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Occurrence and distribution of antibiotics in coastal water of the Bohai Bay, China: Impacts of river discharge and aquaculture activities

Shichun Zou [a], Weihai Xu [b], Ruijie Zhang [c], Jianhui Tang [c], Yingjun Chen [c], Gan Zhang [c,d,*]

[a] School of Marine Sciences, Sun Yat-sen University, Guangzhou 510275, China
[b] CAS Key Laboratory of Marginal Sea Geology, South China Sea Institute of Oceanology, The Chinese Academy of Sciences, Guangzhou 510250, China
[c] Yantai Institute of Coastal Zone Research, The Chinese Academy of Sciences, Yantai 264003, China
[d] State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, The Chinese Academy of Sciences, Guangzhou 510640, China

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ABSTRACT

The presence of 21 antibiotics in six different groups was investigated in coastal water of the Bohai Bay. Meantime, to illuminate the potential effects caused by the river discharge and aquaculture activities, wastewater from three breeding plants and surface water from six rivers flowing into the Bohai Bay were also analyzed for the selected antibiotics. The result revealed that measured antibiotics in the North Bobai Bay were generally higher than those in the South, highlighting the remarkable effects of high density of human activities on the exposure of antibiotics in environment. The antibiotics found in the six rivers were generally higher than those in the Bohai Bay reflecting the important antibiotics source of river discharge. This study reveals that the high consumption of some antibiotics in aquaculture activities may pose high ecological risk to the bay.

1. Introduction

Antibiotics have been used for several decades in both human and veterinary medicine and they are often partially metabolized in the organism and excreted as the parent compound or as metabolites in urine and faeces before being discharged into sewage. It is well recognized at the present that the widespread use of antibiotics has led to a growing concern in the fate after their consumption and residues in aquatic environment. This concern is focused on their potential function toward the wide spread resistance of bacterial pathogens, and post-therapeutic effects.

Previous studies have proved that antibiotics are poorly removed by sewage treatment plants (STPs) and may reach surface waters (Gobel et al., 2005; Ternes, 1998; Xu et al., 2007a). A number of studies have shown that the pharmaceutical residues are widespread in the aquatic environment, where some compounds were detected at concentrations up to a few μg L^{-1} (Golet et al., 2002; Hirsch et al., 1998; Sacher et al., 2001). There exists great difference in the types and concentrations of antibiotics detected in different areas and countries, even in different regions of the same country; this can be mainly explained by the prevalence of diseases, treatment habits, or simply market and economic reasons.

The main interest regarding the use of pharmaceuticals as well as antibiotics in human and animal treatment is the development of resistant bacteria strains representing a health risk to humans and animals. Exposure to antibiotics might induce resistance (Kummerer, 2004) and horizontal transfer of resistance genes in field bacterial populations (Davison, 1999). The antibiotic resistance genes (ARGs) have been recognized as a new emerging contaminant in environment. This new contaminant has been confirmed in many studies in different environment media and recognized as one of the main environmental issues that people have to face in the 21st century (Costa et al., 2008; Dantas et al., 2008; Kemper, 2008; Wells et al., 2007). The ARGs in surface water can transfer via estuaries to open sea and induce global pollution.

Bohai Bay is a large, typical semi-enclosed inner sea located in the northeast of China. Besides hundreds of drains, there are more than 50 continental rivers flowing directly into the Bohai Bay. It receives wastewater and municipal sewage from not only many factories located in the vicinity, but also from the city of Beijing. China being the biggest manufacturer and consumer of pharmaceuticals in the world, the pharmaceuticals pollution in Chinese aquatic environment could possibly be more serious than in other regions of the world. The previous investigations on antibiotics in surface water body of the Pearl River Delta (PRD) provide direct evidence for this conclusion. However, to date, there has been no report on the occurrence of antibiotics in the Bohai Bay as well as in North China.

