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Occurrence and risks of antibiotics in the coastal aquatic environment of the Yellow Sea, North China

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HIGHLIGHTS

- Some antibiotics were ubiquitous in coastal seawater of the Yellow Sea, North China.
- Higher concentrations and spatial variations were presented in the semi-enclosed bay.
- Lower concentrations and spatial variations were presented in the open bays.
- Source of the antibiotics in the different bays varied largely.
- Parts of the antibiotics in one bay posed high ecological risks to some organisms.

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ABSTRACT

Eleven antibiotics in three different categories were investigated in two types of coastal bays (a semi-enclosed bay and an open bay) of the Yellow Sea and in fresh water (rivers and sewage treatment plants [STP] effluents) that discharged into the bays. The results revealed the presence of three predominant antibiotics: dehydration erythromycin, sulfamethoxazole and trimethoprim. These antibiotics were detected in the seawater and fresh water with concentrations of <0.23–50.4 ng L^{-1} and <0.25–663.1 ng L^{-1}, respectively. In terms of the regional distribution of the compounds within the two types of bays, higher concentrations (<0.23–50.4 ng L^{-1}) and higher spatial variations (coefficients of variation: 98%–124%) were found in the semi-enclosed Jiaozhou Bay due to the poor water-exchange ability and to fresh-water inputs through rivers and/or STP effluents. In contrast, lower concentrations (<0.23–3.0 ng L^{-1}) and lower spatial variations (coefficients of variation: 36%–75%) were present in the open Yantai Bays due to the strong water-exchange with the open sea. The source apportionment suggested that 1) fresh-water inputs were the primary source of macrolides in the coastal water, and 2) mariculture affected the relative pollution levels of trimethoprim, sulfamethoxazole and sulfathiazole in the bays. In addition, a risk assessment based on the calculated risk quotient (RQ) showed that the dehydrated erythromycin, sulfamethoxazole and clarithromycin detected at most of the sampling sites in Jiaozhou Bay could pose high (RQ>1) risks to the most sensitive aquatic microorganisms, such as *Synechococcus leopoliensis* and *Pseudokirchneriella subcapitata*, whilst in the Yantai Bays, the compounds could pose medium risks (1≥RQ>0.1) to the same aquatic microorganisms.

1. Introduction

Antibiotic residues are new pollutants in the environment. These compounds can cause ecological harm to organisms and promote antibiotic-resistance genes in bacterial populations (Eguchi et al., 2004; Kummerer, 2004). Antibiotic residues are widely present in faeces, medical waste, soil and all types of aquatic environments due to the extensive and long-term use of antibiotics in human therapy and veterinary medicine as well as in promoting the growth of animals in livestock production (Kummerer, 2009). Terrestrial antibiotic residues could be transported to marine environments via riverine inputs (Jia et al., 2011; Zhang et al., 2012b; Zou et al., 2011) and sewage treatment plant (STP) effluents (Gulkowska et al., 2007; Minh et al., 2009). These antibiotics and/or the residues used in mariculture (Jia et al., 2011) cause various degrees of antibiotic pollution in the coastal environment. For example, as shown in Table 1, the maximum concentration (c_{max}) of roxithromycin (RTM) was up to 630 ng L^{-1} in Bohai Bay (Zou et al., 2011) of the Bohai Sea (BS), China, the c_{max} of trimethoprim (TMP) was up to 330 ng L^{-1} in Laizhou Bay (Zhang et al., 2012b) of the BS, the c_{max}

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Table 1
Global comparison of eight antibiotics in the marine aquatic environment (concentrations given in ng L^{-1}).

Study area	Sampling time	TMP		SMX		SDM		SDZ		ETM		RTM		AZM		CTM		Reference
		Max	Mean/ median	Max	Mean/ median	Max	Mean/ median	Max	Mean/ median	Max	Mean/ median	Max	Mean/ median	Max	Mean/ median	Max	Mean/ median	
Jiaozhou Bay of the Yellow Sea	04/2010	14.1	4.7/2.7	50.4	9.6/5.3	0.35	0.04/ nd	nd	nd	25.2	4.5/2.2	6.9	1.4/0.4	2.5	0.53/ <0.26	2.6	0.58/ <0.25	This study
Yantai Bays of the Yellow Sea	04/2010	2.6	1.4/1.3	3.0	1.4/1.2	<0.24	0.02/ nd	0.24	0.01/ nd	2.6	0.82/ 0.66	0.96	0.34/ <0.62	0.32	0.09/ <0.26	0.34	0.03/ <0.25	This study
Laizhou Bay of the Bohai Sea	09/2009	330	53/18	82	19/13	1.5	0.13/ nd	0.43	0.02/ nd	8.5	2.6/2.4	1.5	0.38/ <0.62	1.2	0.14/ nd	0.82	0.19/ <0.25	Zhang et al. (2012b)
Bohai Bay of the Bohai Sea	05/2009	120	5.6/	140	35	130	6.4/	41	3.4/	150	25/	630	27/	na		na		Zhang (2011)
Liaodong Bay of the Bohai Sea	05/2009	18.2	/3.6	76.9	/25.2	1.1	/0.3	9.1	/2.4	8.8	/7.9	3.4	/0.4	0.8	/0.5	0.9	/0.1	Jia (2011) and Jia et al. (2011)
Victoria Harbour, Hong Kong	12/2004	na		nd		nd		nd		5.2	/3.3	21.1	/6.1	na		na		Xu et al. (2007b)
Victoria Harbour, Hong Kong	06-08/ 2008	216	52/	47	13/	na		na		1730	213/	47	19/	na		na		Minh et al. (2009)
Victoria Harbour & Hong Kong coasts	12/2006	21.8	7.9/	na		na		na		486	91/	na	na	na		na		Gulkowska et al. (2007)
Shenzhen Bay, South China Sea	11/2005	na		880	/[a]	469	/	292	/	1340		206	/	na		na		Xu (2007)
Belgian coastal harbours	05,12/ 2007 04/2008 06/2009	29	/	43	/	na		na		Na		na		na		na		Wille et al. (2010)

