Environmental Science and Pollution Research (2018) 25:11063–11073
https://doi.org/10.1007/s11356-018-1290-1

RESEARCH ARTICLE

Occurrence, source, and ecological risk of antibiotics in Dongting Lake, China

Xiaohui Liu[1,2] · Shaoyong Lu[2] · Wei Meng[2] · Weiliang Wang[3]

Received: 26 October 2017 / Accepted: 15 January 2018 / Published online: 6 February 2018

Abstract
The pollution characteristics and ecological risk of 12 classified as sulfonamide, trimethoprim, quinolone, and tetracycline antibiotics in Dongting Lake, China, were studied. The total concentrations of the antibiotics ranged from 1.06 to 135.40 ng L^{-1} for all sampling sites. The highest average concentration was observed for sulfadiazine, followed by sulfamethoxazole. The detection frequencies (over 60%) of sulfonamides were higher than those of other antibiotics. The direct discharge of the aquaculture, livestock, and poultry wastewater might be the main pollution sources of antibiotics in the Dongting Lake. The pollution levels of antibiotics decreased in the order of East Dongting Lake > South Dongting Lake > West Dongting Lake, which may be related to the distribution and the scale of the aquaculture, livestock, and poultry sources. The seasonal changes of antibiotic concentration were relatively diversified, with the dry season generally having higher concentrations than the wet season. The results of the ecological risk assessment indicated that sulfamethoxazole, ciprofloxacin, and sarafloxacin might pose a significant risk to the aquatic organisms in Dongting Lake, especially in Potou and Nandu. This study enriches the research of emerging pollutants in freshwater lake.

Keywords Antibiotics · Dongting Lake · Aquatic environment · Pollution source · Ecological risk

Introduction

Antibiotics, a class of pharmaceuticals that are extensively used worldwide, have raised significant concerns (Shen et al. 2015; Zhang et al. 2015a, b; Ling 2010) in recent decades due to their potential threat to the ecological environment and human health. Antibiotics are widely used to treat or prevent human and animal diseases, as well as to promote the growth of animals in the livestock and aquacultural operations (Shea 2003; Xu et al. 2015). They are often partially metabolized in organisms and may be excreted as the parent compounds or metabolites into environment via urine and feces, resulting in higher concentrations of antibiotics in the sewage, treated urban wastewater, and wastewater from the livestock, poultry, and aquaculture activities. As a result of the incomplete removal of antibiotics during wastewater treatment and the direct discharge of the wastewater into receiving water (Xu et al. 2014), the detection frequencies of antibiotics in aquatic environments are high.

Although the concentrations of antibiotics in water range from nanograms per liter to micrograms per liter, and although many antibiotics are unstable, having short half-life periods (Christen et al. 2010), antibiotics cause long-term potential harm to the environment and health due to their continuous input. Inducing and spreading antibiotic-resistant bacterial strains is the most serious risk to the ecological environment and human health (Zhang et al. 2014). Therefore, the environmental risk of antibiotics should not be ignored. The consumption and production of antibiotics in China are the highest in the world. According to the study results of

Responsible editor: Ester Heath

Electronic supplementary material The online version of this article (https://doi.org/10.1007/s11356-018-1290-1) contains supplementary material, which is available to authorized users.

✉ Shaoyong Lu
lushy2000@163.com

✉ Weiliang Wang
sunboyhood@163.com

1 School of Environment, Tsinghua University, Beijing 100084, China

2 State Environmental Protection Scientific Observation and Research Station for Lake Dongting, Chinese Research Academy of Environmental Sciences, Beijing 100012, China

3 Shandong Normal University, Jinan, Shandong 250358, China

Zhang et al. (2015a, b), the total antibiotic usage in 2013 was estimated to be approximately 1.60×10^5 t, and human consumption accounts for approximately 48%, with the rest shared by animals. The antibiotic emissions into water are up to 5.0×10^4 t/year, which results in the high detection frequency of antibiotics in water, such as Pearl (Liang et al. 2013), Haihe (Luo et al. 2011), and Yangtze Rivers (Yan et al. 2014; Shi et al. 2014). In addition, the concentrations of some antibiotics are determined to be thousands of nanograms per liter, which are higher than those in the water of the developed countries.

Dongting Lake, the second largest freshwater lake in China, plays an important role in the water supply for fisheries and agriculture, and it is also a water source for drinking water production (Yuan et al. 2015; Hu et al. 2015). However, there are a large number of highly polluting industries including paper mills and chemical plants within the Dongting Lake basin, and their discharge causes the deterioration of the quality of water of the Dongting Lake. In addition, Dongting Lake receives a large quantity of sewage, treated urban wastewater, and wastewater from the livestock, poultry, and aquaculture activities, which are the main sources of antibiotics and could pose a substantial threat to the environment and human health (Yang et al. 2015). According to the research results of Zhang et al. (2015a, b), the emissions of antibiotics (2190–3560 t year^{-1}) in the Dongting Lake basin are the highest in China, with an emission density of 22.2–32.4 kg (km^2· year^{-1}). The results of Wu et al. (2014) show that there are various antibiotics (trimethoprim, lincomycin, clindamycin, and erythromycin) in the surface water of Dongting Lake. However, the pollution level of antibiotics in the lake and its ecological risk are not well known due to limited sampling locations and types of antibiotics studied, which could not comprehensively reflect the antibiotic pollution status of Dongting Lake.

The main objectives of this study are the following: (1) to investigate the pollution levels of antibiotics in Dongting Lake, (2) to assess the potential ecological risk associated with the antibiotics present by the risk quotient (RQ) method, (3) to examine the seasonal and spatial trends. The results could provide reliable information regarding the pollution characteristics, sources, and risk levels of antibiotic contamination in Dongting Lake.

Materials and methods

Chemicals

A total of 12 antibiotics, classified into four classes, were selected as target compounds and are given in Table 1.

Table 1 Selected antibiotics and their classification

Antibiotics	Acronym	CAS number	Classification
Sulfadiazine	SDZ	68-35-9	Sulfonamides (SAs)
Sulfamethoxazole	SMX	723-46-6	
Sulfamethazine	SMZ	57-68-1	
Trimethoprim	TMP	738-70-5	Trimethoprim (TMP)
Norfloxacin	NOR	70458-96-7	Quinolones (QNs)
Ciprofloxacin	CIP	85721-33-1	
Enrofloxacin	ENR	93106-60-6	
Ofloxacin	OFLO	82419-36-1	
Sarafloxacin	SFLO	98105-99-8	
Tetracycline	TC	60-54-8	Tetracyclines (TCs)
Oxytetracycline	OTC	79-57-2	
Chlortetracycline	CTC	57-62-5	

The selection of the target analytes was based on their high detection frequencies in other lakes and rivers and their high consumption. Analytical standards were purchased from Dr. Ehrenstorfer GmbH (Germany). The internal standards (ciprofloxacin (CIP)-D_8, sulfamethoxazole (SMX)-D_4, trimethoprim (TMP)-$^{13}C_3$, and demeclocycline (DMC)) were obtained from Sigma-Aldrich (St. Louis, MO, USA), except for sulfamethazine-$^{13}C_6$ (SMZ-$^{13}C_6$) which was from Cambridge Isotope Laboratories (Andover, MA, USA). All other chemicals and solvents were purchased from Fisher Chemicals (Fair Lawn, NJ, USA). The SPE cartridges used were Oasis HLB (500 mg/6 mL) purchased from Waters Corporation (Milford, MA, USA). Glass fiber filters were from Sigma-Aldrich (St. Louis, MO, USA). Stock standards and internal standard solutions were prepared in methanol at 1 g L-1 and stored at − 20 °C, which gave a shelf-life of at least 3 months and were diluted before use.

