Marine Pollution Bulletin 83 (2014) 317–323

Contents lists available at ScienceDirect

Marine Pollution Bulletin

journal homepage: www.elsevier.com/locate/marpolbul

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

ARTICLE INFO

Article history:
Available online 10 May 2014

Keywords:
Antibiotics
TOC
Sediments
Distribution

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 ($0.10\ \mathrm{mg\ kg^{-1}}$) 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).

http://dx.doi.org/10.1016/j.marpolbul.2014.04.034
0025-326X/

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

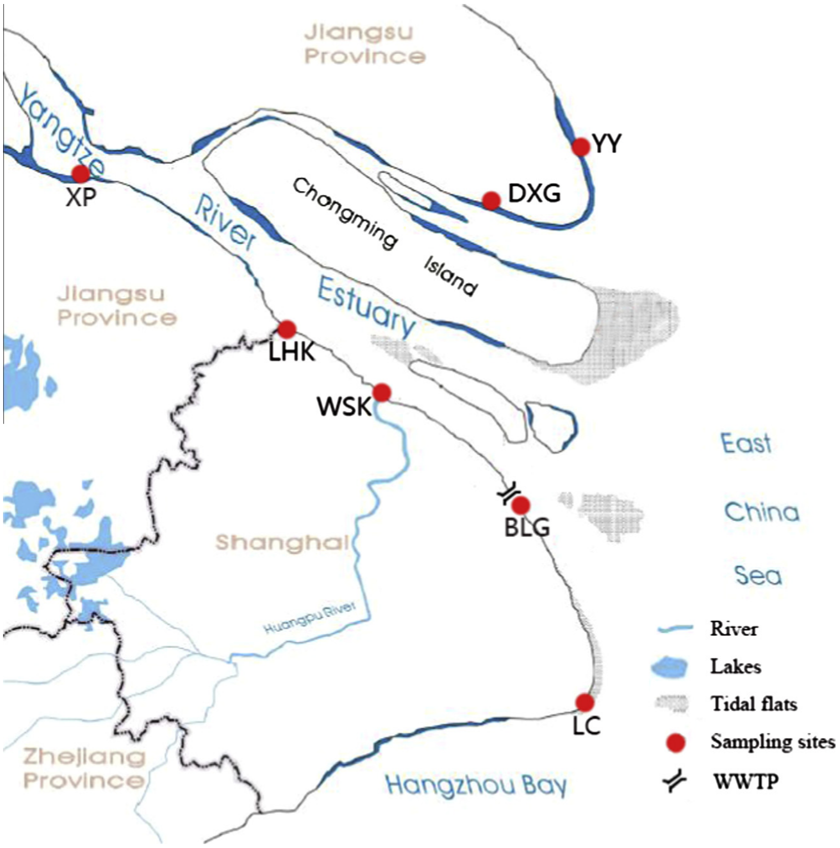

Fig. 1. Sampling sites along the Yangtze Estuary and its coastal area.

voltage, 6–100 V; source temperature, 150 °C; desolvation gas temperature, 500 °C; desolvation gas flow, 800 L/h nitrogen; cone gas flow, 150 L/h nitrogen; argon collision gas flow, 0.17 mL/min for MS/MS.

Quantitative analysis of the compounds was performed using UPLC–MS/MS in multiple reaction monitoring (MRM) mode. The linear calibration curves were performed by analyzing standard solutions ranging from 0.05 ng/mL to 500 ng/mL followed by calculating the ratios of the analyte peak area to those of the internal standards. Table 1 summarizes the information including the limit of detection (LOD), limit of quantification (LOQ) and recovery of individual antibiotic compound. The LOD and LOQ for each antibiotic were defined as the concentrations corresponding to signal-to-noise (S/N) values of 3 and 10, respectively. The LOD and LOQ of antibiotics in sediment were 0.01–1.18 ng/g and 0.03–1.68 ng/g, respectively. The recoveries of 20 target compounds spiked to the sediment samples (100 ng/g) ($n = 3$) were between 64.1% and 126.4%. Analysis of laboratory blanks showed no detectable amount of contamination.

The total organic carbon (TOC) concentration in sediment samples was analyzed using the potassium dichromate oxidation method. Sediment samples were ground to 0.175 mm (80 mesh, and dried at 80 °C for 3 h. For each sample, 0.40 g was placed in a glass test tube (50 mL), and a little solid Ag_2SO_4 and 10.00 mL $K_2Cr_2O_7$–H_2SO_4 standard solution were added. All tubes were heated at 175 ± 5 °C for 5 min in an oil bath. Two to three drops of phenanthroline indicator were added to each test tube and titrated with $FeSO_4$ standard solution from light green to bright green, and then mutated brick red as the end point.

