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Baseline

Occurrence and distribution of antibiotics in the surface sediments of the Yangtze Estuary and nearby coastal areas

Hao Shi [a], Yi Yang [a,b,*], Min Liu [a], Caixia Yan [b], Haiying Yue [a], Junliang Zhou [b]

[a] Key Laboratory of Geographic Information Science of the Ministry of Education, Shanghai Key Lab for Urban Ecological Processes and Eco-Restoration, School of Resource and Environmental Sciences, East China Normal University, 3663 North Zhongshan Road, Shanghai 200062, China
[b] State Key Laboratory of Estuarine and Coastal Research, East China Normal University, 3663 North Zhongshan Road, Shanghai 200062, China

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ABSTRACT

The occurrence and distribution of five groups of antibiotics were investigated in the surface sediments of the Yangtze Estuary over four seasons. Four tetracyclines (TCs), sulfaquinoxaline (SQ), enrofloxacin (EFC) and thiamphenicol (TAP) were detected in all the samples, while sulfamerazine (SM) and sulfathiazole (ST) showed the lowest detection frequency. The detection frequencies and antibiotic concentrations were generally higher in January and May, indicating that low flow conditions and low temperature might enhance the persistence of antibiotics in sediment. Antibiotic levels varied with location, with the highest concentrations being observed around river discharges and sewage outfalls. Furthermore, a positive correlation between the concentration of quinolones and TOC revealed the significant role played by TOC. The concentration of quinolones at Wusongkou exceeded the trigger value (0.10 mg kg^{-1}) of the Steering Committee of the Veterinary International Committee on Harmonization (VICH), which should be paid attention to in future studies.

The discovery and application of antibiotics has played an extremely important role in the prevention and treatment of human and animal diseases, and they are applied widely in livestock and aquaculture as additives to accelerate the growth of animals and to increase yields (Schlüsener and Bester, 2006). The annual usage of antibiotics has been estimated to be between 100,000 and 200,000 tons globally, with more than 25,000 tons per year in China (Xu et al., 2007). As much as 80–90% of these compounds can be excreted into the environment as parent compounds by humans via urine and feces (Kümmerer, 2009; Bound and Voulvoulis, 2004). The pharmaceutically active compounds in livestock manure, which is used as fertilizer on farmland, may accumulate in the soil surface or flow into surface water or seep into groundwater (Carballo et al., 2007). Antibiotics are ubiquitous and have been detected in the influent and effluent of sewage treatment plants, surface water and even groundwater (Sacher et al., 2001; Kolpin et al., 2002; Golet et al., 2001). Induction of drug-resistant bacteria (Michal and Alvarez, 2004) can affect growth of plants and microorganisms (Richardson et al., 2005; Migliore et al., 1996). Moreover, antibiotics in food and drinking water can pose a threat to human health (Li et al., 2004).

As a highly developed region, the Yangtze Delta has become an important industrial and economic center in China. It has a population of more than 75 million, an area of approximately 99 thousand square kilometers, and makes up 18.7% of the national GDP. At the same time, high-speed development has placed a heavy environmental burden on this area. Estuarine areas receive considerable pollutant inputs from land-based sources via river runoff and sewage outfalls. Recently, the occurrence of hydrophobic organic compounds (HOCs) including polycyclic aromatic hydrocarbons (PAHs) (Yang et al., 2008), polychlorinated biphenyls (PCBs) (Zhang et al., 2011) and dichlorodiphenyltrichloroethanes (DDTs) (Liu et al., 2006) has been reported in tidal surface sediments from the Yangtze Estuary. However, to our knowledge, until now no study has comprehensively dealt with antibiotic residues in the surface sediments of the Yangtze Estuary and its coastal zone. The overall objectives of this study are to investigate the concentration, the spatial and seasonal distribution, and assess the risk of 20 antibiotics in the sediments of the Yangtze Estuary and its coastal area.

Antibiotic standards of chloramphenicols (CPs), including chloramphenicol (CAP), thiamphenicol (TAP), and florfenicol (FF); sulfonamides (SAs), including sulfadiazine (SD), sulfapyridine (SP),

* Corresponding author at: Key Laboratory of Geographic Information Science of the Ministry of Education, Shanghai Key Lab for Urban Ecological Processes and Eco-Restoration, School of Resource and Environmental Sciences, East China Normal University, 3663 North Zhongshan Road, Shanghai 200062, China. Tel.: +86 21 62232439.
E-mail address: yyang@geo.ecnu.edu.cn (Y. Yang).

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sulfamethoxazole (SMX), sulfathiazole (ST), sulfamerazine (SM), sulfamethazine (SMT), and sulfaquinoxaline (SQ); fluoroquinolones (FQs), including norfloxacin (NFC), ciprofloxacin (CFC), enrofloxacin (EFC), and ofloxacin (OFC); tetracyclines (TCs), including tetracycline (TC), oxytetracycline (OTC), doxycyclinehyclate (DXC), and chlorotetracycline (CTC); and macrolides (MLs), including erythromycin (ETM) and roxithromycin (RTM), were purchased from Dr. Ehrenstorfer (GmbH, Germany). The physicochemical properties of these 20 compounds are summarized in Table S1, supplementary material. The compounds chloramphenicol-d5, sulfamethoxazole-d4, norfloxacin-d5, demeclocycline and roxithromycin-d7 were used as the internal standards for CPs, SAs, FQs, TCs and MLs, respectively. All solvents used were of HPLC grade.