Study area and sample collection

Dongting Lake (27° 39′–29° 51′ N, 111° 19′–113° 34′ E), located in Hu'nan Province and Hubei Province China, is the second largest freshwater lake in China. Currently, the lake is split into several parts, including West Dongting Lake, South Dongting Lake, and East Dongting Lake. Dongting Lake covers a large surface water area of 2691km^2, with the watershed area of 2.57×10^5 km^2. The annual water level of the lake changes by as much as 15 m (Li et al. 2000). The area, whose total capacity is 1.78×10^{10} m^3, receives an annual average rainfall of 1302 mm, and the average water depth is 6.39 m. Dongting Lake plays an important role in regulating the amount of water in the Yangtze River.

To better reflect the antibiotic pollution in the aquatic environment of the Dongting Lake, 18 samples (Fig.1 and

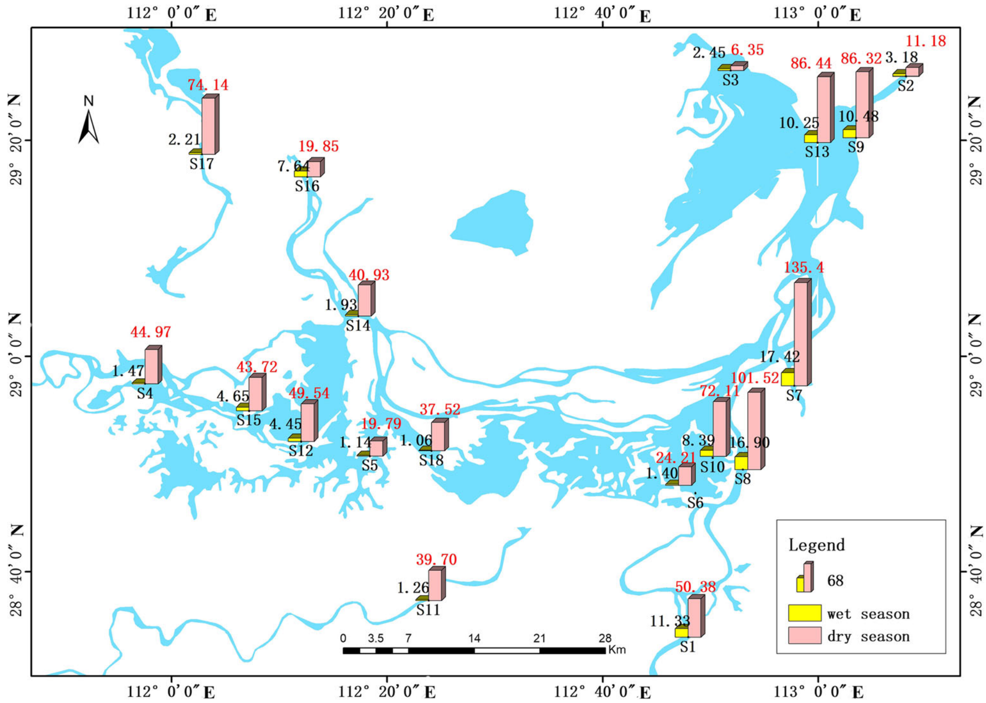


Fig. 1 Distribution of the total antibiotics in the water from Dongting Lake, ng L^{-1}

Table S1) covering the entire lake were collected in December 2015 (dry season) and August 2016 (wet season). The surface water samples were collected at a depth of 1.0 m and placed in pre-rinsed brown glass bottles. Three parallel samples were collected from each sample location, then kept in the brown glass bottle at 4 °C before laboratory analysis. The surface water samples were treated within 12 h after being transported to the laboratory.

Sample preparation and instrumental analysis

The water samples (2 L) were filtered through glass microfiber filters (0.45 μm) (Whatman GF/F, 0.45 μm, USA) to remove suspended particles. Then, the pH value was adjusted to 3 using 0.1 mol L^{-1} sulfuric acid, Na_2EDTA (0.5 g), and 100 μL of 1 mg L^{-1} surrogate standards (CIP-D_8, SMX-D_4, TMP-$^{13}C_3$, DMC, SMZ-$^{13}C_6$) was added to water samples. The treated solutions were extracted using Waters Oasis HLB cartridges (500 mg, 6 mL), which were sequentially preconditioned with 10 mL of methanol and 10 mL of ultrapure water, after which the water samples were loaded into the cartridges at a flow rate of 3–5 mL min^{-1}. The cartridges were rinsed with 10 mL of a 1% methanol aqueous solution and 10 mL of ultrapure water and dried for 2 h under vacuum. The antibiotics retained on the Oasis HLB cartridges were eluted with 6 mL of methanol and 6 mL of a 5% NH_4–H_2O methanol solution, and the eluents were concentrated to near dryness under a gentle stream of nitrogen, after which the resulting residues were re-dissolved in 1 mL of a 10% methanol aqueous solution. After filtration through a 0.22-μm membrane to remove particles, the final extracts were transferred to 2-mL amber glass vials in preparation for analysis.

The analysis of the antibiotics was performed by ultra-performance liquid chromatography–tandem mass spectrometry (ACQUITY UPLC-XEVO-TQMS) (USA, Waters) equipped with an UPLC BEH–C_{18} column (50 × 2.1 mm, 1.7 μm). The column was maintained at 40 °C during sample analysis. The mobile phase consisted of eluent A (0.3% formic acid and 0.1% ammonium formated in ultrapure water) and eluent B (acetonitrile/methanol = 1:1). The separation of the antibiotics was achieved with the gradient program given in Table S2.

The results of the mass spectrometric analyses are provided in Table S3.

Quality assurance and quality control

Quantification using internal standard was the approach to determine the concentration of antibiotics. The calibration curves (0.1~500 μg L^{-1} concentrations) for the antibiotic detection exhibited good linear relationship ($R^2 > 0.98$). The recoveries of the antibiotics from the surface water samples were ranged from 80 to 121% (Table S4). The limit of quantification calculated with a signal/noise ratio of 10 was 0.1 to 0.92 ng L^{-1}. Duplicates, method blanks, and solvent blanks were used for quality control. The target antibiotics were not detected in the method blanks and solvent blanks.

