Desalination and Water Treatment
www.deswater.com

doi:10.5004/dwt.2018.22255

115 (2018) 249–260
May

Occurrence, distribution and risk assessment of antibiotics in the surface water of Hongze Lake: a typical water exchanging lake in the South-to-North Water Diversion Project

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Received 20 September 2017; Accepted 23 March 2018

ABSTRACT

This study investigated the presence and distribution of antibiotics and assessed their ecological risk to aquatic organisms in surface water from Hongze Lake, China. The concentrations of 16 antibiotics, including six sulfonamides, five quinolones, and five tetracyclines and macrolides were analyzed by liquid chromatography–tandem mass spectrometry (UPLC-MS/MS), and the RQ value method was used for the risk assessment. The results indicated that sulfamethoxazole (SMX) and sulfa-chloropyridazine (SCP) were the main antibiotics in the surface water of Hongze Lake, with maximum concentrations of 48.1 ng/L and 36.5 ng/L, respectively. The concentration of antibiotics was higher in June than in October. The sulfonamide distribution was generally higher in the eastern water transfer area than the west lake area, whereas that of quinolones, tetracyclines and macrolides was higher in the north lake area than in the other areas. The results of the risk assessment suggested that SMX might pose a high ecological risk to algae. The RQ value of SMX in algae of Hongze Lake was determined to be 1.60. This study will enrich the water quality system of Hongze Lake and supplement the water quality data of the South-to-North Water Diversion Project.

Keywords: Antibiotics; Hongze Lake; Risk assessment; Concentration; Distribution

1. Introduction

The occurrence, fate and persistence of antibiotics in the water environment have attracted widespread attention given the close link between antibiotics with their water solubility and anti-degradation characteristics [1,2]. China is a major producer and consumer of antibiotics, and the total consumption of antibiotics in the world is estimated to be between 100,000 and 200,000 ton/y [3], of which approximately 25,000 tons are used in China annually [4,5]. In particular, the consumption of prescription antibiotics in China accounts for 70% of the global total compared to 30% in Western countries; therefore, the abuse of antibiotics is a serious issue in China [6]. Agriculture, animal husbandry and aquaculture are important economic activities in developing countries. However, livestock and aquaculture are among the main sources of PPCP pollution in the local water environment. Antibiotics such as sulfonamides, fluoroquinolones and tetracycline are widely used in pharmaceuticals or feed additives, and they are ultimately released to the water environment through farm waste-water and animal residues, medical waste-water, agricultural manure irrigation runoff and soil infiltration, domestic sewage discharge and industrial waste water [7,8], usually in the form of the parent compounds or metabolites [9]. The irrational use of antibiotics and their continued transport increase the residual levels in aquatic environments, which affect the growth and development of crops after irrigation through contaminated lakes and flowing water [10–12].

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Antibiotics may be toxic to certain aquatic organisms. Robinson tested the toxicity of five fluoroquinolones and found that *Pseudomonas aeruginosa* is the most sensitive organism, followed by duckweed and green algae [13]. González-Pleiter tested the toxicity of five antibiotics and reported that quinolones levofloxacin and norfloxacin were more toxic to cyanobacteria than green algae [14]. Antibiotics are retained in the bodies of animals and plants, ultimately affecting all organisms involved in a food chain [13]. Therefore, antibiotic contamination has the potential to destroy the balance of an entire ecosystem. Antibiotic contaminations in water bodies is a serious issue, as it can lead to the development of antibiotic resistance genes (ARGs) and induce a large number of antibiotic-resistant bacteria; with the breeding and propagation of such bacteria, human health and local ecological environments are exposed to unpredictable hazards [14–16]. In particular, the occurrence, fate, and persistence of antibiotics in aquatic environments have attracted widespread attention given their solubility in water and anti-degradation characteristics [2].

Previous studies about the aquatic antibiotics concentration have been conducted around the world. Managaki found sulfonamides were at concentrations of 7–360 ng/L in the Mekong River Delta in Vietnam [19]. Tamtam conducted a six-month survey of water bodies around the Seine River in France and detected at least 17 compounds, with sulfamethoxazole concentrations of up to 544 ng/L [20]. Arikan detected antibiotics in the Choptank Rivers of Maryland in the United States and reported that agriculture could serve as a source of antibiotic residues in the aquatic environment [21]. Xu detected chloramphenicol, two quinolones and three sulfonamides in seawater near Victoria Harbor, Hong Kong, with concentrations ranging from 11 to 67 ng/L in the wet season and from 66 to 460 ng/L in the dry season [22]. Li investigated Baiyangdian Lake and found that sulfonamides were the main antibiotic, with concentrations ranging from 0.86 to 1563 ng/L [23]. Luo found 24–385 ng/L of sulfonamides in the Haihe River Basin [24]. The frequency and concentration of sulfonamides and sulfamethoxazole in the Yangtze River and the Pearl River were 56.8 and 616 ng/L, respectively [25,26], and antibiotics in some parts of the Pearl River reached mg/L levels. Investigating the Chaohu Lake Basin, Tang found that the antibiotics were mainly sulfamethoxazole and ofloxacin with maximum concentrations of 95.6 and 383.4 ng/L, respectively [8]. It can be concluded that the highest content of sulfonamides in bodies of water occurred in Baiyangdian, followed by the Pearl River and the Haihe River Basin; the lowest contents were located in the Chaohu Lake and the Yangtze River. Antibiotic concentration may be related to the amount of water in the river, the self-purification capacity of the river, the degradation of antibiotics as well as environmental behavior such as adsorption, migration, and degradation in the aquatic environment [7,27].