Twenty antibiotics were investigated in surface sediments of the Yangtze Estuary and its coastal areas (Table 2). FQs, TCs, MLs, and CPs were detected at more than half of the sampling sites in the four seasons. Four TCs (TC, OTC, DXC and CTC), SQ, EFC, and TAP were the most frequently detected compounds, with a detection frequency of 100% in all the samples, while SM and ST showed the lowest detection frequency, and were not detected at all the sampling sites in three sampling campaigns. In addition, the concentrations of all target antibiotics were at the ng/g level. FQs were the predominant antibiotics, contributing 58.5–85% of the total amount of antibiotics, while TCs and MLs accounted for 4–25% and 9.3–13.5%, respectively. SAs only accounted for 1.8–4.5%. All the concentrations of CPs were below the LOQ.

Compared to other antibiotics, the levels of SAs in the surface sediments in the study area were in general low, with medium concentrations lower than 1 ng/L or even less than the LOQ for most of the samples. Although SQ had a detection frequency of 100%, its maximum concentrations were lower than 1 ng/g at all the sampling sites. Due to their relatively high water solubility, SAs showed weak affinity to soils/sediments (Karcı and Balcıoğlu, 2009; Thiele, 2000), while they have frequently been detected as the dominant antibiotics in surface water in the Yangtze Estuary (Yan et al., 2013). Among SAs, the highest concentration was found for SP (9.1 ng/g) in May. The concentrations of SAs in this study were at comparable levels to those in the Yellow River, the Hai River, and the Liao River (China), but lower than those in the Pearl River (China) (Table 3).

Four FQs (NFC, CFC, EFC and OFC) were detected at more than half of the sampling sites in the four seasons. The maximum concentrations of FQs ranged from 20.2 ng/g to 69.3 ng/g (NFC), from 12.1 ng/g to 42.9 ng/g (CFC), from <LOQ to 4.8 ng/g (EFC), and from 48.1 ng/g to 458.2 ng/g (OFC). This antibiotic group is frequently used by humans and animals, and has been detected in vegetables from Guangzhou (Li et al., 2010). With high sorption affinity to solids (Picó and Andreu, 2007), FQ were detected with elevated concentrations in the sediments revealing that these antibiotics were applied in a large amount in the study area. The concentration of FQs in the Yangtze Estuary was lower than those in the Hai River and the Pearl River (China), but comparable to those in the Yellow River and the Liao River (China).

In the TC group, TC, OTC, DXC, and CTC had detection frequencies of 100% in the Yangtze Estuary, indicating widespread use of these antibiotics in this region. The highest concentrations of TCs were 6.8 ng/g of TC in June, 14 ng/g of OTC in October, 18.6 ng/g of DXC in May, and 12 ng/g of CTC in May. The TCs concentrations in this study were comparable to those in the Dagu River (China), but much lower than those in the Tiaoxi River, the Yellow River, the Hai River, and the Liao River (China), and the Cache La Poudre River (USA). Because of their side effects and bacterial resistance, TCs are rarely used clinically (Zou et al., 2011). Although the use of TCs as animal growth promoters has been limited in European Union countries, the Chinese government has so far not prohibited adding them to animal feed. Consequently, the main source of these contaminants was veterinary antibiotic applications.

For the two MLs, ETM had detection frequencies of 100% in the Yangtze Estuary, while RTM was detected at more than half of all sites in the four seasons. The concentrations were lower than those reported in the Pearl River (China), and fell within the range of those in the Yellow River (China) and the Cache La Poudre River (USA). MLs are large complex molecules with a number of stereocenters (Stepanić et al., 2012), and are widely used in humans (Murata et al., 2011).

Three CPs (CAP, TAP, and FF) were widely identified, but at low concentrations. There have been few studies reporting CP concentrations, especially in sediment. As these chloramphenicol antibiotics can cause aplastic anemia, hemolytic anemia, and other side effects (Turton et al., 2000), the European Union and the United States have prohibited the use of these drugs in animal husbandry and aquaculture. However, the application of CAP and TAP in livestock and aquaculture is still practiced in China, due to their low price and steady antibiosis effectiveness (Chen et al., 2009), and they have been detected in agricultural products (Feng et al., 2013).

Fig. 2 shows the seasonal distribution of four groups of antibiotics at different sampling sites of the Yangtze Estuary. As the dominant antibiotics, the highest value of FQs was in January. The

Table 1
The LOD (ng/g), LOQ (ng/g) and Recovery (%) of individual antibiotic compound.