Ecological risk

The ecological risks of the antibiotics were based on the RQ method (Ma et al. 2016; Vryzas et al. 2011). The RQ values were calculated using the formula below:

$$\mathrm{RQ} = \frac{\mathrm{MEC}}{\mathrm{PNEC}} \quad (1)$$

$$\mathrm{PNEC} = \frac{\mathrm{TD}}{\mathrm{AF}} \quad (2)$$

$$\mathrm{RQ}_{\mathrm{com}} = \sum \mathrm{RQ} \quad (3)$$

where MEC is the measured environmental concentration, nanograms per liter. PNEC is the predicted no effect concentration in water, nanograms per liter. PNECs were based on the reported acute or chronic toxicity data. The TD is toxicity data, milligrams per liter. AF is assessment factor. According to the calculated RQ values, the environmental risks were classified into four levels: no risk (RQ < 0.01), low risk (0.01–0.1), medium risk (0.1–1), and high risk (> 1) (Zheng et al. 2012; Sassman and Lee 2005). The RQcom is the combined risk quotient at each point.

Results and discussion

Occurrence of antibiotics in lake water and comparisons between areas

The concentrations of antibiotics in surface water of Dongting Lake are provided in Table 2. Eleven of the 12 antibiotics were detected in the 18 sampling sites, where oxytetracycline was the only antibiotic not detected. The antibiotic concentrations ranged from ND (not detected) to 61.28 ng L^{-1}. The sulfonamides (SAs) were the main components among the tested analytes in Dongting Lake. There was a distinct seasonal variation in the antibiotic concentration. Overall, the contamination by antibiotics in Dongting Lake was relatively low compared to that in other lakes in China. As the Yangtze River-connected Lake and the second largest freshwater lake in China, the fluidity of the water body is large in Dongting Lake, which has strong dilution effect.

The concentration of SAs was in the range of ND–61.8 ng L^{-1}, with detection frequencies of over 60%. Sulfamethazole was the most frequently detected compound. The concentration of sulfamethoxazole was in the range of 0.47–47.41 ng L^{-1} (11.8 ng L^{-1}) in the dry season and ND–5.63 ng L^{-1} (1.36 ng L^{-1}) in the wet season, with detection frequencies of over 80%.The average concentration of sulfadiazine was 24.35 ng L^{-1} in the dry season which was nearly 23 times as high as that in the wet season. Among the three SAs, the average concentration and detection frequencies of sulfamethazine were relatively low. Compared to other lakes in China (see Table 3), the pollution level of sulfamethazine and sulfamethoxazole in Dongting Lake was lower. However, the pollution level of sulfadiazine was much higher than that in Bosten Lake, Chaohu Lake, and Wulungu Lake, except Baiyangdian Lake. Trimethoprim was in a range of ND–2.25 ng L^{-1}. Trimethoprim, an antibacterial synergists, was most commonly used in combination with sulfa-drugs, especially sulfamethoxazole and sulfadiazine, in a ratio of 1:5 (Grossman and Remington 1979; Qin et al. 2015), which led to the relatively high detection frequency in detected antibiotics. The mean concentrations of TMP in both dry and wet seasons are quite close.

Table 2 Statistical characteristics of the concentrations of antibiotics in surface water in wet season and dry season of Dongting Lake (ng L^{-1})

Analytes	Min		Max		Mean		Detection frequency	
	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet
SDZ	0.77	ND	61.28	8.73	24.35	1.07	100%	78%
SMX	0.47	ND	47.41	5.63	11.8	1.36	100%	83%
SMZ	ND	ND	14.88	2.46	3.46	0.67	61%	67%
TMP	ND	ND	2.25	2.12	0.32	0.39	28%	50%
NOR	ND	ND	1.65	1.11	0.1	0.15	11%	28%
CIP	ND	ND	36.17	2.7	3.25	0.18	11%	6%
ENR	ND	ND	0.73	4.61	0.04	0.89	6%	44%
OFL	ND	ND	0.53	ND	0.09	ND	22%	0%
SFLO	ND	ND	21.29	5.59	4.91	0.66	39%	28%
TC	ND	ND	21.51	ND	2.17	ND	28%	0%
OTC	ND	ND	ND	ND	ND	ND	0%	0%
CTC	ND	ND	6.5	4.08	1.79	0.66	50%	28%

ND not detected

Among the five QNs, the detection frequency of sarafloxacin was higher in both dry and wet seasons. The concentration of sarafloxacin was in the range of ND–21.29 ng L^{-1}. As a class of dedicated animal veterinary products, sarafloxacin is becoming increasingly widespread in clinical animal applications (Pulgarín et al. 2012), which might be one of the major reasons for its high concentration and detection frequency in Dongting Lake. Although the detection frequency of ciprofloxacin was low, its concentration was higher than that of some of the detected antibiotics. Ciprofloxacin was widely used in aquaculture, livestock, and poultry, and the usage in the medical field is at the top (Zhang and Liu. 2010). Although the concentrations of norfloxacin and enrofloxacin were low, the concentration and detection frequencies of these two antibiotics were higher in the wet season than in the dry season, especially for enrofloxacin, which was similar to the trend observed in Hongze Lake (Sun 2015). In the wet season, the fish and livestock were in a period of rapid growth, which corresponds to an increase in the usage of norfloxacin and enrofloxacin to treat or prevent diseases and promote the growth of animals. However,

Table 3 The concentration of antibiotics in typical lakes, China (ng·L^{-1})

Antibiotics	Bosten Lake		Wulungu Lake		Baiyangdian Lake		Chao Lake		Taihu Lake		Poyang Lake	Dongting Lake	
	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Mean	Range	Mean
SDZ	2.88–37.27	10.54	1.03–3.68	1.84	0.86–505	118	ND–48	7	–	–	–	0.17–61.28	24.35
SMZ	1.12–13.28	5.91	ND–1.87	0.90	ND–16.1	5.25	ND–171.6	56.1	ND–654	252.7	0.9	ND–14.88	3.46
SMX	–	–	–	–	ND–940	240	ND–9.9	4.5	ND–114.7	48.4	ND	0.47–47.41	11.8
TMP	–	–	–	–	–	–	–	–	ND–40.8	12	–	ND–2.25	0.32
CIP	17.33–112.3	39.22	2.56–28.65	13.62	ND–60.3	9.45	ND~13.6	10.4	ND–43.6	8.8		ND–36.17	3.25
ENR	ND–15.22	6.03	ND–0.58	0.18	ND–4.42	1.28	ND~82.7	13.7	–	–	–	ND–0.73	0.04
OFLO	1.3–32.24	9.29	ND–9.41	2.42	0.38–32.6	9.23	1.2~182.7	18.8	ND–82.8	32.2	–	ND–0.53	0.09
TC	ND–2.84	0.45	0.69–4.7	1.22			ND~9.8	5.5	ND–87.9	43.2	–	ND–21.51	2.17
CTC	ND–3.11	1.03	ND–6.67	1.54	–	–	ND~4.4	3.5	ND–142.5	67.9	–	ND–6.5	1.79
References	Lei. 2014				Li et al. 2012		Tang et al. 2013; Tang et al. 2014		Xu et al. 2014		Wu et al. 2014	This study	

norfloxacin and ofloxacin were prohibited from being produced and used in food animals after September 1, 2015, according to the regulations of the Ministry of Agriculture, and these antibiotics were no longer circulated after December 1, 2015. The detection frequencies of norfloxacin rebounded during the wet season, which may indicate that the norfloxacin in the water of Dongting Lake was mainly from human medication. The lower concentration of norfloxacin may be related to the prohibited use in juveniles (Li et al. 2016), which limits its usage. Generally, the pollution levels of QNs in Dongting Lake were much lower than those reported for other lakes of China.