* Corresponding author.
E-mail address: zhanggan@gig.ac.cn (G. Zhang).

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The target antibiotics in present study belong to six groups, fluoroquinolones, macrolides, sulfonamides, tetracyclines and chloramphenicoles, polypeptides and β-lactam. Fluoroquinolones, macrolides and β-lactam are the most frequently prescribed antibiotics for human treatment in China. The most antibiotics selected in this study were widely present in surface waters in Europe, the U.S.A., and in China (Hirsch et al., 1999; Kolpin et al., 2002; Lindsey et al., 2001; McArdell et al., 2003; Xu et al., 2007b). Sulfonamides and tetracyclines were detected up to several hundreds μg L^{-1} in poultry farms or aquaculture ponds (Kemper, 2008; Le and Munekage, 2004). It is known that antibiotics are often used in aquaculture for disease prophylaxis and treatment, and/or for growth promotion. The unconsumed food and fish faeces containing antibiotics reach the bottom of the raising pens; antibiotics are gradually leached from the food and faeces, diffuse into the sediment and finally can be washed by currents to distant sites.

The purpose of this study was to document the occurrence and distribution of selected antibiotics in the coastal water of the Bohai Bay. A systematic survey on inputs of antibiotic pollutants from main continental rivers flowing into Bohai Bay was also conducted. Specific objective was to demonstrate the effects of widely distributed aquaculture activities in this area on the Bohai Bay.

2. Materials and methods

2.1. Chemicals and standards

21 compounds belonging to reference six groups, ampicillin (AMP), oxacillin (OXA), penicillin G (PEN G), ceftazidime (CTD), cefazolin (CFZ), cefotaxime (CTX), cefalexin (CLX), sulfadiazine (SDZ), sulfamethazine (SMZ), sulfamethoxazole (SMX) trimethoprim (TMP), norfloxacin (NOR), ciprofloxacin (CIP), ofloxacin (OFL), tetracycline (TC), oxytetracycline (OTC), chlortetracycline (CTC), chloramphenicol (CHP), roxithromycin (ROX), erythromycin (ERY) and vancomycin (VCM), were purchased from Sigma–Aldrich Company. The detailed information of these compounds, such as CAS No., molecular formula, pKa and structure had been illustrated in the previous studies (Li et al., 2009). $^{13}C_3$-caffeine solution was obtained from Cambridge Isotope Labs (1 mg mL^{-1} in methanol, USA). All the antibiotic compounds were dissolved in methanol and stored in a freezer. Erythromycin–H_2O (ETM–H_2O), a major degradation product of erythromycin, was obtained by acidification from erythromycin (McArdell et al., 2003). Ultra-pure water was prepared with a Milli-Q water purification system (Millipore, Bedford, MA, USA). Unless otherwise indicated, chemicals used in the analysis were purer than the analytical grade.

2.2. Sample collection

The sampling was carried out during May 5–10, 2008. A total of 28 sampling stations in the Bohai Bay with sector distribution were selected (see Fig. 1). Besides, 23 water samples were collected from 6 main rivers among the 53 ones pouring into the Bohai Bay. Except for the Dou River, the other four rivers including Suyun River, Yongding River, Duliujian River and Ziya River are four main tributaries of the Haihe River. All water samples were collected (~1 m below the surface) using a water grab sampler and stored in precleaned brown glass bottles. The bottles were rinsed with water sample three times before the final sample was collected.

In addition, a total of 12 effluent samples from three aquafarms (fish pond, breeding farm and nursery plant, respectively) around the Bohai Bay were collected. The samples were kept at 5 °C in a cold storage room for further treatment and analysis in laboratory.