The Yangtze Estuary (121°50′–122°30′ E and 31°45′–30°50′ N) is situated on the east coast of China and extensive tidal flats develop along the area with the substantial transportation of suspended sediment by the Yangtze River (Hou et al., 2008). Whilst, the estuary is divided into the north and south branches by Chongming island. Seven surface sediment samples were collected along the Yangtze Estuary and its nearby coastal areas (Fig. 1) in July 2011, October 2011, January 2012 and May 2012, respectively. The sampling sites included Yinyang (YY), Daxingang (DXG), Xupu (XP), Liuhekou (LHK), Bailonggang (BLG), Wusongkou (WSK) and Luchao (LC), among which LHK is the junction of the Liu River and the Yangtze River, WSK is the junction of Huangpu River to Yangtze River. In addition, at BLG site there is the largest waste water treatment plant in Asia. To ensure a greater homogeneity, triplicate sediment samples were combined, rendering the total sediment wet mass of at least 2 kg for each sample. All sediment samples were packed in brown glass bottles (pre-heated at 400 °C, 5 h) and immediately stored at −20 °C until further processing.

One-gram sediment samples were placed in glass vials (20 mL), and were spiked with 20 ng of internal standard in triplicate. In each bottle 1 mL of buffer (dissolving 0.552 g of trisodium phosphate dodecahydrate, 0.258 g of sodium citrate, 2 g of EDTA in 20 mL of Milli-Q) and 9 mL acetonitrile were added. Each sample was mixed at 200 rpm for 20 min using a mechanical shaker before being sonicated in an Ultra wave sonic bath for 15 min. The samples were mixed with 3 g anhydrous sodium sulfate (to remove water) and centrifuged for 5 min at 2500 rpm to separate the solid and liquid phases. The liquid phase was poured into a test tube, and the same extraction procedure was repeated twice to obtain a complete extraction of target compounds, and the third extraction was analyzed and showed undetectable levels of antibiotics. The extracts were reduced to 0.5 mL by evaporation under gentle N_2 and filled to the final analysis volume of 1.0 mL with additional pure water.

The target antibiotics were analyzed using a Waters Acquity™ ultra performance liquid chromatograph-tandem mass spectrometry (UPLC-MS/MS) system. After the sample extracts (4 μL) were injected, the target compounds were separated using a Waters HSS T3 column (100 mm × 2.1 mm i.d., 1.8 mm). Ultra-pure water containing 0.1% formic acid (V/V) (eluent A) and acetonitrile containing 0.1% formic acid (V/V) (eluent B) was used as the mobile phase. The gradient program was as follows: 85% A (0 min), 83% A (3 min), 70% A (7 min), 35% A (1 min), 100% B (10 min), and finally 85% A (12 min). The column temperature was set at 40 °C and the flow rate was 0.4 mL/min. Mass spectrometric analysis was conducted using a Waters triple quadrupole tandem mass spectrometer with a Z-spray electrospray interface (Waters Corp., Manchester, UK). Both positive (SAs, FQs, TCs, MLs) and negative ion (CPs) modes were applied in the determination of the antibiotics, with the following parameters: capillary voltage, 3.0 kV; cone

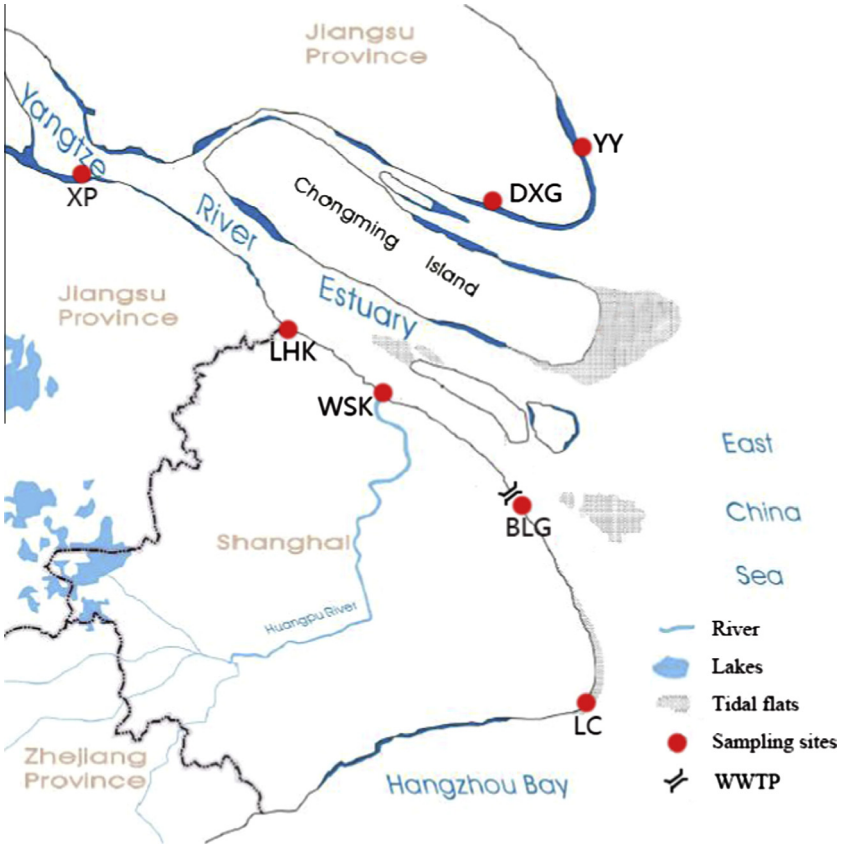

Fig. 1. Sampling sites along the Yangtze Estuary and its coastal area.

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