In the dry season, the concentration of tetracycline ranged from ND to 21.51 ng L^{-1} with a mean value of 2.17 ng L^{-1}, and chlortetracycline ranged from ND to 6.5 ng L^{-1} with a mean value of 1.79 ng L^{-1}. Tetracyclines are widely used to treat diseases and protect the health of animals. They are also added at subtherapeutic levels to animal feed to prevent infection and act as growth promoters. Tetracyclines are also the most widely used veterinary drugs and food additives in the aquacultural and livestock industries of China. In 2010, the chlortetracycline usage reached approximately 7.19×10^4 t, which was 22 times the annual usage of tetracycline antibiotics in America (Guo et al. 2014). The usage of tetracycline antibiotics is enormous in Dongting Lake which is as an important aquacultural, livestock, and poultry breeding base. Therefore, the detection frequencies of tetracycline (26.32%) and chlortetracycline (47.37%) were higher than those of the other antibiotics except for the SAs. The concentrations of chlortetracycline and tetracycline were much lower than those of Taihu Lake, and of the same order of magnitude as those of Chaohu Lake, Bosten Lake, and Wulungu Lake. In the wet season, tetracycline and oxytetracycline were not detected. As the only detectable tetracycline antibiotic, the concentration of chlortetracycline declined drastically in the wet season, compared to the dry season.

Overall, the concentrations of antibiotics in the dry season were significantly higher than in the wet season. This phenomenon is similar to the Poyang Lake (Ding et al. 2017), the Victoria Harbor and the Pearl River (Xu et al. 2006), the Honghu Lake (Wang et al. 2017), and the Xiang River (Fan et al. 2015). The conclusions of these studies reached a consensus that the significantly lower concentrations of antibiotics in the wet season mainly resulted from the dilution effect of water flow. The average water level of Dongting Lake has been increasing two times between December 2015 and August 2016 (http://www.yymsa.gov.cn/yymsa/xxgk/xxgkml/aqxx/swgg/).On the other hand, the cold water temperatures, low microbial activity, and low dissolved oxygen might enhance the persistence of antibiotics (Yan et al. 2013; Kümmerer. 2009). In addition, winter was the peak incidence of diseases, which resulted in larger usage of antibiotics.

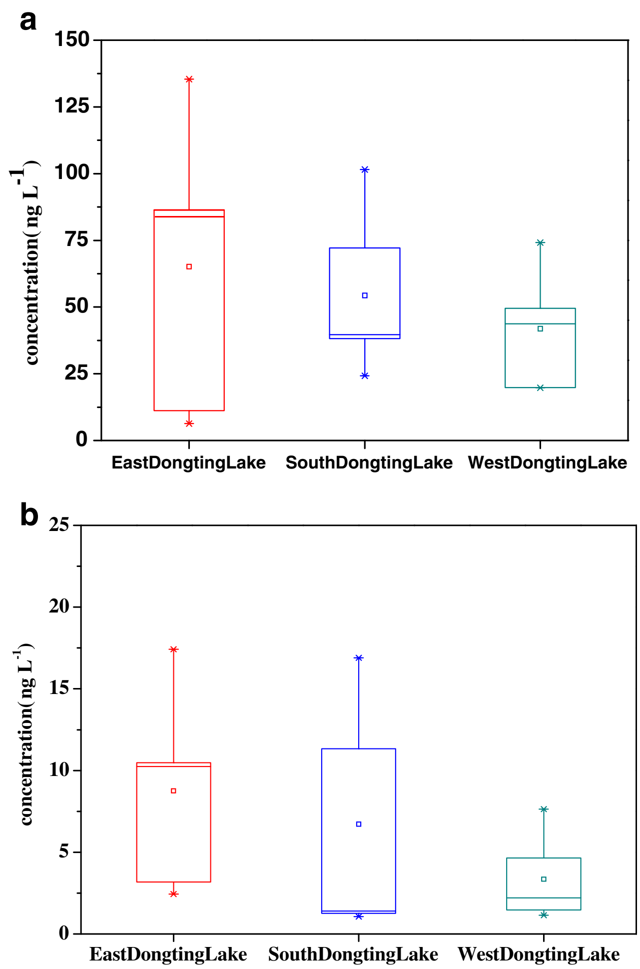


Fig. 2 Spatial distribution in the dry (A) and wet season (B) between East Dongting, West Dongting, and South Dongting Lake

Spatial distribution and source identification

The total concentrations of the antibiotics in Dongting Lake are shown in Fig.1. The total concentrations of the detected antibiotics at each sampling site ranged from 6.35 to 135.40 ng L^{-1} in the dry season and 1.06 to 17.42 ng L^{-1} in the wet season. In Nandu, the total concentration was the highest. The difference in the distribution of the antibiotics was obvious, in which the highest pollution level of antibiotics was observed in East Dongting Lake (mean value of 65.14 ng L^{-1} in the dry season and 8.76 ng L^{-1}in the wet season), followed by South Dongting Lake (mean value of 54.35 ng L^{-1} in the dry season and 6.72 ng L^{-1}in the wet season) and West Dongting Lake (mean value of 41.85 ng L^{-1} in the dry season and 3.36 ng L^{-1}in the wet season) (see Fig.2). The spatial distribution of antibiotics in Dongting Lake was similar to the distribution of Pharmaceuticals and Personal Care Products (PPCPs) (Ma et al. 2016). The objective reasons were as follows: (1) as the convergence site of lake water, a large number of pollutants gathered in East Dongting Lake (Bu 1991); (2) the outlet of Dongting Lake near East Dongting Lake was easily affected by the backwater effect of the Yangtze river (Wang et al. 2012), which facilitated the accumulation of pollutants; (3) the populations around East Dongting Lake was 1,783,000, which had high population density, and the two wastewater treatment plants of Yueyang City were very close to East Dongting Lake (Yang et al. 2016). The spatial distribution pattern of the antibiotics in Dongting Lake was closely related to the distribution of the pollution sources. Sulfadiazine, sulfamethoxazole, sulfamethazine, and sarafloxacin, the major pollutants of the Dongting Lake, are used in aquaculture, livestock, and poultry. From 2003 to 2013, the use of veterinary drugs increased from 46 to 52% of the total usage. Furthermore, more than 60 to 90% of the ingested antibiotics may be excreted by animals without modification, resulting in a potential pollution risk for the water environment (Boundj and Voulvoulis 2004).