Hongze Lake is one of the four major freshwater lakes in China. It has many functions such as flood storage, irrigation, shipping, aquaculture, drinking water source, and ecological protection. The lake is one of the major agricultural and aquaculture production areas in China. The southern part of the lake also hosts the internationally famous lobster breeding base Xuyi. Fish and crab farming is also very well developed. Investment in a certain amount of antibiotics is required to prevent diseases and promote the growth of aquaculture organisms during the aquaculture process. The lake is prone to pollution through domestic sewage, industrial waste-water, and non-point source pollutants, thus affecting ecological security. With the implementation of the South-to-North Water Diversion Project in the eastern part of the lake, the downstream drinking water safety has become very important. In recent years, a great deal of research and investigation has been conducted on the environmental pollution in Hongze Lake by pesticides, organic pollutants, heavy metals and eutrophication. Wang [28] found that most anomalies point of heavy metals in Hongze Lake occurred in the area seriously affected by pollution in Huaihe River. Gao [29] found that DDT and HCH were the major among pesticides in the sediments of Hongze Lake. Huang [30] discussed the public awareness about both cyanobacteria and ecological changes, and from the perspective of environmental management, Wang [31] explored the use of nutrient balance to estimate nitrogen and phosphorus loadings and emissions from cage culture in Hongze Lake. However, studies on antibiotic pollution in Hongze Lake have been rarely conducted. This study analyzed sulfonamides, quinolones, and tetracyclines and macrolides in Hongze Lake at temporal and spatial scales. In addition, the ecological risk of antibiotics in the water was analyzed to provide scientific reference for water environment protection and water resources management of Hongze Lake.

2. Materials and methods

2.1. Study sites and sampling

Hongze Lake (33º06′–33º40′N and 118º10′–118º52′E) is located in the eastern part of the Huaihe River, west of Jiangsu Province. It lies southeast of the North China Plain, west of Huai'an, and south of Suqian. As shown in Fig. 1, this lake can be divided into three parts: the sub-Lake, Li River Lake, and Huaihe Lake Bay. The Huaihe River Basin is fed by two major perennial rivers that flow from west to east, Huaihe River and Sui River, of which the Huaihe River accounts for more than 70% of the total inflow. This inflow is an important factor in controlling the water quality of Hongze Lake. Three rivers flow mainly flow in the eastern part of the lake, and in the northern part, irrigation and drainage channels are common. The water level in the study area is usually 0.5–3.5 m. Under the impact of strong interaction between groundwater and surface water, groundwater usually flows from south to north. The eastern part of Hongze Lake is mainly woodland and pastures, whereas the northern part experiences heavy pollution mainly by urban domestic sewage. In the west, there are more woodland and farms, which contribute to agricultural non-point source pollution; however, pollution in the south mainly occurs through pollutants transferred by the Huaihe River.

In this study, 14 representative sampling points were established. The distribution of sampling points is shown in Fig. 1 and Table 1. Most of the samples in the first category (S1, S2, S3) were collected at relatively close points in the northern part of Hongze Lake, where the water velocity is slow. The nitrogen and phosphorus content in this area is relatively low, the water transparency is high, and the indicators of water quality are relatively high. Water quality is