	SD	SP	SMX	ST	SM	SMT	SQ	NFC	CFC	EFC
LOD	0.21	0.05	0.1	0.15	0.1	0.07	0.01	0.17	0.30	1.18
LOQ	0.41	0.41	0.34	0.42	0.04	0.45	0.03	0.46	0.41	1.68
Recovery	117.1	106.2	98.8	94.2	104.8	103.4	64.1	116.4	122.0	126.4
RSD[a]	2.9	5.8	5.8	3.7	5.4	3.0	4.4	6.9	5.3	7.7
	OFC	TC	OTC	DXC	CTC	ETM	RTM	CAP	TAP	FF
LOD	0.11	0.07	0.05	0.19	0.23	0.08	0.01	0.29	0.61	0.02
LOQ	0.16	0.87	0.19	1.2	0.29	0.03	0.17	0.76	1.28	0.25
Recovery	123.8	84.2	81.5	77.5	91.4	101.5	122.2	103.0	69.1	96.4
RSD	4.7	7.1	9.0	7.7	6.1	9.6	6.1	1.0	2.6	1.7

[a] RSD – relative standard deviation (%).

Table 2
Summary of antibiotic concentrations (ng/g) and detection frequencies (%) in Yangtze Estuary from July 2011 to May 2012.

Group		SAs ($n = 7$)							FQs ($n = 7$)				TCs ($n = 7$)				MLs ($n = 7$)		CPs ($n = 7$)		
Compounds		SD	SP	SMX	ST	SM	SMT	SQ	NFC	CFC	EFC	OFC	TC	OTC	DXC	CTC	RTM	ETM	CPA	TAP	FF
2011–07	Freq.	28.6	57.1	14.3	0	0	28.6	100	100	100	100	100	100	100	100	100	100	100	100	100	100
	Max.	0.20	3.71	0.515	n.d	n.d	1.54	0.469	20.2	13.1	2.34	61	<LOQ	2.68	3.53	4.3	1.59	5.84	<LOQ	<LOQ	<LOQ
	Med.	0.12	1.36	0.515	n.d	n.d	0.768	0.269	2.44	2.61	1.17	2.78	<LOQ	0.99	<LOQ	0.628	0.65	3.27	<LOQ	<LOQ	<LOQ
	Min.	0.045	0.32	0.515	n.d	n.d	<LOQ	0.202	0.771	<LOQ	<LOQ	0.63	<LOQ	0.520	<LOQ	<LOQ	0.176	1.06	<LOQ	<LOQ	<LOQ
2011–10	Freq.	0	42.9	0	0	0	14.3	100	71.4	57.1	100	100	100	100	100	100	71.4	100	100	100	100
	Max.	n.d	4.38	n.d	n.d	n.d	0.559	0.608	25.6	12.1	<LOQ	48.1	6.15	14	14.6	11	0.966	17.5	<LOQ	<LOQ	<LOQ
	Med.	n.d	0.602	n.d	n.d	n.d	0.559	0.373	8.30	3.93	<LOQ	11.2	<LOQ	0.951	<LOQ	0.623	0.522	2.26	<LOQ	<LOQ	<LOQ
	Min.	n.d	<LOQ	n.d	n.d	n.d	0.559	0.082	0.87	1.32	<LOQ	1.22	<LOQ	0.525	<LOQ	<LOQ	0.205	0.653	<LOQ	<LOQ	<LOQ
2012–01	Freq.	0	71.4	28.6	0	0	42.9	100	100	100	100	85.7	100	100	100	100	57.1	85.7	100	100	71.4
	Max.	n.d	3.28	1.13	n.d	n.d	4.84	0.959	69.3	42.9	2.26	458.2	6.84	8.13	2.37	5.37	3.61	51.5	<LOQ	<LOQ	<LOQ
	Med.	n.d	0.759	0.515	n.d	n.d	2.42	0.427	3.53	2.14	<LOQ	12	<LOQ	0.765	<LOQ	0.76	0.859	6.05	<LOQ	<LOQ	<LOQ
	Min.	n.d	<LOQ	<LOQ	n.d	n.d	<LOQ	0.042	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.305	<LOQ	<LOQ	0.305	<LOQ	<LOQ	<LOQ	<LOQ
2012–05	Freq.	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	85.7	100	100
	Max.	0.469	9.12	0.516	<LOQ	0.408	1.3	0.117	39.6	20.1	4.84	206.3	2.16	13.9	18.6	12	3.22	28.5	<LOQ	<LOQ	<LOQ
	Med.	0.452	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.04	2.64	4.75	<LOQ	3.22	0.914	4.02	<LOQ	1.3	0.694	4.64	<LOQ	<LOQ	<LOQ
	Min.	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.552	<LOQ	0.118	<LOQ	0.483	<LOQ	<LOQ	<LOQ

concentrations of SAs and MLs were higher in January and May than in July and October. TCs were rarely detected in July.