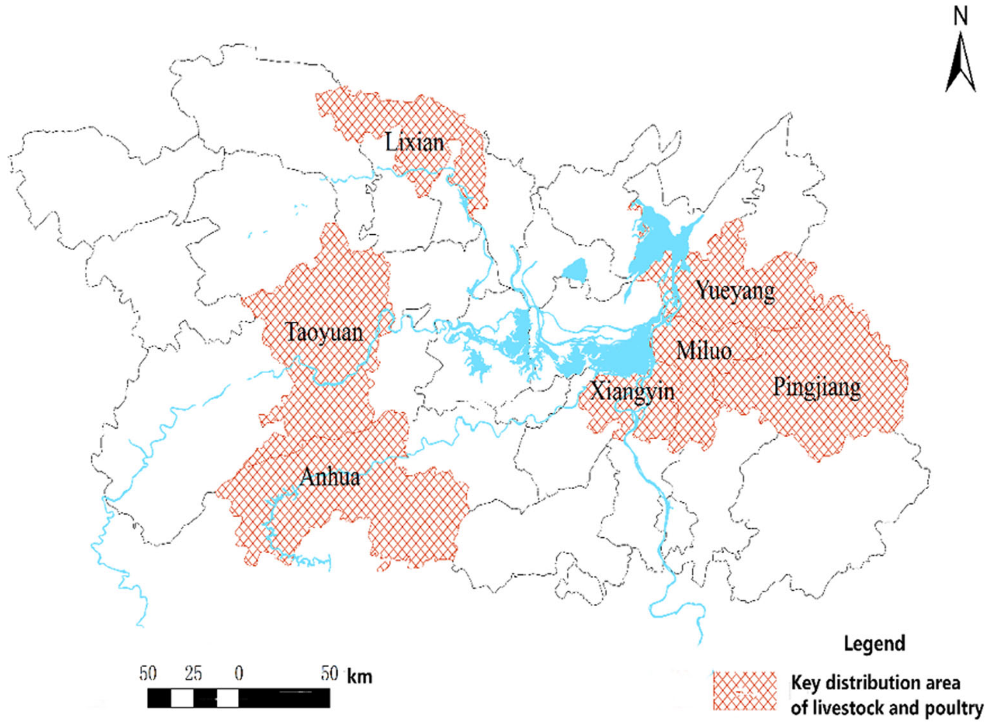
The key distribution areas of aquaculture, livestock, and poultry are seen in Fig.3, and Fig. 4. In the West Dongting Lake basin, the key distribution areas of livestock and poultry are located in Taoyuan county, Anhua county, and Lixian. However, as an important risk source of antibiotics, this area is far from West Dongting Lake. During the migration of antibiotics, photodegradation and hydrolysis become important environmental factors, which caused lower antibiotic concentrations in West Dongting Lake. In the East and South Dongting Lake basins, the key distribution areas are in Xiaoyin county, the downtown area, Miluo City, and the Pingjiang county of Yueyang City. As the second largest producer of livestock and poultry in the Dongting Lake Basin, Yueyang City is an important risk source of antibiotics. However, the phenomenon of direct discharge of aquaculture, livestock, and poultry wastewater still existed (http://www.hbzhan.com/news/detail/109718.html).

The regulatory controls are weak and antibiotics are often overused in aquaculture in China. In 2014, the total aquacultural production of Dongting Lake was 1.31×10^6 t. The key distribution areas of aquaculture are located in Hanshou county (3.0×10^5 acres), Xiangyin county (1.5×10^5 acres), Huarong county (the aquaculturing areas are 2.0×10^5–3.0×10^5 acres), and Nan county (the aquaculturing areas are over 1.0×10^5–2.0×10^5 acres), which are mainly located in East Dongting Lake.

Ecological risk

Based on the worst case scenario, the RQs were estimated based on the PNECs of the most sensitive species (see Table 4), and conducted, using the maximum concentrations of the antibiotics according to Yan et al. (2013) and Xue et al. (2013). The results are displayed in Table 5. Due to their trace residue, the RQs for most of the antibiotics were below 0.1 in

Fig. 3 Key distribution area of livestock and poultry in Dongting Lake



the dry season. However, the RQs of sulfamethoxazole, ciprofloxacin, and sarafloxacin were over 1, indicating that they pose a significant environmental risk to Dongting Lake. Furthermore, ciprofloxacin had the highest RQ (up to 7.23) due to its low PNEC, which may pose adverse ecological effects. Sulfadiazine, the target compound with the highest concentration and detection frequency, showed the low risk. The rest of the antibiotics exhibited low or no environment

Fig. 4 Key distribution area of aquaculture in Dongting Lake

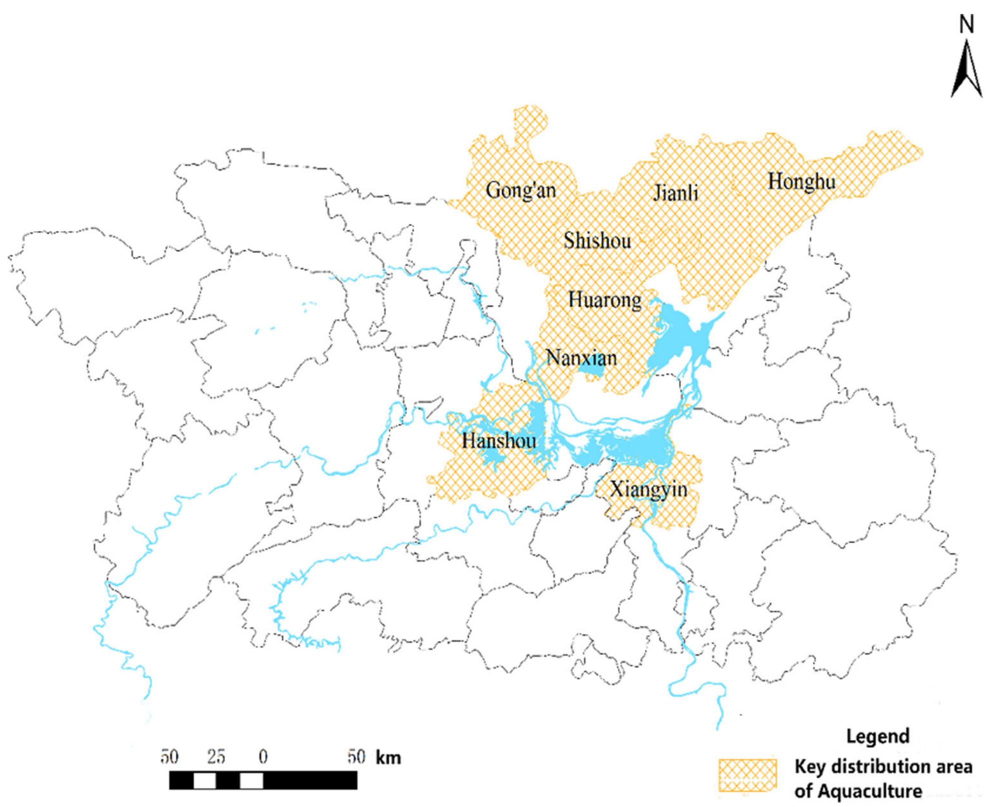


Table 4 Aquatic toxicity data of antibiotics to the most sensitive aquatic species