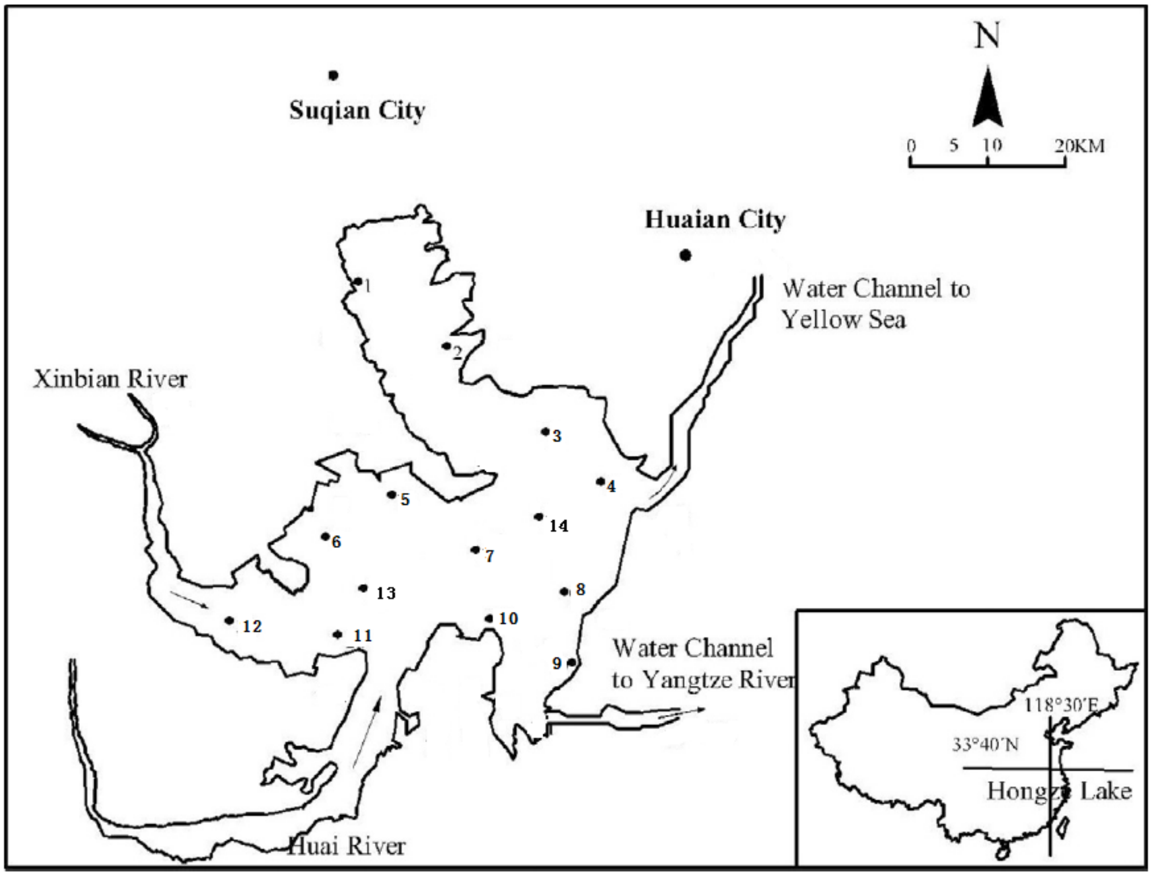

Fig. 1. Locations of sampling sites in Hongze Lake China.

Table 1
Coordinates of sampling points in Hongze Lake

	Site	North Latitude	East Longitude
North Lake Area	1	33°32′45 ″	118°29′37″
	2	33°28′17″	118°35′36″
	3	33°24′18″	118°45′3″
Eastern water Transfer Area	4	33°19′16″	118°48′54″
	7	33°17′7″	118°38′23″
	8	33°13′12″	118°47′17″
	9	33°8′50″	118°45′29″
	10	33°10′26″	118°43′49″
	14	33°18′34″	118°43′59″
West Lake Area	5	33°18′11″	118°34′14″
	6	33°17′41″	118°27′45″
	11	33°11′37″	118°27′52″
	12	33°10′34″	118°21′54″
	13	33°14′42″	118°30′38″

mainly affected by fence pollution. The samples in the second category (S4, S8, S9 and S10) were collected from open waters of the eastern and southern parts of Hongze Lake. This area comprises a channel and the Huaihe River water discharge channel; the water flow rate is high, the water is deep, and the transparency is low. Water quality is mainly affected by the inflow of the Huaihe River into the lake and the impact of ship activity. Samples in the third category (S5, S6, S12 and S11) were collected from the western part of Hongze Lake, away from the channel, where water quality is mainly affected by aquaculture waste water and urban sewage. The fourth category samples were mainly from the center of the lake (S7, S13 and S14).

The samples of Hongze Lake (S1–S7) were obtained in June 16 and October 27 in 2015, respectively, and the other samples (S8–S14) were collected in the corresponding next day. In this study, 14 representative water samples were collected without a field blank. Water samples for antibiotic testing were stored in a head space sterile amber glass vial and treated within 24 h after sample collection. The amber glass vial (1500 ml) can prevent the destruction of antibiotics upon exposure to light conditions. Physical and chemical indicators were determined using a portable water quality analyzer (HACH); temperature, pH conductivity (EC), oxidation-reduction potential (ORP), and dissolved oxygen (DO) were also measured. A 50 mL sample of surface water was collected and filtered through a 0.45 μm nylon membrane and the filtered water was adjusted to pH < 2 using 8 M HCl in the laboratory for further DOC analysis. The procudure of checking membrane performance for analyzed the concentration of DOC was not required [26]. Besides, it didn't need a pretreatment before the filtration for water sample. The material of membranes applied the type of nylon film. The aperture of membranes is 0.45 μm and the diameter is 50 mm, which was producted by Shanghai Xinya purification equipment.