The concentration of the individual antibiotic varied greatly at different seasons, except for BLG. Antibiotic enrichment in the sediment was greatly influenced by hydrodynamic and temperature changes (Luo et al., 2011). The lower detected antibiotic concentrations in the summer can be attributed to higher runoff (increased flow rate), faster photolysis (Thiele-Bruhn, 2003), thermal degradation (the summer water temperature was approximately 28 °C, versus 8 °C in winter), and biodegradation associated with higher microbial activity during the summer season (Radka et al., 2004; Jerold and Roger, 2003; Ingerslev and Halling-Sørensen, 2000). The other reason for the temporal variation in antibiotic concentrations might be differences in the amounts and types of antibiotics used for livestock at different times, such as different growth stages (Hamscher et al., 2000; Hu et al., 2010). However, at the BLG site, which is located near the BLG WWTP, the antibiotic concentrations were relatively high and did not show significant seasonal change, which indicated the continuous influence by the WWTP effluent.

Compared to antibiotics detected in water in the Yangtze Estuary (Yan et al., 2013), the contributions of FQs and TCs to the total antibiotics were markedly greater, while there was a significant reduction in SAs and CPs. It has been reported that TCs show high sorption affinity to sediments, followed by FQs and MLs. SQs exhibit weak to moderate adsorption to soils (Li et al., 2012).

The TOC concentration showed seasonal variation, with high levels in January and May, followed by July and October. The temperature and hydrodynamic condition could affect the TOC contents spatially and temporally. In January due to low temperatures, a relatively weakened biodegradation could result in a relatively high TOC content (Wang and Xian, 2011). A positive correlation was observed between TOC and the FQs concentrations of the Yangtze Estuary (WSK, a R^2 value of 0.831, $P < 0.05$; LHK, a R^2 value of 0.999, $P < 0.01$; BLG, a R^2 value of 0.918, $P < 0.05$), but no correlation was found between TOC concentrations and the concentrations of other types of antibiotics. This suggests that different types of antibiotics in sediments have very different adsorption mechanisms. TOC could be an important factor controlling the level and distribution of FQs in the sediments.

Generally, the antibiotic concentrations at WSK were the highest among all the sites in the four seasons. The remaining sites were in the following order: LHK > BLG > LC > DXG > XP > YY. Antibiotics showed a general trend of higher concentrations at the junctions of rivers (WSK and LHK) and WWTP effluent (BLG) than those in other coastal sites. This indicates that rivers and WWTP effluents were important sources of antibiotics. For example, as the dominant antibiotics, FQs, which is often used to treat diseases by both human and livestock in China, were detected in high levels at WSK, LHK and BLG sites. The upstream Huangpu River runs through the countryside areas of Shanghai with a large population and highly developed industry and agriculture, and the downstream river runs through the urban area. While the Liu River mainly runs through agricultural areas, where many animal feeding and fish farming operations are located. The total TCs concentrations at LHK were higher than WSK, especially in May and October. TCs are widely used in the treatment of livestock and weight gain which could be used in larger amounts in May and October compared to January and July in the Liu River basin.

At present, ecological risk assessments of antibiotics are mainly focused on water bodies, but seldom on sediments/soils. Soil/sediments are considered as a potential sink or source of contaminants. Whether from water desorption, thereby threatening aquatic organisms (Lützhøft et al., 1999; Xue et al., 2013), or through the food chain (Du and Liu, 2012), antibiotics in sediments pose a great potential danger. Antibiotics in soil can easily become concentrated in plants, with an enrichment rate as much as more than 10,000 times (Sarmah et al., 2006). The antibiotic concentrations measured in this study were evaluated with respect to the trigger value of 0.10 mg kg^{-1} in soil set by the Steering Committee of the Veterinary International Committee on Harmonization (VICH), on the ecotoxic effects of antibiotic compounds on a range of organisms (Karcı and Balcıoğlu, 2009). The concentration of quinolones in WSK exceeded the trigger value (0.10 mg kg^{-1}), indicating that there was a potential risk from such contaminants.