nd: not detected.
na: not analysed.
[a] No data.

of sulfamethoxazole (SMX) was up to 77 ng L^{-1} in Liaodong Bay (Jia et al., 2011) of the BS, the c_{max} of dehydrated erythromycin (ETM-H_2O) was up to 1730 ng L^{-1} in Victoria Harbour of Hong Kong, China (Minh et al., 2009), the c_{max} of SMX was up to 43 ng L^{-1} in Belgian coastal harbours (Wille et al., 2010), and so on. However, the most recent studies mainly pay attention to semi-enclosed areas with poor water-exchange ability, such as the coastal areas of the three main bays (Bohai Bay, Laizhou Bay and Liaodong Bay) of the BS (Jia et al., 2011; Zhang et al., 2012b; Zou et al., 2011) and Victoria Harbour of Hong Kong (Gulkowska et al., 2007; Minh et al., 2009; Xu et al., 2007b). Limited information is available regarding the presence of antibiotics in open coastal areas, which usually have stronger water-exchange ability and less serious pollution than semi-enclosed areas. The detection of antibiotics in the open sea would confirm their ubiquitous character and could lead to new insights into their persistence. In this work, emphasis is placed upon the antibiotics in some parts of selected open bays in the Yellow Sea (YS), an open sea of China (Fig. 1A-2) near the BS, which is the only semi-enclosed sea in China. The open bays include Taozi Bay, Zifu Bay and Sishili Bay near Yantai City (Fig. 1A-3). For convenience, in the present study, the bays are named together as the "Yantai Bays" (YTBs). Because the YTBs are close to Bohai Strait, they are affected by the current from the BS. As an interesting comparison, one semi-enclosed bay (Jiaozhou Bay [JZB]) (Fig. 1A-4) in the open YS was also studied concurrently. The objectives of the present study are as follows: 1) to address the data gap regarding the occurrence of antibiotics in the open coastal environment; 2) to analyse the different levels of antibiotics in the open bay and the semi-enclosed bay; 3) to assess the sources of the antibiotics in these bays based on the antibiotic usage, distributions and correlations between antibiotic concentrations; and 4) to assess the ecological risk of the antibiotics in the two different coastal environments using calculated risk quotients (RQs) (Hernando et al., 2006).

Eleven antibiotics belonging to three groups, macrolides, sulfonamides and diaminopyrimidines, were selected as the target compounds in this study. Information regarding the target compounds, including the physicochemical properties and primary usage, are given in Supplementary Table S1. Most of the target antibiotics are frequently prescribed for human treatment and veterinary medicine in China. These antibiotics are also present in surface waters in many countries in Europe, in the USA, and in China (Hirsch et al., 1999; Kolpin et al., 2002; McArdell et al., 2003; Xu et al., 2007b; Zou et al., 2011).

2. Materials and methods

2.1. Standards and chemicals

The eleven target compounds belong to three different antibacterial families: 1) macrolides, including erythromycin (ETM), spiramycin (SRM), azithromycin (AZM), clarithromycin (CTM) and roxithromycin (RTM); 2) sulfonamides, consisting of sulfadiazine (SDZ), sulfamethoxazole (SMX), sulfadimidine (SDM), sulfathiazole (STZ) and sulfacetamide (SAAM); and 3) diaminopyrimidines, only including trimethoprim (TMP). The synergist TMP is often prescribed in combination with sulfonamides and has similar properties to sulfonamides; therefore, TMP is usually grouped with the sulfonamides when discussing the results. All of the target compounds were purchased from Sigma-Aldrich Co. (St. Louis, MO, USA). The $^{13}C_3$-caffeine solution was obtained from