2.2. Standards and chemicals

The antibiotics for study were selected on the basis of sixteen typical antibiotics used frequently in China: sulfonamides (SDZ, 99.5%), sulfamethoxazole (SMX, 98.7%), sulfamethazine (SMZ, 99.0%), sulfachloropyridazine (SCP, 98.0%), sulfaquinoxaline (SDM, 99.0%), sulfa dimethoxypyrimidine (SM2, 98.5%), norfloxacin (NOR, 99.0%), ciprofloxacin (CIP, 99.5%), ampicillin (AMP, 98.0%), ofloxacin (OFL, 98.0%), difloxacin(DIF, 99.5%), doxycycline (DOC, 99.0%), tetracycline (TC, 97.0%), erythromycin (ERY, 99.0%),azithromycin (AZM, 98.0%) and roxithromycin (ROX, 97.9%), all of which were of highest purity available and were purchased from Dr. Erenstorfer (Augsburg, Germany). Simatone was purchased from Accu-Standard Inc. (USA) and used as the internal standard (purity>99.0%).

All antibiotic compounds were purchased from Dr. Erenstorfer (Augsburg, Germany); simatone was purchased from Accu-Standard Inc. (USA) and used as the internal standard. A variety of antibiotic standard solutions and internal standard solutions were prepared in methanol at a concentration of 1000 mg/L and stored in the dark at –20°C. The 25 different antibiotic mixtures of different concentrations were prepared by gradually diluting the various stock solutions in methanol for using in the next day. All individually prepared mixtures were updated every six months. The 25 antibiotics with individual initial concentration of 1000 mg/L were mixed together. The 25 kinds of antibiotics were sulfonamides (SDZ), sulfamethoxazole (SMX), sulfamethazine (SMZ), sulfachloropyridazine (SCP), sulfaquinoxaline (SDM), sulfa dimethoxypyrimidine (SM2), norfloxacin (NOR), ciprofloxacin (CIP), ampicillin (AMP), ofloxacin (OFL), difloxacin (DIF), doxycycline (DOC), tetracycline (TC), erythromycin (ERY), azithromycin (AZM), roxithromycin (ROX), leucomycin (LCM), oleandomycin (ODM), roxithromycin (RTM), tylosin (TYL), salinomycin (SAL), narasin (NAR), monensin (MON), lincomycin (LIN), florfenicol (FF). The mixed antibiotics were diluted to 25 ng/L, 160 ng/L, and 400 ng/L. However, only 16 common antibiotics, SDZ, SMX, SMZ, SCP, SDM, SM2, NOR, CIP, AMP, OFL, DIF, DOC, TC, ERY, AZM and ROX, were chosen for analysis in this study.

2.3. Water chemistry analysis

Temperature, pH, EC, ORP, and DO were measured in situ using a water quality analyzer HQ40D Field Case. cat (NO. 58258-00, HACH, Colorado, USA) equipped with four probes. Water was filtered through a 0.45 μm filter using a total organic carbon analyzer (N/C 3100, Germany) for the determination of dissolved organic carbon (DOC) with a detection limit of 0.004 mg/L.

2.4. Extraction and detection of target antibiotics in water samples

2.4.1. Solid phase extraction (SPE)

Based on previous studies, the SPE method was improved by means of standard additions including a single internal standard (simatone) analysis of multiple antibiotics. First, 1000 mL of groundwater was obtained by extraction of sufficient antibiotics through the plunger. Before loading the SPE column, the water samples were filtered through a 0.45 μm glass fiber filter to remove granules, adjusted to pH 4 with 1 mol/L hydrochloric acid, and 10 mL of 5% (v/v) chelating agent Na_2-EDTA was added to prevent tetracycline and divalent cation binding. The water samples were equilibrated at 23°C and filtered through a nylon membrane (0.45 μm). The target analyte was extracted on an Oasis HLB box. The HLB column was pretreated with 6 mL of MeOH, 6 mL of MQ, and 6 mL of buffer solution. Before loading the sample onto the SPE column, the sample was acidified to pH 3.0 with 50% SA (v/v) and then 1.0 g Na_2EDTA was added to increase the extraction efficiency of the antibiotic. Each water sample was loaded onto the HLB column at 3–5 mL/min. After the sample was loaded, the HLB column was washed with 6 mL of MQ, and dried in vacuum for 60 min. The SPE column was eluted with 6 mL MeOH. The extract was then dried under a mild nitrogen stream using an evaporation system (N-Evap, Organermation Associates, MA, USA) at 40°C. The analyte was reconstituted using a 2 mL sample diluent (15:85 MeOH: MQ) and transferred to an autosampler vial for analysis. After solid phase extraction, simatone was added to the final extract prior to LC-MS/MS analysis.