The concentrations and distributions of 20 different antibiotics from seven sites in the Yangtze Estuary and nearby coastal areas were determined. Four TCs, SQ, EFC and TAP were detected in all the samples, indicating that these antibiotics are widespread in the sediments of Yangtze Estuary area; while SM and ST showed the lowest detection frequency. The contributions of FQs to total antibiotic burden were relatively high compared to the other groups of antibiotics. At the WSK and LHK sites, significant seasonal variations were investigated. The concentration of the same antibiotic varied greatly in different seasons, probably as a result of a combination of factors such as high consumption, low dilution due to low river flow, and slow degradation due to low temperature. The levels of antibiotics at different sites were generally, in

Table 3
Comparison of antibiotic concentrations in surface sediments with other studies (ng/g).

	Yangtze Estuary, China ($n = 7$)	Baiyangdian Lake, China ($n = 45$)	Tiaoxi River, China ($n = 7$)	Dagu River, China ($n = 8$)	Yellow River, China ($n = 15$)	Hai River, China ($n = 11$)	Liao River, China ($n = 21$)	Pearl River, China ($n = 14$)	Cache La Poudre River USA ($n = 5$)
SD	n.d.[a]-0.5	n.d.-2.07	n.d.-1.1		n.d. (22.0)[b]	n.d. (1.18)[b]	n.d. (11)[b]	3.16 (83.9)[b]	
SP	n.d.-9.1	n.d.-1.40		1.6–8.1	n.d.	n.d.	n.d.	n.d. (<LOQ)	
SMX	n.d.-1.1	n.d.-7.86	n.d.-0.3	9.7–14.7	n.d.	n.d.	n.d. (<LOQ)	n.d. (<LOQ)	1.6 (1.9)[c]
ST	n.d.-<LOQ	n.d.-5.94		n.d.-13.4					
SM	n.d.-0.4	n.d.-2.47		n.d.-1.4					
SMT	<LOQ-4.8	n.d.-6.92	n.d.-2.6	n.d.-1.8	n.d.	n.d. (5.67)	n.d.	19.7 (248)	5.2 (13.7)
SQ	n.d.-1.0								
NFC	<LOQ-69.3	49.4–1140	n.d.-2.8	n.d.	8.34 (141)	32.0 (5770)	3.32 (176)	88.0 (1120)	
CFC	<LOQ-42.9	n.d.-46.0		n.d.	n.d. (32.8)	16.0 (1290)	n.d. (28.7)	21.8 (197)	
EFC	<LOQ-4.8	n.d.-13.0		n.d.-114.8	n.d.	n.d. (2.34)	n.d.		
OFC	<LOQ-458.2	n.d.-362	0.1–1.2	n.d.-14.2	3.07 (123)	10.3 (653)	3.56 (50.5)	156 (1560)	
TC	<LOQ-6.8		0.1–55.7	n.d.-16.3	n.d. (18.0)	2.0 (135)	n.d. (4.82)	4.05 (72.6)	17.9 (102.7)
OTC	0.3–14.0		0.7–276.6	n.d.-7.9	n.d. (184)	2.52 (422)	2.34 (652)	7.15 (196)	14.8 (56.1)
DXC	<LOQ-18.6		6.0–15.6						
CTC	<LOQ-12.0		6.5–131.6	n.d.-27	n.d.	n.d. (10.9)	n.d. (32.5)		10.8 (30.8)
RTM	<LOQ-3.6	n.d.-302	0.1–1.2		n.d. (6.8)	2.29 (11.7)	5.51 (29.6)	24.7 (133)	1.9 (5.9)
ETM	<LOQ-51.5	n.d.-3.04	n.d.-0.1		1.28 (49.8)	<LOQ (67.7)	3.61 (40.3)	24.4 (385)	7.6 (25.6)
CPA	<LOQ		n.d.-0.2						
TAP	<LOQ		n.d.-0.2						
FF	<LOQ								
Ref.	This study	Li et al. (2012)	Chen et al. (2011)	Hu (2011)	Zhou et al. (2011)	Zhou et al. (2011)	Zhou et al. (2011)	Yang et al. (2010)	Kim and Carlson (2007)

[a] n.d.: not detected.
[b] Median concentration (maximum concentration), ng/g.
[c] Mean concentration (maximum concentration), ng/g.

