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# Levels, distributions and sources of veterinary antibiotics in the sediments of the Bohai Sea in China and surrounding estuaries

Xinghua Liu [a,c], Haibo Zhang [a,c,*], Lianzhen Li [a], Chuancheng Fu [a,c], Chen Tu [a], Yujuan Huang [b], Longhua Wu [b,c], Jianhui Tang [a,c], Yongming Luo [a,c,*], Peter Christie [b]

[a] Key Laboratory of Coastal Environmental Processes and Ecological Remediation, Yantai Institute of Coastal Zone Research, Chinese Academy of Sciences, Yantai 264003, China
[b] Key Laboratory of Soil Environment and Pollution Remediation, Nanjing Institute of Soil Science, Chinese Academy of Sciences, Nanjing 210008, China
[c] University of Chinese Academy of Sciences, Beijing 100049, China

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ABSTRACT

Veterinary antibiotics are emerging contaminants of concern. A total of 139 samples comprising 104 marine sediments and 35 estuarine sediments were collected from the Bohai Sea area and analyzed for seventeen antibiotics. The results reveal that the presence and concentration of antibiotics were generally higher in the estuaries than in the sea. The highest antibiotic concentration, 4695 μg $kg^{-1}$ of oxytetracycline, occurred in the estuarine sediment from Ziya New River. Bohai Bay and Laizhou Bay and the surrounding estuaries had higher concentrations of antibiotics. However, low levels of antibiotics detected were detected in Liaodong Bay in contrast to the high concentrations present in the surrounding estuaries. Spatial heterogeneity and principal component analysis suggest a large impact of terrestrial sources of the antibiotics contaminating the Bohai Sea. Risk quotients indicate that current levels of norfloxacin and oxytetracycline might be potentially hazardous to sensitive biota both in the Bohai Sea and in its surrounding estuaries.



Veterinary antibiotics are emerging contaminants in both terrestrial and marine environments of increasing concern in recent years. Antibiotic residues in the environment are mainly derived from the extensive and long-term use of both human and veterinary medicines (Kümmerer, 2009). China leads the world in volume of antibiotic production and usage. Although some antibiotics have been regulated in animal feeds since 1989, the amount used was up to 92,700 tonnes in 2013 (Zhang et al., 2015b). Antibiotics are poorly adsorbed in the gut of the animals and as much as 90% of each dose is excreted in urine and 75% remains unchanged in the feces (Halling-Sørensen, 2000; Sarmah et al., 2006). Thus, a substantial proportion of administered antibiotics enters the environment through wastewater discharge and the land application of manures and sludges, eventually entering the marine environment by riverine input (Jia et al., 2011; Zhang et al., 2012; Zou et al., 2011) and sewage discharge (Gulkowska et al., 2007; Minh et al., 2009). It was reported that over thirty-five main rivers surrounding the Bohai Sea were severely polluted (Jun, 2007; Mao et al., 2009) and transported 36% of wastewaters and 47% of the solid pollutants to the Bohai Sea (Wang and Wang, 2007). Increasing use of antibiotics in aquaculture is another important source for the marine environment (Jia et al., 2011; Kümmerer, 2009; Martins et al., 2008; Minh et al., 2009; Wille et al., 2010; Xu et al., 2007; Zou et al., 2011). The Bohai Sea is the only continental sea in China and has a low exchange rate of seawater, resulting in the long-term residence of pollutants in the sea (Li et al., 2014). Several studies have indicated the presence of high antibiotic contamination in the surface waters of the Bohai Sea (Zhang et al., 2013; Zhang et al., 2012). More than ten antibiotics were found at high detectable frequencies in the surface waters with maximum concentrations of roxithromycin (RTM), trimethoprim (TMP) and sulfamethoxazole (SMX) of 0.63, 0.33 and 0.077 μg $L^{-1}$, respectively (Zhang et al., 2012; Zou et al., 2011). Many antibiotics have a high $K_d$ value and are liable to be adsorbed by solid particles such as sediments (Wang and Wang, 2015).

Antibiotic residues in the marine sediments are also very important in terms of the fate of antibiotics in the marine environment and their ecological risks (Bu et al., 2013; Eguchi et al., 2004; Kümmerer, 2004). However, until now to our knowledge no available data have been reported regarding the antibiotic contamination in the sediments of the Bohai Sea. The purposes of the present study were therefore to fill the knowledge gap regarding the occurrence of antibiotics in the marine and estuarine sediments and to identify the potential sources of the antibiotics in this area.

Surface sediment (0–10 cm depth) samples were collected using a stainless steel sediment sampler from 139 sites comprising 104 marine sites and 35 estuarine sites on one research cruise covering the whole Bohai Sea from August 11 to September 5, 2014 (Fig. 1). All the samples

* Corresponding authors at: Yantai Institute of Coastal Zone Research, Chinese Academy of Sciences, Yantai 264003, China.
*E-mail addresses:* hbzhang@yic.ac.cn (H. Zhang), ymluo@yic.ac.cn (Y. Luo).