2.4.2. HPLC-MS/MS analysis

The 16 target compounds and internal standards were detected by high- performance liquid chromatography-tandem mass spectrometry (HPLC-MS/MS) using an Extend-C18 column (1.8 μm, 2.1 mm i.d. × 100 mm, Agilent, USA). A sample volume of 5 μL was injected into a C18 column and maintained at 40°C. The analyte was eluted with a gradient of 0.25 mL/min with ultrapure water of acetonitrile (eluent A) and 0.1% formic acid and 5 mM ammonium acetate (eluent B). The initial percentage of eluent A was 15%, which was maintained for 2 min, linearly increased to 90% over 3 min, held for 2 min; then, the eluent A was returned to 15% over 3 min and was held for 5 min to complete the entire cycle, which was respected a total of 15 times). The identification of target antibiotics was achieved by comparing the retention time of two optimized ionic pairs with the corresponding standard compounds. For each antibiotic, the ion pair with a relatively high abundance was selected for quantitative use.

2.5. Quantification and method validation

An external standard method was used to quantify the concentration of the selected antibiotics. The solvent blank, program blank and mixed standard solutions were run regularly to monitor system performance and potential contamination. The analyte was identified based on the corresponding parent ion and product ions as well as the retention time. The analyte was quantified based on the calibration standard curve constructed from the SPE and calibration of the labeled water sample. The calibration curve showed strong linearity ($r^2 > 0.99$) over the wide antibiotic concentration range of 0.1–1000.0 μg/L. To simplify the and analysis and make the process more convenient, tetracyclines and macrolides were classified as one group in spite of the differences. The recoveries of T-sulfonamides (SM), T-quinones (QNL), and T-tetracycline and T-macrolides (TC and MLs) were 58%–103%, 63%–122% and 82%–107%, respectively.

The limit of detection (LOD) and limit of quantitation (LOQ) were determined as the minimum detectable concentration of the analyte at signal-to-noise (S/N) ratios of 3 and 10, respectively. The S/N ratio (10) was obtained from the recovery data for the lowest concentration (25 ng/L). The LOD and LOQ ranges for the antibiotics in water were 0.17–1.93 ng/L and 0.57–6.42 ng/L, respectively.

2.6. Environmental risk assessment

According to the EU environmental risk analysis and guidance, the risk of antibiotics in Hongze Lake was analyzed using the risk quotient (RQ) method [7]. The RQ values were calculated using the following formula

$$RQs = MEC/PNEC \quad (1)$$

where the measured environmental concentration (MEC) is the measured ambient concentration (ng/L) and the predicted no effect concentration (PNEC) is the predicted effective concentration (ng/L). PNEC values were obtained by reviewing the literature, or by collecting acute or chronic toxicology experimental data and assessment factors. The survey is based on the "worst case" plan, using the maximum measured antibiotic concentration to calculate the corresponding RQ value. The environmental risk of 16 antibiotics was assessed in the most conservative manner.

To better distinguish the ecological risk of antibiotics in the surface water, the RQ value was divided into four grades: RQs < 0.01 indicate risk free, 0.01 < RQs < 0.1 indicate low risk, 0.1 < RQs < 1 indicate moderate risk, and 1 < RQs indicate high risk [32]. This study selected three different levels of aquatic organisms, namely, green algae, plants, and invertebrates.

3. Results and discussion

3.1. Antibiotic concentration

It can be seen from Table 2 that the concentration of antibiotics in Hongze Lake varies with changes in seasons. Only SM2, AMP, and AZM were not detected; the other 13 kinds of antibiotics could be detected throughout the different seasons. The detection rates of T-sulfonamides (SM), T-quinones (QNL), and T-tetracycline and T-macrolides (TC and MLs) were 21.40–100%, 78.57–100%, and 35.71–100%, respectively, in June and October. Overall, the detection rate of the 13 kinds of antibiotics was 21.40–100%, with average concentrations of 0.20–21.30 ng/L in June and 0.08–10.79 ng/L in October. The highest detection values were found for SMX at 48.10 and 24.03 ng/L, with a detection rate of 100%, whereas the lowest detection values were found for SDM at 0.20 and 0.08 ng/L, with a detection rate of 21.40%. These results indicate

Table 2
Summary of antibiotics in Hongze Lake (ng/L)