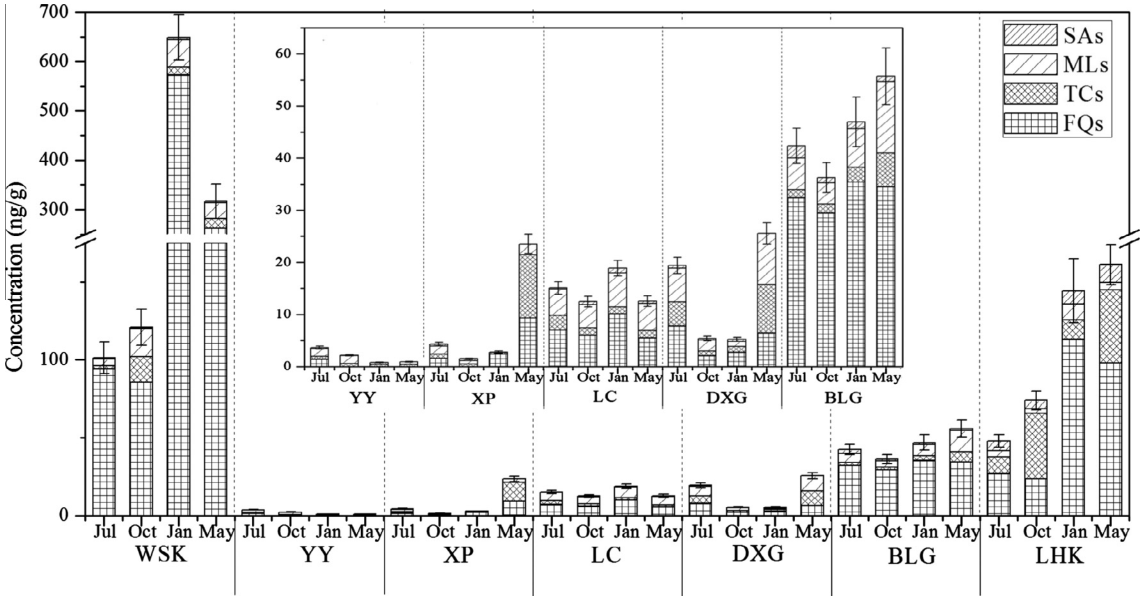

Fig. 2. Total concentrations of five classes of antibiotics in the Yangtze Estuary over four seasons.

descending order, as follows: WSK > LHK > BLG > LC > DXG > XP > YY. The input of contamination from the upstream rivers or WWTPs might be responsible for the higher levels of antibiotics at WSK, LHK and BLG. In addition, a positive correlation was observed between the TOC concentration and the FQ concentration of the rivers and WWTP effluent. The concentration of quinolones in WSK exceeded the VICH trigger value ($0.10\ \mathrm{mg\ kg^{-1}}$), and further monitoring and detailed investigations on the ecological risks of these antibiotics are urgently needed.

Acknowledgements

The work was funded by the National Natural Science Foundation of China (41271473; 41130525; 41371451) and the Fundamental Research Funds for the Central Universities. Additional support was provided by the Large Instruments Open Foundation of East China Normal University.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.marpolbul.2014.04.034.

References

Bound, J.P., Voulvoulis, N., 2004. Pharmaceuticals in the aquatic environment – a comparison of risk assessment strategies. Chemosphere 56, 1143–1155.

Carballo, E.M., Barreiro, C.G., Scharf, S., Gans, O., 2007. Environmental monitoring study of selected veterinary antibiotics in animal manure and soils in Austria. Environ. Pollut. 148 (2), 570–579.

Chen, H.X., Chen, H., Ying, J., Huang, J.L., Liao, L., 2009. Dispersive liquid–liquid microextraction followed by high-performance liquid chromatography as an efficient and sensitive technique for simultaneous determination of chloramphenicol and thiamphenicol in honey. Anal. Chim. Acta 632, 80–85.

Chen, Y.S., Zhang, H.B., Luo, Y.M., 2011. Investigation of 14 selected antibiotics in sediments of the typical cross sections of Tiaoxi River. Environ. Sci. 32 (3), 667–672.

Du, L., Liu, W., 2012. Occurrence, fate, and ecotoxicity of antibiotics in agro-ecosystems. A review. Agron. Sustain. Dev. 32 (2), 309–327.

Feng, M., Wei, Y.J., Zhu, Z.Y., He, J., Wang, X.J., Liu, H., Ding, T., Wu, B., 2013. Simultaneous determination of chloramphenicol, thiamphenicol and florfenicol residues in feed by high performance liquid chromatography-tandem mass spectrometry. J. Instrumental Anal. 32 (1), 117–121.

Golet, E.M., Alder, A.C., Hartmann, A., Ternesi, T.A., Giger, W., 2001. Trace determination of fluoroquinolone antibacterial agents in urban wastewater by solid-phase extraction and liquid chromatography with fluorescence detection. Anal. Chem. 73, 3632–3638.

Hamscher, G., Abu-Quare, A., Sczesny, S., Hoper, H., Nau, H., 2000. Determination of tetracyclines and TYL in soil and water samples from agricultural areas in Lower Saxony. In: Van Ginkel, L.A., FRuiter, A (Eds.), Proceedings of the Euroside IV Conference. National Institute of Public Health and the Environment (RIVM), Bilthoven, Netherlands, pp. 522–526.