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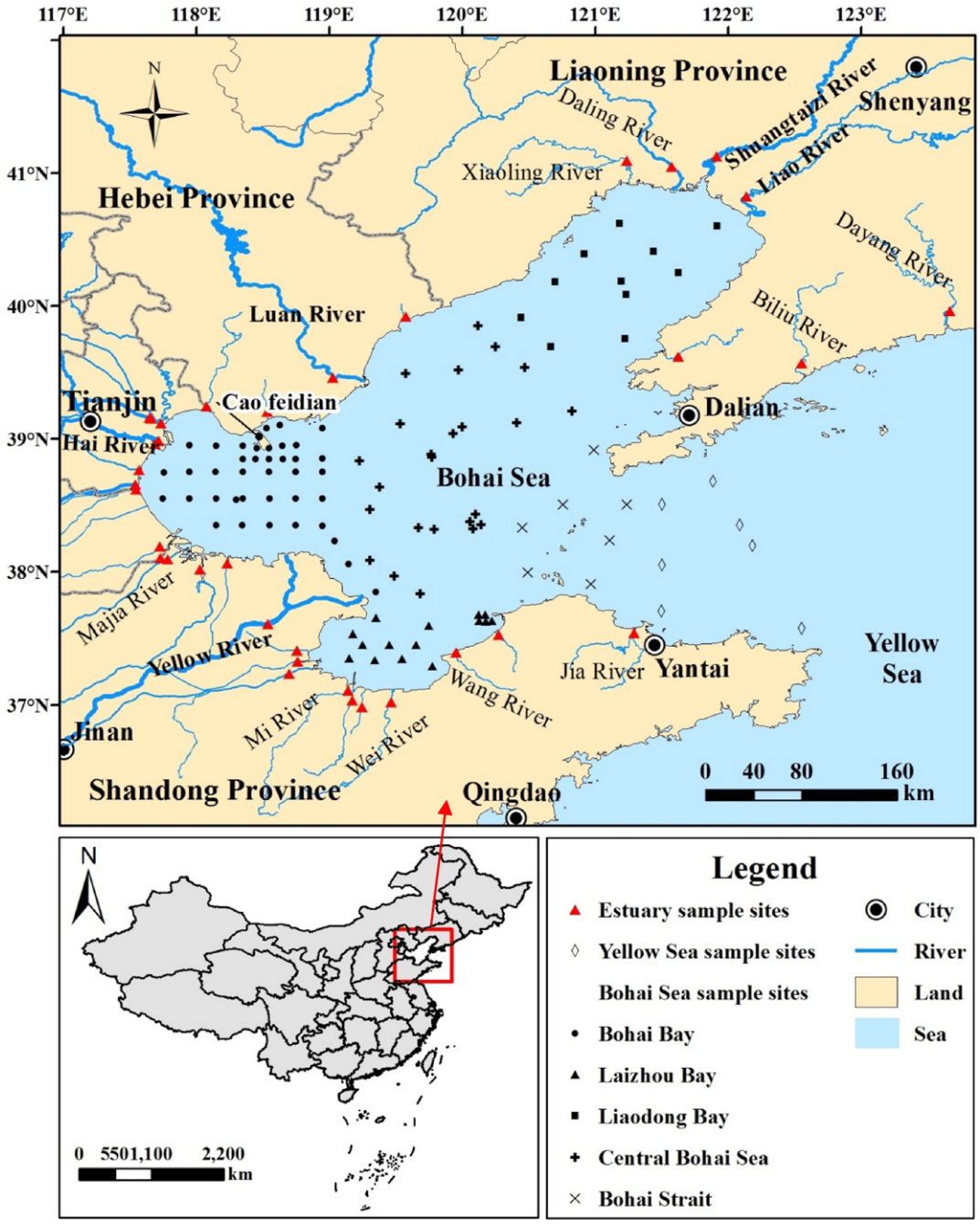


**Fig. 1.** Map of the Bohai Sea showing the surrounding estuaries and sampling sites.

were immediately transferred to clean plastic closure pockets, chilled to near freezing, transported to the laboratory, and stored at −20 °C in the dark. Before extraction, the samples were freeze-dried, large calcareous debris and rocks and plant fragments were removed, and the samples were ground with an agate mortar and homogenized by sieving through a 0.15-mm mesh.

Sample preparation and antibiotics analysis were based on previously developed methods (Huang et al., 2013). The 17 target veterinary antibiotics belong to four different classes of compound: (1) four tetracyclines comprising tetracycline (TC), oxytetracycline (OTC), chlortetracycline (CTC), and doxycycline (DOC); (2) eight sulfonamides comprising sulfadiazine (SDZ), sulfamethoxazole (SMX), sulfamethazine (SMZ), sulfamonomethoxine (SMM), sulfachinoxalin (SCX), sulfadimethoxine (SDM), sulfameter (SM), and sulfaclozine (SCZ); (3) the four fluoroquinolones norfloxacin (NFC), ofloxacin (OFC), ciprofloxacin (CFC), and enrofloxacin (EFC), and (4) the one macrolide roxithromycin (RTM). Four isotope-labelled antibiotics consisting of tetracycline-D6, enrofloxacin-D5, sulfamethazine-D4, and sulfadimethoxine-D6 and demeclocycline were selected as internal standards. All target compounds were simultaneously extracted with $Mg(NO_3)_2$-$NH_3 \cdot H_2O$ solution coupled with ethylenediaminetetraacetic acid-sodium perborate (EDTA-SPB) at 3:1 (v/v). The $Mg(NO_3)_2$-$NH_3 \cdot H_2O$ solution was prepared by mixing the 50% $Mg(NO_3)_2$ and 2.5% $NH_3 \cdot H_2O$ at 96:4 (v/v). The SPB solution was prepared by dissolving 10.56 g of $NaH_2PO_4$ and 0.82 mL of $H_3PO_4$ to 1 L with ultrapure water. The EDTA-SPB (pH 4) mixture was obtained by dissolving 80.0 g of $Na_2EDTA$ to 1 L in SPB. The 2.5000 (±0.0005) g aliquots of sediment sample spiked with internal standards (100.0 μg $kg^{-1}$) were extracted ultrasonically three times using 20 mL extraction solvent for the first extraction and 10 mL for each of the remaining two. All the 40 mL extracts were purified and