		June					October				
		Fre[a]	Min[b]	Max[c]	Mean	Med[d]	Fre[a]	Min[b]	Max[c]	Mean	Med[d]
SM	SDZ	100	0.50	5.50	2.30	1.80	100	0.25	2.76	1.15	0.82
	SMX	100	5.00	48.10	21.30	17.00	100	2.51	24.03	10.79	8.50
	SMZ	93.00	nd[e]	3.40	1.60	1.20	92.90	nd	1.71	0.76	0.62
	SCP	78.60	nd	36.50	4.60	1.10	78.60	nd	18.24	2.28	0.54
	SDM	21.40	nd	0.60	0.20	nd	21.40	nd	0.28	0.08	nd
	SM2	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
QNL	NOR	78.57	nd	11.99	2.92	1.84	78.60	nd	5.99	1.46	0.92
	CIP	100	0.43	7.15	1.94	1.21	100	0.21	3.58	0.97	0.60
	AMP	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
	OFL	100	0.23	4.68	1.22	0.79	100	0.12	2.34	0.61	0.40
	DIF	100	0.23	5.65	1.47	0.88	100	0.12	2.82	0.74	0.44
TC&MLs	DOC	100	0.43	3.28	1.30	1.09	100	0.21	1.64	0.65	0.55
	TC	100	0.23	2.37	0.95	0.76	100	0.12	1.18	0.48	0.38
	ERY	35.70	nd	1.12	0.39	0.54	35.70	nd	0.56	0.19	0.27
	AZM	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
	ROX	100	nd	0.30	0.16	0.16	100	nd	0.15	0.08	0.08

Nd: below the limit of detection.
[a] Frequency(%).
[b] Minimum.
[c] Maximum.
[d] Median.
[e] Not detected.

that the use of different types of antibiotics and their usage ratio are somehow consistent in this region.

It can be seen from Table 3, the concentration of SMZ, NOR and CIP are at a lower level, while the concentration of SMX and SCP is at a moderate level compared with existing data on rivers and lakes in China and abroad. Beside, SMX was found to be the main component of sulfonamides and had the highest concentration. SMX is widely used in the aquaculture industry in large amounts probably because it is cheaper and has stronger effects [33]. However, due to its high detection rate and difficult degradation, we should take measures against the potential ecological risk of SMX.

Overall, antibiotics in Hongze Lake are at a moderate level compared with antibiotic levels reported for rivers and lakes in China and abroad. Hongze Lake is one of the main water diversion lakes along the east route of the South-to-North Water Diversion Project. Therefore, research on the potential risks of antibiotics on water quality is particularly important for this area and is essential for water security.

3.2. Seasonal changes in antibiotic content

Although the detection rate of various antibiotics in June and the proportion of use for the entire year and October were basically flat, antibiotics concentration was approximately 2 times higher in October. The concentrations of sulfonamides were 6.45–88.23 ng/L and 3.32–44.12 ng/L in June and October, respectively. In 6 months, the concentrations of the antibiotics changed by 0.89–29.46 ng/L and 0.44–14.73 ng/L, respectively, and the concentrations of tetracycline and macrolide antibiotics were 1.26–5.75 ng/L and 0.63–2.88 ng/L, respectively. The higher antibiotic concentration in June could be attributed to the existence of the world famous lobster breeding base in Xuyi County, south of Hongze Lake, where a large amount of antibiotics is used. Although the breeding of crabs is concentrated in the eastern part of the lake, the use of antibiotics does not significantly affect the lake because the lake is discharged mainly from the eastern section. At the same time, a large amount of water is used for agricultural purposes, accounting for approximately 65% of the total water resources [38], and the area around Hongze Lake is mainly used for the cultivation of rice. On June 16, which falls under the rice plantation period, the water demand was at 11.1–16.7% [39]. In contrast, yellowing of rice occurs during late October for which sunny conditions are required without any irrigation. The water level of Hongze Lake may decline in June due to irrigation, leading to the higher antibiotic concentration. Therefore, the use of antibiotics in the Huaihe River Basin should be strictly controlled.

The detection rate of various antibiotics in the lake generally follow the order sulfonamides > quinolone > tetracycline and macrolide. This shows differences in the use of antibiotics and environmental response. Sulfonamides are mainly used in the breeding industry to prevent the occurrence of animal diseases; the use and frequency of use of sulfonamides are much higher than those of other antibiotics. Li [23] studied antibiotics in river sediments, and reported the following order of adsorption of tetracycline: cyclohexanoids > quinolones > sulfonamides. Sulfonamides are highly soluble in natural water bodies and are less susceptible to adsorption or degradation reactions [23, 40]. These may contribute to their high detection rate in surface water; the antibiotic content is more likely to be high in June, during which waste and wastewater are discharged into water bodies without complete treatment. In contrast, fluoroquinolones are susceptible to photodegradation and are easily adsorbed by sediments [40]. In addition, NOR is strictly regulated for minors, and its usage is an important cause of residual content in the lake [41]. TC and macrolides had low concentrations, which are more likely to be related to the photolysis and hydrolysis of antibiotics in the water environment [42,43]. In addition, because TC treatment of humans and animals has not been as prevalent in the past 20 years, it has been gradually enhanced by binding with particles and interacting with cations or it has been replaced by other antibiotics such as lactam [44].