Hou, L.J., Liu, M., Xu, S., Yan, H., Ou, D., Cheng, Su., Lin, X., 2008. Distribution and accumulation of biogenic silica in the intertidal sediments of the Yangtze estuary. J. Environ. Sci. 20, 543–550.

Hu, W., 2011. The Study on Occurrence and Distribution of Typical Pharmaceuticals and Personal Care Products (PPCPs) in Tianjin Urban Aqueous and Soil Enviroment and the Combined Estrogenic Effects. D. Nankai University.

Hu, X., Zhou, Q., Luo, Y., 2010. Occurrence and source analysis of typical veterinary antibiotics in manure, soil, vegetables and groundwater from organic vegetable bases, northern China. Environ. Pollut. 158 (9), 2992–2998.

Ingerslev, F., Halling-Sørensen, B., 2000. Biodegradability properties of sulfonamides in activated sludge. Environ. Toxicol. Chem. 19 (10), 2467–2473.

Jerold, S.T., Roger, D.M., 2003. Aerobic degradation of tylosin in cattle, chicken, and swine excreta. Environ. Res. 93 (1), 45–51.

Karcı, A., Balcıoğlu, I.A., 2009. Investigation of the tetracycline, sulfonamide, and fluoroquinolone antimicrobial compounds in animal manure and agricultural soils in Turkey. Sci. Total Environ. 407 (16), 4652–4664.

Kim, S.C., Carlson, K., 2007. Temporal and spatial trends in the occurrence of human and veterinary antibiotics in aqueous and river sediment matrices. Environ. Sci. Technol. 41, 50–57.

Kolpin, D.W., Furlong, E.T., Meyer, M.T., Thurman, E.M., Zaugg, S.D., Barber, L.B., Buxton, H.T., 2002. Pharmaceuticals, hormones and other organic wastewater contaminants in U. S. streams, 1999–2000: a national reconnaissance. Environ. Sci. Technol. 36 (6), 1202–1211.

Kümmerer, K., 2009. Antibiotics in the aquatic environment – a review – part I. Chemosphere 75, 417–434.

Li, C.Z., Liu, Y.H., Guo, J., 2004. Hazardous effects of antibiotics and other veterinary drug residues in milk. China Dairy Ind. 32 (10).

Li, Y.W., Zhang, Y., Mo, C.H., Tai, Y.P., Wu, X.L., Wang, J.Y., Su, Q.Y., 2010. Preliminary study on occurrence and health risk assessment of quinolone antibiotics in vegetables from Guangzhou, China. Environ. Sci. 31 (10), 2445–2449.

Li, W., Shi, Y., Gao, L., Liu, J., Cai, Y., 2012. Occurrence of antibiotics in water, sediments, aquatic plants, and animals from Baiyangdian Lake in North China. Chemosphere 89 (11), 1307–1315.

Liu, M., Yang, Y., Xu, S., Liu, H., Hou, L., Ou, D., Liu, Q., Cheng, S., 2006. HCHs and DDTs in salt marsh plants (Scirpus) from the Yangtze estuary and nearby coastal areas, China. Chemosphere 62, 440–448.

Luo, Y., Xu, L., Rysz, M., Wang, Y., Zhang, H., Alvarez, P.J., 2011. Occurrence and transport of tetracycline, sulfonamide, quinolone, and macrolide antibiotics in the haihe river basin, China. Environ. Sci. Technol. 45 (5), 1827–1833.

Lützhøft, H.C.H., Halling-Sørensen, B., Jørgensen, S.E., 1999. Algal toxicity of antibacterial agents applied in Danish fish farming. Arch. Environ. Contam. Toxicol. 36, 1–6.

Michal, R., Alvarez, P.J.J., 2004. Amplification and attenuation of tetracycline resistance in soil bacteria: aquifer column experiments. Water Res. 38, 3705–3712.

Migliore, L., Brambilla, G., Gasoria, P., Civitareale, C., Cozzolino, S., Gaudio, L., 1996. Effects of sulphadimethoxine on barley (Hordeum distichum L., Poaceae, Liliposida). Agr. Ecosyst. Environ. 60 (2), 121–128.

Murata, A., Takada, H., Mutoh, K., Hosoda, H., Harada, A., Nakada, N., 2011. Nationwide monitoring of selected antibiotics: distribution and sources of sulfonamides, trimethoprim, and macrolides in Japanese rivers. Sci. Total Environ. 409 (24), 5305–5312.

Picó, Y., Andreu, V., 2007. Fluoroquinolones in soil-risks and challenges. Anal. Bioanal. Chem. 387 (4), 1287–1299.