Antibiotics	Sensitive aquatic species	Toxicity types	AF	Toxicity data (mg L^{-1})		Assessment factor	PNEC (ng L^{-1})	References
				EC50	NOEC			
SDZ	*S. capricornutum*	Acute	1000	2.2		1000	2200	Eguchi et al. 2004
SMX	*S. leopoliesis*	Acute	1000	0.027		1000	27	Ferrari et al. 2004
SMZ	*Lemna minor*	Acute	1000	1.74		1000	1740	Białk-Bielińska et al. 2011
TMP	*R. salina*	Acute	1000	16.4		1000	16,400	Lützhøft et al. 1999
CIP	*M. aeruginosa*	Acute	1000	0.005		1000	5	Isidori et al. 2005
ENR	*M. aeruginosa*	Acute	1000	0.049		1000	49	Backhaus et al. 2000
OFLO	*P. subcapitata*	Chronic	100		0.00113	100	11.3	Robinson et al. 2005
SFLO	*M. aeruginosa*	Acute	1000	0.015		1000	15	Lützhøft et al. 1999
TC	*P. subcapitata*	Acute	1000	3.31		1000	3310	González-Pleiter et al. 2013
OTC	*P. subcapitata*	Acute	1000	1.04		1000	1040	Kolar et al. 2014
CTC	*Chlorella pyrenoidosa*	Acute	1000	9.31		1000	9310	Xu et al. 2013

EC50 is the concentration for 50% of maximal effect, NOEC is the no-observed effect concentration

risk, except for ofloxacin (medium risk). In the wet season, ciprofloxacin (RQ = 0.54) had the highest risk factor as in the dry season, followed by sarafloxacin (RQ = 0.37) and sulfamethoxazole (RQ = 0.21) with these antibiotics exerting medium ecological risk. The RQ of rest antibiotics were in the range of 10^{-2}~10^{-4}, which would not cause obvious risk to ecological environment.

Table 5 RQs and RQcom for the antibiotics in surface water from the Dongting Lake

Antibiotics	RQ_{dry}	RQ_{wet}
SDZ	2.79×10^{-2}	3.97×10^{-3}
SMX	1.76	0.21
SMZ	8.55×10^{-3}	1.41×10^{-3}
TMP	1.37×10^{-4}	1.29×10^{-4}
NOR	1.59×10^{-2}	0.01
CIP	7.23	0.54
ENR	1.49×10^{-2}	0.14
OFLO	0.53	–
SFLO	1.42	0.37
TC	6.5×10^{-3}	–
CTC	6.98×10^{-4}	4.38×10^{-4}
Sampling sites	$RQcom_{dry}$	$RQcom_{wet}$
S1	1.52	0.21
S2	0.18	4.45×10^{-2}
S3	0.19	4.00×10^{-2}
S4	6.09	3.01×10^{-2}
S5	0.38	6.00×10^{-4}
S6	1.32	1.73×10^{-2}
S7	8.73	0.89
S8	1.58	0.62
S9	0.45	0.19
S10	1.36	0.34
S11	0.18	4.31×10^{-2}
S12	5.38×10^{-2}	9.71×10^{-2}
S13	1.5	4.90×10^{-2}
S14	0.15	2.76×10^{-2}
S15	0.63	3.35×10^{-2}
S16	7.18×10^{-2}	8.60×10^{-3}
S17	1.77	5.05×10^{-2}
S18	0.39	2.20×10^{-3}

Furthermore, antibiotics in the actual environment often exist as mixtures, which can enhance the effect on the environment due to cocktail effects (Cleuvers 2004). However, most of the toxicity researches on antibiotics only analyze individual compounds. Therefore, it is assumed that the effects of antibiotics on biological system fail to exhibit antagonistic or synergistic relationship, and the simple accumulation model was used to calculate the combined risk in this study, see Formula (3). The calculated results of the combined risk assessment are shown in Table 5. In the dry season, the combined risk index at the different sites were significantly different, ranging from 0.05 to 8.73. Of the sites, S7 (Nandu) had the highest combined risk (up to 8.73), followed by S4 (Hanshouyuanshui bridge) (up to 6.09), which posed a substantial threat to the ecological security of Dongting Lake. The combined risk for S1, S6, S8, S10, S13, and S17, which were all located in the East and South Dongting Lake, ranged from 1 to 2, whereas the combined risk indexes in the rest of the sites were below 1, which corresponded to a medium or low risk. Compared to the dry season, the combined risk index of all sites were lower in the wet season, with values below 1. Of the sites, S7 (Nandu) had the highest combined risk as dry season (0.89), followed by the sites in the order of S8 > S10 > S1 > S9, which showed a medium risk. The risk index of other sites exhibited low or no environmental risk. In the cumulative risk for S7, ciprofloxacin accounted for over 80%. Although the detection frequency of ciprofloxacin was low, its risk to the Dongting Lake was not ignored.

Although the ecological risk of most of the antibiotics was low, the antibiotic risk to human health should be not ignored. Antibiotics could lead to a selective pressure on the water bacteria and induce the formation of antibiotic-resistant bacteria. Additionally, antibiotic-resistant genes (ARGs) can be transferred between non-pathogens, pathogens, and even distantly related organisms, such as Gram-positive and Gram-negative bacteria, through horizontal gene transfer, and the resulting antibiotic-resistant bacteria are considered a potential threat to human health through the food chain (Pruden et al. 2006). In Peking Union Medical College Hospital, the fungal infection rate was 0% in the 1980s and increased to 7–8% in 2000, which was caused by the appearance of pandrug-resistant nonfermenters (ChinaIRN, 2012). Xiao (2008) found that the mortality rate (11.7%) of patients infected by drug-resistant bacteria was more than twice that in patients with a common infection (5.4%). In addition, related studies showed that the highest resistance rates of tetracycline, sulfamethoxazole, and cefalotin sodium have reached 57, 13, and 35%, respectively (Dai et al. 2009). The antibiotic-resistant bacteria and genes are abundant in the Pearl (Tao et al. 2010), Haihe (Luo et al. 2010), and Huangpu rivers (Shen et al. 2012). However, relevant studies on the risk assessment of ARGs are limited. In Dongting Lake, the pollution characteristics and ecological risk of ARGs in water were still absent, which relevant research should be conducted.

Conclusions and suggestions

This study reported the occurrence of 10 individual antibiotics in the surface water of the second largest freshwater lake in China. The results showed that the concentrations of sulfonamides were relatively higher than other antibiotics in Dongting Lake. Compared to other lakes in China, the pollution level of antibiotics was relatively low. The pollution level of antibiotics in the dry season was significantly higher than in the wet season except for trimethoprim, enrofloxacin, and norfloxacin. The concentrations showed an obvious spatial difference, which followed the trend of East Dongting Lake> South Dongting Lake > West Dongting Lake. The spatial distribution of antibiotics in Dongting Lake may be related to the distance of risk sources (aquaculture, livestock, and poultry) from Dongting Lake and their scale. The risk assessment revealed that sulfamethoxazole, ciprofloxacin, and sarafloxacin had higher ecological risk to the Dongting Lake. Therefore, a risk warning system should be built. Further study is needed to investigate the usage and emission of typical antibiotics in Dongting Lake basin, and the rates of contribution from different sources should be quantified in detail, especially in the aquacultural, livestock, and poultry industries. The occurrence, distribution, and environmental risk in multimedia samples from Dongting Lake should be researched. In addition, the mechanisms and routes of the migration and transformation of the antibiotics from West Dongting Lake to East Dongting Lake, and the types and toxic effects of the derivatives and transformation products should be analyzed. These properties have important theoretical and practical significance for evaluating and diagnosing the environmental safety of Dongting Lake.