3.3. Distribution characteristics of antibiotics

The southeastern part of the Huaihe River was the most affected by antibiotics, whereas the total concentration of antibiotics in the northern and western areas of the lake was relatively low. With the rapid development of the economy around Hongze Lake and the high population density, the pollution problem of the Hongze Lake water is becoming increasingly serious. Although much has been invested to manage water quality, our research shows that antibiotic pollution in Hongze Lake is still serious. To understand the source of antibiotics and to develop appropriate management measures, the spatial distribution of antibiotics in Hongze Lake was analyzed. As shown in Fig. 2, Fig. 3, Fig. 4 and Fig. 5, sulfonamides were generally low in the western area and high in the eastern water transfer area, while quinones antibiotics and tetracycline and macrolide antibiotics showed high distribution characteristics in the northern area. In June and October, the concentration of antibiotics was 18.65–29.46 ng/L and 9.33–14.73 ng/L, respectively. The antibiotic content in the northern and southern areas was higher than in the northern area. This difference is mainly because the northern lake area is relatively closed, with the main source of pollution from non-point emissions in Suqian City. This implies that quinolones are mainly derived from Suqian City, and the relatively high concentration of residual pollutants is a serious issue. Sulfonamides had the highest concentrations, ranging from 8.90–88.24 ng/L and 4.56–44.12 ng/L in June and October, respectively. The content of antibiotics in the eastern part of the area and for 4–14 sampling points in the western area followed the order sulfonamides > quinolone > tetracycline and macrolide, with sulfonamides having much higher values than those of tetracyclines and macrolides by up to 4.3–50 times. At the midpoint of the northern and eastern areas, the content of quinolone and sulfonamides in sampling sites 3 and 4 were different. Sulfonamide content was higher than tetracycline and macrolide content by 4.8–6.1 times, and quinolone content was up to 4.5–22 times greater at points 5–14; quinolone content was higher than tetracycline and macrolide content by 3.3–5.2 times at points 1–4, but less at other sites. Many types of antibiotics were detected in Hongze Lake, of which sulfonamides had the highest concentration.

Table 3
Comparison of antibiotic concentrations in surface waters across the world (ng/L)

Compounds	Hongze Lake , China	Taihu Lake, China	Bosten Lake, China	Poyang Lake, China	Caohu Lake, China	Lake Erie, United States	Baiyangdian Lake, China	Huangpu River, China	Yangtze Estuary, China	Seine River France	Urban water, Australia	139 streams, United States
SDZ	0.50–5.50		2.88–37.27		n.d–45.60		0.90–505.00	1.40–40.60	0.30–71.80	n.a.	n.a.	n.a.
SMX	5.00–48.10	n.d.–114.70		n.d.–14.70	n.d.–171.60	201.00–211.00	n.d.–940.00	4.90–55.20	0.30–56.80	544.00	2000.00	520.00
SMZ	n.d.–3.40	n.d.–654.00	1.22–13.28	n.d.–22.20	n.d.–9.90	8.50–17.00	n.d.–16.10	2.00–623.30	0.50–89.10	<10.00	n.a.	120.00
SCP	n.d.–36.50	n.d.–89.40			n.d.–4.60		n.a.	3.20–58.30	n.a.	n.a.	n.a.	n.d.
SDM	n.d.–0.60				n.d.–8.80		n.d.	n.a.[b]	n.a.	n.a.	n.a.	60.00
NOR	n.d.–11.99	n.d.–6.50			n.d.–70.20		n.d.–156.00	n.d.	n.d.–14.20	163.00	1150.00	120.00
CIP	0.42–7.15	n.d.–43.60	17.33–112.30	n.d–8.60	n.d.–23.20		n.d.–60.30	blq.	n.d.–2.30	<10.00	1300.00	30.00
OFL	0.23–4.68	n.d.–82.80	1.30–32.24		n.d.–182.70		0.4–32.60	blq.	n.d.–12.40	55.00	n.a.	n.a.
DIF	0.23–5.64			n.d.–5.30	n.d.–10.40		n.d.	n.a.	n.a.	<10.00	n.a.	n.a.
DOC	0.42–3.28		n.d.–4.92	n.d.–39.70	n.d.–42.30		n.a.	n.d.–46.90	n.d.–5.60	n.a.	400.00	n.d.
TC	0.23–2.36	n.d.–87.90	n.d.–2.84	n.d.–10.80	n.d.–17.80		n.a.	n.d.–113.90	n.d.–2.40	n.a.	80.00	110.00
ERY		n.d.–624.80		n.d–10.70								
ROX		n.d.–218.30		n.d.–11.10								
References	This Study	[4]	[35]	[33]	[8]	[36]	[23]	[2]	[26]	[20]	[34]	[37]

