Pruden et al., 2006). Hundreds of various ARGs encoding resistance to a broad range of antibiotics have been found in various environments resulting directly from an intensive use of antibiotics in both human and veterinary medicine (Luo et al., 2011; Storteboom et al., 2010; Vignesh et al., 2012). More importantly, ARGs can horizontally transfer and amplify in the environment under certain conditions by genetic mechanisms (Rysz and Alvarez, 2004; Sedgley et al., 2008).

Oceans and coastal zones in particular, are acting as reservoir for many contaminants originating from various sources. It has been documented that riverine runoff is the most important contributor of contaminants transported from terrestrial sources into coastal regions (Lu et al., 2009; Shimizu et al., 2013). Therefore, knowledge on specific contaminant mass fluxes from rivers into coastal regions should be valuable for identifying their possible sources and understanding their effects on marine systems. The Pearl River Delta (PRD) is one of the most developed and urbanized areas in China, connecting the Pearl River Estuary (PRE) to the South China Sea (SCS) via eight major riverine runoff outlets. The PRD generates 64% of the industrial sewage and 74% of the domestic sewage within the entire Guangdong Province (Ma et al., 2005). It was estimated that about 1.73×10^{10} t per year of wastewater are discharged from the PRD into the PRE and the SCS.

The global annual application of antibiotics has been estimated between 100,000 and 200,000 tons (Kummerer, 2003). More than 22,000 tons of antibiotics are consumed in China each year, with equal distribution between human and veterinary applications. The

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* Corresponding author.
E-mail address: whxu@scsio.ac.cn (W. Xu).

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PRD region has more than 25 million permanent residents and 10 million temporary inhabitants. Resulting from the large population and intensified poultry/fish farming activities, this region has become one of the largest antibiotics consumption regions in China as well as in the whole world. More than 20 antibiotic compounds can be found in sewage water and sediment, vegetable and soil, river water, and even in tap water and drinking water resources in the PRD (Hu et al., 2010; Richardson et al., 2005; Xu et al., 2007a; Zhang et al., 2012). There is no data so far on the riverine mass loadings of antibiotics in the same region. We believe that this study will contribute to the understanding of the current situation of antibiotics in surface waters and in the coastal environment in the PRD.

Main objectives of this study are (1) to examine the occurrence and seasonal variations of common antibiotics in the riverine runoff of the Pearl River system; (2) to investigate annual mass flux of antibiotics from the PRD to the PRE and coastal environments; (3) to assess the ecological risks in the riverine and coastal environments using calculated risk quotients (RQs).

2. Materials and methods

2.1. Materials

Ten in China frequently used and earlier in the Pearl River detected antibiotics (Xu et al., 2007a; Zhang et al., 2012), were selected in this study. These are ofloxacin (OFL), norfloxacin (NOR), enrofloxacin (ENR), ciprofloxacin (CIP), roxithromycin (RTM), erythromycin (ETM), sulfadiazine (SDZ), sulfadimidine (SMZ), sulfamethoxazole (SMX) and chloramphenicol (CAP). Standards were purchased from Sigma–Aldrich Co. $^{13}C_3$-caffeine solution was obtained from Cambridge Isotope Labs ($1\ mg\ mL^{-1}$ in methanol, USA). It should be noted that erythromycin was detected as its dehydration product (ETM-H_2O) because this compound is readily dehydrated by loss of one water molecule (Gobel et al., 2005).

2.2. Samples collection

The Pearl River is the largest and most complex water system in South China. It has a catchment area of more than 450,000 km^2, with an annual mean runoff volume of 326 billion m^3. The river water finally enter the SCS via eight major outlets, Humen (HM), Jiaomen (JM), Hongqilimen (HQ), Hengmen (HE) on the eastern side, and Modaomen (MD), Jitimen (JT), Hutiaomen (HT), and Yamen (YM) on the western side (Fig. 1). Detailed information of the eight outlets was present elsewhere (Ni et al., 2008) (Table S1).

Sampling campaigns at the eight outlets were conducted in three different periods, June 2009, October 2009 and January 2010, which are representative months for the wet season, intermediate season and dry season, respectively. All sampling work was conducted during nip tides in order to avoid tidal influences (Ni et al., 2008). At each sampling outlet, three duplicated water samples, distributed horizontally along the river cross section were collected as 1-h composite samples using a peristaltic pump (BT50b, Prefluid). Later, the three duplicated water samples were combined into one composite sample. The water samples were kept at 5 °C in a cold storage room and analyzed within one week. The sampling campaigns in the PRE were conducted in wet season and dry season. A total of 16 sampling sites widely distributed in the PRE were selected during the two sampling campaigns (Fig. 1). Three replicate samples were collected at each station in the PRE.