Acknowledgments This work was financially supported by the Ministry of Science and Technology of China (grant no. 2015FY110900) and the National Natural Science Foundation of China (41672340). The authors would like to thank the assistance of Prof. Weihao Zhang and Dr. Yixiao Wu from Wuhan University and Prof. Fang Yang from Tsinghua University.

References

Białk-Bielińska A, Stolte S, Arning J et al (2011) Ecotoxicity evaluation of selected sulfonamides. Chemosphere 85(6):928–933

Backhaus T, Scholze M, Grimme LH (2000) The single substance and mixture toxicity of quinolones to the bioluminescent bacterium Vibrio fischeri. Aquat Toxicol 49(1):49–61

Bu YX (1991) Statistical analysis of Dongting Lake water quality and its time and space distribution indexes. Environ Pollut Control 13(3):2–4

Boundj P, Voulvoulis N (2004) Pharmaceuticals in the aquatic environment: a comparison of risk assessment strategies. Chemosphere 56(11):1143–1155. https://doi.org/10.1016/j.chemosphere.2004.05.010

Christen V, Hickmann S, Rchenberg B et al (2010) Highly active human pharmaceuticals in aquatic systems: a concept for their identification based on their mode of action. Aquat Toxicol 96(3):167–181

Cleuvers M (2004) Mixture toxicity of the anti-inflammatory drugs diclofenac, ibuprofen, naproxen and acetylsalicylic acid. Ecotoxicol Environ Saf 59(3):309–315. https://doi.org/10.1016/S0147-6513(03)00141-6

ChinaIRN. http://www.chinairn.com, 2012

Dai CM, Zhou XF, Zhang YL et al (2009) Research advancements in potential risk of PPCPs of environmental media. Environ Pollut Control 31(2):77–80 (in Chinese)

Ding H, Wu Y, Zhang W, Zhong J, Lou Q, Yang P, Fang Y (2017) Occurrence, distribution, and risk assessment of antibiotics in the surface water of Poyang Lake, the largest freshwater lake in China. Chemosphere 184:137–147. https://doi.org/10.1016/j.chemosphere.2017.05.148

Eguchi K, Nagase H, Ozawa M et al (2004) Evaluation of antimicrobial agents for veterinary use in the ecotoxicity test using microalgae. Chemosphere 57(11):1733–1738

Ferrari B, Mons R, Vollat B et al (2004) Environmental risk assessment of six human pharmaceuticals: are the current environmental risk assessment procedures sufficient for the protection of the aquatic environment? Environ Toxicol Chem 23(5):1344–1354

Fan CZ, Wang C, Lu LH et al (2015) Occurrence and seasonal changes of tetracycline antibiotics and antibiotic resistance genes in the xiang river. k 42(o):107–112 (in Chinese)

González-Pleiter M, Gonzalo S, Rodea-Palomares I et al (2013) Toxicity of five antibiotics and their mixtures towards photosynthetic aquatic organisms: implications for environmental risk assessment. Water Res 47(6):2050–2064

Grossman PL, Remington JS (1979) The effect of trimethoprim and sulfamethoxazole on Toxoplasma gondii in vitro and in vivo. Am J Trop Med Hyg 28(3):445–455. https://doi.org/10.4269/ajtmh.1979.28.445

Guo XY, Wang N, Xu J et al (2014) Research progress on environmental exposure levels and environmental fate of veterinary antibiotics. Environ Sci Technol 37(9):76–86 (in Chinese)

Hu Y, Huang J, Du Y, Han P, Huang W (2015) Monitoring spatial and temporal dynamics of flood regimes and their relation to wetland landscape patterns in Dongting Lake from MODIS time-series imagery. Remote Sens 7(6):7494–7520. https://doi.org/10.3390/rs70607494

Isidori M, Lavorgna M, Nardelli A et al (2005) Toxic and genotoxic evaluation of six antibiotics on non-target organisms. Sci Total Environ 346(1):87–98

Kolar B, Arnuš L, Jeretin B et al (2014) The toxic effect of oxytetracycline and trimethoprim in the aquatic environment. Chemosphere 115:75–80

Kümmerer K (2009) Antibiotics in the aquatic environment–a review–part I. Chemosphere 75(4):417–434. https://doi.org/10.1016/j.chemosphere.2008.11.086

Ling BD (2010) Multidrug resistance in Acinetobacter baumanni mechanisms and anti-infective therapy. Chin J Antibiot 4:241–254 (in Chinese)

Liang X, Chen B, Nie X et al (2013) The distribution and partitioning of common antibiotics in water and sediment of the Pearl River Estuary, South China. Chemosphere 92(11):1410–1416

Luo Y, Xu L, Rysz M, Wang Y, Zhang H, Alvarez PJJ (2011) Occurrence and transport of tetracycline, sulfonamide, quinolone, and macrolide antibiotics in the Haihe River Basin, China. Environ Sci Technol 45(5):1827–1833. https://doi.org/10.1021/es104009s

Li Y, Sleigh A, Ross AG et al (2000) Epidemiology of schistosma japonicum in China: morbidity and strategies for control in the Dongting Lake of region. Int J Parasitol 30(3):273–281

Lei X N. 2014 Distribution and pollution levels of antibiotics from typical lakes in Xinjiang. Guangxi Univ. (in Chinese)

Li WH, Shi YL, Gao LH et al (2012) Occurrence of antibiotics in water, sediments, aquatic plants, and animals from Baiyangdian Lake in North China. Chemosphere 89:1307–1315

Lützhøft HCH, Halling-Sørensen B, Jørgensen SE (1999) Algal toxicity of antibacterial agents applied in Danish fish farming. Arch Environ Contam Toxicol 36(1):1–6

Li J, Zhang RJ, Wang RM et al (2016) Distribution characteristics and ecological risk assessment of antibiotic pollution in Xiaoqing River watershed. J Agro-Environ Sci 35(7):1384–1391 (in Chinese)

Luo Y, Mao D, Rysz M, Zhou Q, Zhang H, Xu L, J. J. Alvarez P (2010) Trends in antibiotic resistance genes occurrence in the Haihe River, China. Environmental Science & Technology 44(19):7220–7225. https://doi.org/10.1021/es100233w

Ma R, Wang B, Lu S, Zhang Y, Yin L, Huang J, Deng S, Wang Y, Yu G (2016) Characterization of pharmaceutically active compounds in Dongting Lake, China: occurrence, chiral profiling and environmental risk. Sci Total Environ 557-558:268–275. https://doi.org/10.1016/j.scitotenv.2016.03.053