Radka, A., Tina, K., Klaus, K., 2004. Assessment of degradation of 18 antibiotics in the closed bottle test. Chemosphere 57 (6), 505–512.

Richardson, B.J., Lam, P.K.S., Martin, M., 2005. Emerging chemicals of concern: pharmaceuticals and personal care products (PPCPs) in Asia, with particular reference to Southern China. Mar. Pollut. Bull. 50, 913–920.

Sacher, F., Lange, F.T., Brauch, H.J., Blankenhorn, I., 2001. Pharmaceuticals in groundwater analytical methods and results of a monitoring program in Baden-Württemberg, Germany. Chromatography A 938, 199–210.

Sarmah, A.K., Meyer, M.T., Boxall, A.B.A., 2006. A global perspective on the use, sales, exposure pathways, occurrence, fate and effects of veterinary antibiotics (VAs) in the environment. Chemosphere 65 (5), 725–759.

Schlüsener, M.P., Bester, K., 2006. Persistence of antibiotics such as macrolides, tiamulin and salinomycin in soil. Environ. Pollut. 143 (3), 565–571.

Stepanić, V., Žiher, D., Gabelica-Marković, V., Jelić, D., Nunhuck, S., Valko, K., Koštrun, S., 2012. Physicochemical profile of macrolides and their comparison with small molecules. Eur. J. Med. Chem. 47, 462–472.

Thiele, S., 2000. Adsorption of the antibiotic pharmaceutical compound sulfapyridine by a long-term differently fertilized loess chernozem. J. Soil Sci. Plant Nutr. 163, 589–594.

Thiele-Bruhn, S., 2003. Pharmaceutical antibiotic compounds in soils – a review. J. Soil Sci. Plant Nutr. 166 (2), 145–167.

Turton, J.A., Havard, A.C., Robinson, S., Holt, D.E., Andrews, C.M., Fagg, R., Williams, T.C., 2000. An assessment of chloramphenicol and thiamphenicol in the induction of aplastic anaemia in the BALB/c mouse. Food Chem. Toxicol. 38 (10), 925–938.

Wang, H.X., Xian, W.W., 2011. Distribution of the total organic carbon of surface sediment and its influence factors in the Yangtze River Estuary. Mar. Sci. 35 (5), 24–31 (in Chinese).

Xu, W.H., Zhang, G., Zou, S.C., Li, X.D., Liu, Y.C., 2007. Determination of selected antibiotics in the Victoria Harbour and the Pearl River, South China using high performance liquid chromatography–electrospray ionization tandem mass spectrometry. Environ. Pollut. 145, 672–679.

Xue, B., Zhang, R., Wang, Y., Liu, X., Li, J., Zhang, G., 2013. Antibiotic contamination in a typical developing city in south China: Occurrence and ecological risks in the Yongjiang River impacted by tributary discharge and anthropogenic activities. Ecotoxicol. Environ. Safe. 92, 229–236.

Yan, C.X., Yang, Y., Zhou, J.L., Liu, M., Nie, M., Shi, H., Gu, L., 2013. Antibiotics in the surface water of the Yangtze estuary: occurrence, distribution and risk assessment. Environ. Pollut. 175, 22–29.

Yang, Z., Feng, J., Niu, J., Shen, Z., 2008. Release of polycyclic aromatic hydrocarbons from Yangtze River sediment cores during periods of simulated resuspension. Environ. Pollut. 155 (2), 366–374.

Yang, J.F., Ying, G.G., Zhao, J.L., Tao, R., Sua, H.C., Chen, F., 2010. Simultaneous determination of four classes of antibiotics in sediments of the Pearl Rivers using RRLC-MS/MS. Sci. Total Environ. 408, 3424–3432.

Zhang, L., Shi, S., Dong, L., Zhang, T., Zhou, L., Huang, Y., 2011. Concentrations and possible sources of polychlorinated biphenyls in the surface water of the Yangtze River Delta, China. Chemosphere 85 (3), 399–405.

Zhou, L.J., Ying, G.G., Zhao, J.L., Yang, J.F., Wang, L., Yang, B., Liu, S., 2011. Trends in the occurrence of human and veterinary antibiotics in the sediments of the Yellow River, Hai River and Liao River in northern China. Environ. Pollut. 159 (7), 1877–1885.

Zou, S., Xu, W., Zhang, R., Tang, J., Chen, Y., Zhang, G., 2011. Occurrence and distribution of antibiotics in coastal water of the Bohai Bay, China: impacts of river discharge and aquaculture activities. Environ. Pollut. 159 (10), 2913–2920.