2.3. Samples preparation and extraction

The methods for treatment and analysis of river water and seawater samples were earlier reported (Xu et al., 2007a), and only a brief description is given here. In summary, 1 L of water sample was filtered through 0.45 μm glass fiber filters and acidified to pH 3.0. Then the water was extracted by an Oasis HLB cartridge (6 mL, 500 mg, Waters). 100 ng $^{13}C_3$-caffeine was added as a surrogate to monitor the recovery before extraction. The HLB cartridge was then rinsed with 10 mL of ultra-pure water, and dried under nitrogen gas for 1 h. After being dried, the cartridge was eluted by methanol. For the recovery experiments, 1 L of filtered artificial seawater and river water were fortified separately with 100 ng of target analytes, and 100 ng of surrogate (Xu et al., 2007a). The solutions were treated in the same procedure as the field samples described above.

2.4. Antibiotics analysis

Antibiotics were analyzed by liquid chromatography–tandem mass spectrometry using multiple reaction monitoring (MRM). Liquid chromatography was performed on an HP 1100 LC (Agilent Technologies, Palo Alto, CA, USA) controlled gradient system. It was equipped with an auto sampler, a pump and a thermostated column oven. An ODS-P (Dikma, USA. 4.6 mm × 250 mm i.d., 3.5 μm) chromatographs column was employed. Mass spectrometric measurements were performed on a Sciex API 4000™ (Applied Biosystems, CA, USA) equipped with an electrospray ionization source (ESI). The conditions of LC system and mass spectrometric are described earlier (Xu et al., 2007a).

Quantitative analysis of each compound was performed using two highest characteristic precursor ion/product ion transitions. Together with the retention times, the characteristic ions were used to ensure correct peak assignment and peak

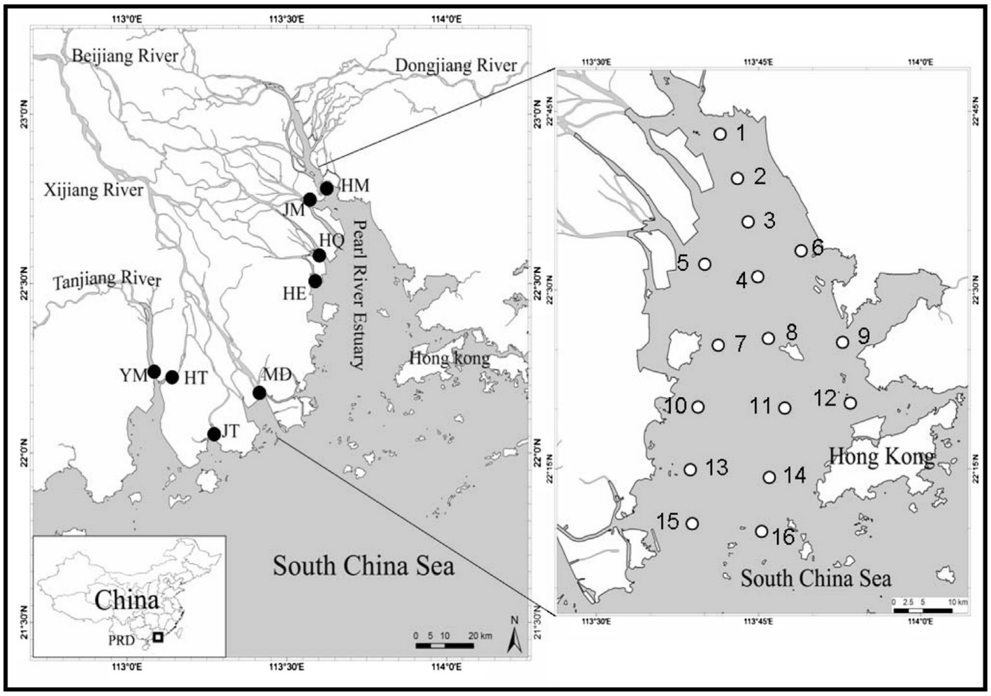

Fig. 1. Maps of the sampling sites in the Pearl River Delta, China. The eight major runoff outlets are labeled with HM (Humen), JM (Jiaomen), HQ (Honqimen), HE (Hengmen), MD (Modaomen), JT (Jitimen), HT (Hutiaomen), and YM (Yamen).