2.3. Sample preparation and extraction

The methods for analyzing river water and seawater samples described in previous studies were used in this study (Li et al., 2009; Xu et al., 2007b). In summary, 1 L water sample was filtered through 0.45 μm glass fiber filters and then extracted by an Oasis HLB cartridge (6 mL, 500 mg, Waters). About 100 ng $^{13}C_3$-caffeine was added as a surrogate to monitor the recovery. The HLB column was then rinsed with 10 mL of ultra-pure water, and dried under nitrogen gas for 1 h. After dried, the cartridge was eluted with 2 mL (×3) of methanol. The analytes were collected in a 10 mL brown glass vial, volume-reduced under nitrogen purge to about 20 μL, and then dissolved in 40% aqueous methanol to a final volume of 1.0 mL.

2.4. Instrumental analysis

The extracted antibiotics were analyzed using ultra performance liquid chromatography tandem mass spectrometry (UPLC-MS/MS) with multiple reaction monitoring (Li et al., 2009). The UPLC system was Acquity™ Ultra performance LC system (Waters) equipped with a BEH™ C_{18} column (1.7 μm, 50 mm × 2.1 mm). Mass spectrometric measurements were performed on a tandem quadrupole mass spectrometer (Waters) equipped with the Zspray™ electrospray ionisation source

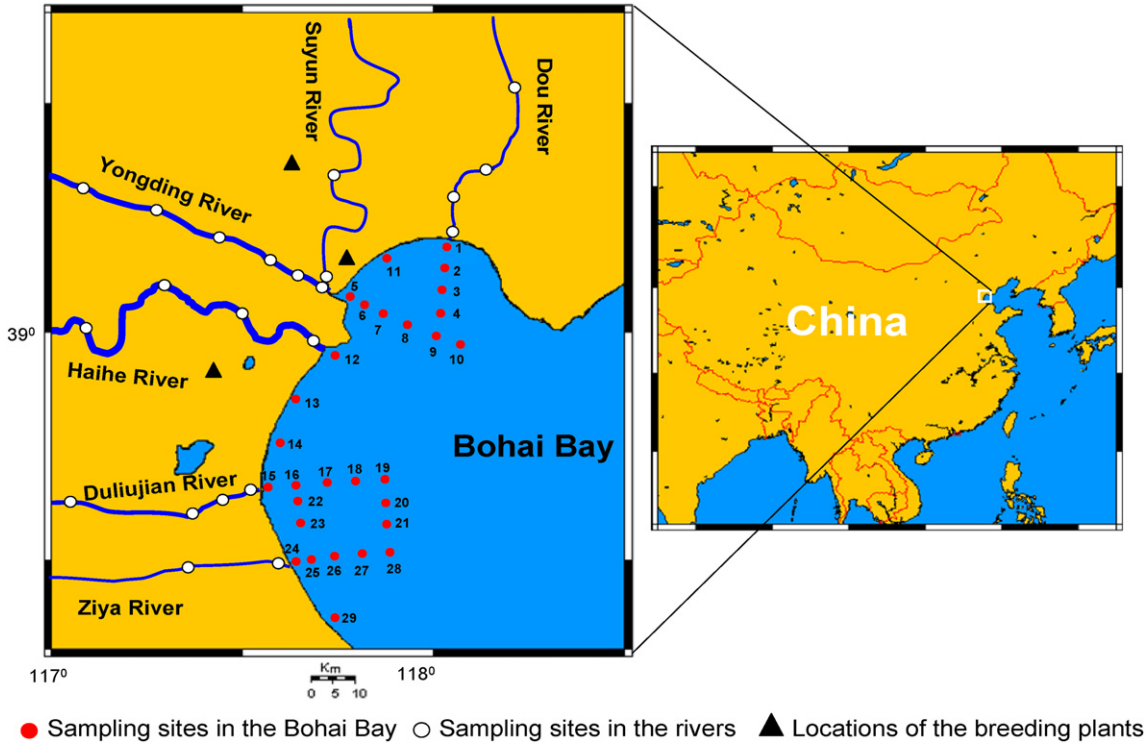

Fig. 1. Sampling locations of water samples from the Bohai Bay and the rivers.