Pulgarín JAM, Molina AA, Ferreras FM et al (2012) Rapid and simple determination of sarafloxacin in egg by time-resolved chemiluminescence. Food Anal Methods 6(4):1153–1161

Pruden A, Pei R, Storteboom H, Carlson KH (2006) Antibiotic resistance genes as emerging contaminants: studies in northern Colorado. Environ Sci Technol 40(23):7445–7450. https://doi.org/10.1021/es0604131

Qin Y, Zhang L, Shi Y et al (2015) Contamination characteristics and ecological risk assessment of typical antibiotics in surface water of the Daliao River, China. Res Environ Sci 28(3):361–368 (in Chinese)

Robinson AA, Belden JB, Lydy MJ (2005) Toxicity of fluoroquinolone antibiotics to aquatic organisms. Environ Toxicol Chem 24(2):423–430. https://doi.org/10.1897/04-210R.1

Shen YW, Huang ZT, Xie B (2015) Advances in research of pollution, degradation and removal of antibiotics and antibiotic resistance genes in the environment. Chin J Appl Environ Biol 21(2):181–187 (in Chinese)

Shea KM (2003) Antibiotic resistance: what is the impact of agricultural uses of antibiotics on children's health. Pediatrics 112(1):253–258

Shi X, Zhou JL, Zhao H et al (2014) Application of passive sampling in assessing the occurrence and risk of antibiotics and endocrine disrupting chemicals in the Yangtze Estuary, China. Chemosphere 111C:344–351

Sassman SA, Lee LS (2005) Sorption of three tetracyclines by several soils; assessing the role of pH and cation exchange. Environ Sci Technol 39(19):7452–7459. https://doi.org/10.1021/es0480217

Shen QH, Ji XL, Fu SJ et al (2012) Preliminary studies on the pollution levels of antibiotic and antibiotic resistance genes in Huangpu River, China. Ecol Environ Sci 21(10):1717–1723 (in Chinese)

Sun K (2015) Contamination characteristics and ecological risk assessment of typical antibiotics in the water of the Hongze Lake. Nanjing Tech University, Nanjing

Tang J, Chen HY, Shi TZ et al (2013) Occurrence of quinolones and tetracyclines antibiotics in the aquatic environment of Chaohu Lake. J Anhui Agric Univ 40(6):1043–1048 (in Chinese)

Tang J, Zhang FH, Wang CC et al (2014) Investigation of sulfonamide antibiotics residue in the water of Chaohu Lake and its inlet rivers. J Saf Environ 14(4):334–338 (in Chinese)

Tao R, Ying GG, Su HC, Zhou HW, Sidhu JPS (2010) Detection of antibiotic resistance and tetracycline resistance genes in Enterobacteriaceae isolated from the Pearl rivers in South China. Environ Pollut 158(6):2101–2109. https://doi.org/10.1016/j.envpol.2010.03.004

Vryzas Z, Alexoudis C, Vassiliou G et al (2011) Determination and aquatic risk assessment of pesticide residues in riparian drainage canals in northeastern Greece. Ecotoxicol Environ Saf 74(2):174–181

Wang Z, Du Y, Yang C et al (2017) Occurrence and ecological hazard assessment of selected antibiotics in the surface waters in and around Lake Honghu, China. Sci Total Environ 609:1423–1432. https://doi.org/10.1016/j.scitotenv.2017.08.009

Wu CX, Huang XL, Witter JD et al (2014) Occurrence of pharmaceuticals and personal care products and associated environmental risks in the central and lower Yangtze river, China. Ecotoxicol Environ Saf 106:19–26. https://doi.org/10.1016/j.ecoenv.2014.04.029

Wang X, Xiao WH, Zhu EY et al (2012) Effects of water level variation on water quality in Dongting Lake. South-to-north Water Transfers Water Sci Technol 10(5):59–62 (in Chinese)

Xu YG, Yu WT, Ma Q et al (2015) The antibiotic in environment and its ecotoxicity: a review. Asian J Ecotoxicol 10(3):11–27 (in Chinese)

Xu W, Zhang G, Zou S et al (2006) Occurrence and seasonal changes of antibiotics in the Victoria Harbour and the Pearl River, South China. Environ Sci 27(12):2458–2462

Xu J, Zhang Y, Zhou CB et al (2014) Distribution, sources and composition of antibiotics in sediment, overlying water and pore water from Taihu Lake, China. Sci Total Environ s497–498(3):267–273

Xiao YH (2008) Medical and social consequences of antibiotics abuse. Symp Qual Saf Antibiot (in Chinese)

Xue B, Zhang R, Wang Y et al (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 Saf 92(3):229

Xu DM, Wang YH, Rao GW (2013) Cellular response of freshwater green algae to the toxicity of tetracycline antibiotics. Environ Sci 34(9):3386–3390 (in Chinese)

Yan C, Yi Y, Zhou J et al (2014) Selected emerging organic contaminants in the Yangtze Estuary, China: a comprehensive treatment of their association with aquatic colloids. J Hazard Mater 283:14–23

Yuan Y, Zeng G, Liang J et al (2015) Variation of water level in Dongting Lake over a 50-year period: implications for the impacts of anthropogenic and climatic factors. J Hydrol 525(10):450–456

Yang Y, Cao X, Zhang M et al (2015) Occurrence and distribution of endocrine-disrupting compounds in the Honghu Lake and East Dongting Lake along the Central Yangtze River, China. Environ Sci Pollut Res 22(22):17644–17652

Yan C, Yang Y, Zhou J et al (2013) Antibiotics in the surface water of the Yangtze Estuary: occurrence, distribution and risk assessment. Environ Pollut 175(8):22–29

Yang Y, Cao X, Lin H et al (2016) Antibiotics and antibiotic resistance genes in sediment of Honghu Lake and East Dongting Lake, China. Microb Ecol 72(4):791–801

Zhang Q, Cheng J, Xin Q (2015a) Effects of tetracycline on developmental toxicity and molecular responses in zebrafish (Danio rerio) embryos. Ecotoxicology 24(4):707–719. https://doi.org/10.1007/s10646-015-1417-9

Zhang Q, Jia A, Wan Y, Liu H, Wang K, Peng H, Dong Z, Hu J (2014) Occurrences of three classes of antibiotics in a natural river basin: association with antibiotic-resistant Escherichia coli. Environ Sci Technol 48(24):14317–14325. https://doi.org/10.1021/es503700j

Zhang QQ, Ying GG, Pan CG, Liu YS, Zhao JL (2015b) A comprehensive evaluation of antibiotics emission and fate in the river basins of China: source analysis, multimedia modelling, and linkage to bacterial resistance. Environ Sci Technol 49(11):6772–6782. https://doi.org/10.1021/acs.est.5b00729

Zheng Q, Zhang R, Wang Y et al (2012) Occurrence and distribution of antibiotics in the Beibu Gulf, China: impacts of river discharge and aquaculture activities. Mar Environ Res 78(8):26–33

Zhang B, Liu YH (2010) Usage analysis of quinolones from 2007 to 2009 in a hospital. Guid China Med 8(26):112–113 (in Chinese)