[a]Not detected(concentration<LOQ)
[b]Not analyzed

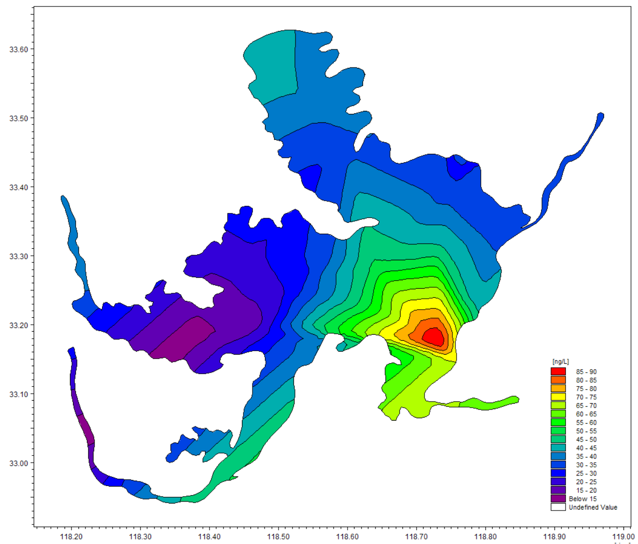

Fig. 2. Spatial distribution characteristics of antibiotics in Hongze Lake in June.

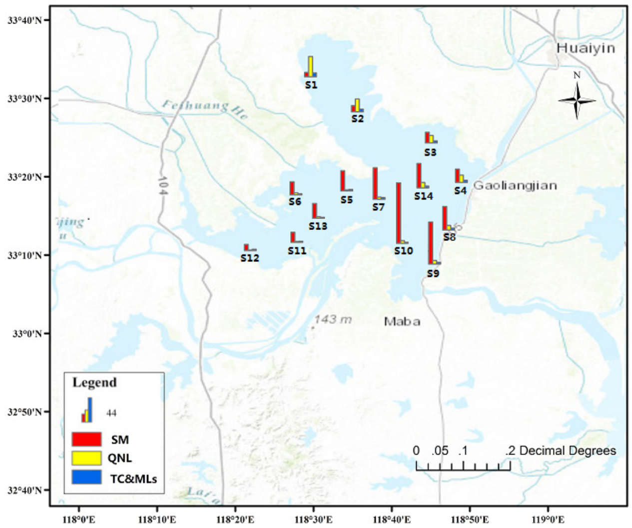

Fig. 4. Spatial distribution of three classes of antibiotics in Hongze Lake in June.

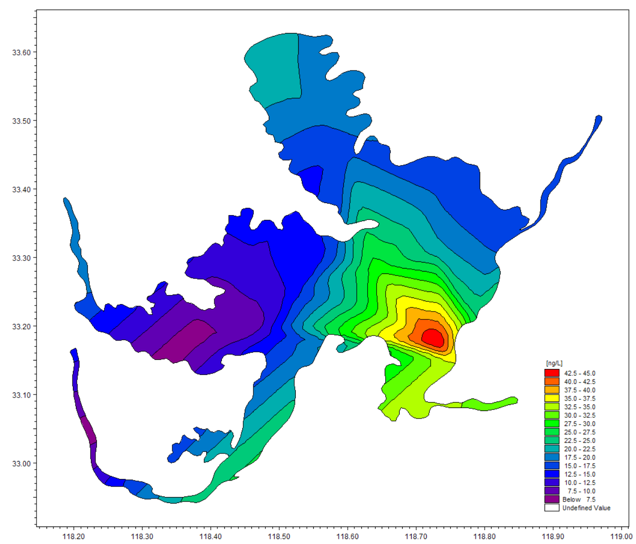

Fig. 3. Spatialdistribution characteristics of antibiotics in Hongze Lake in October.

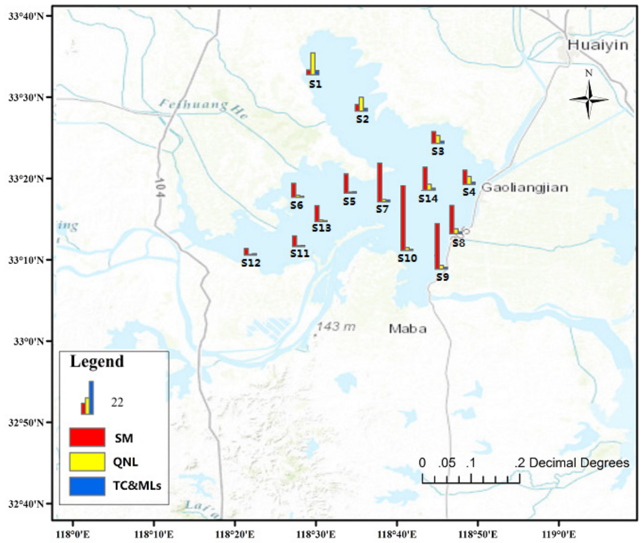

Fig. 5. Spatial distribution of three classes of antibiotics in Hongze Lake in October.

The highest concentrations of quinolone and tetracycline and macrolide were found at the first site, and the concentrations of quinolone and tetracycline at sites (1, 2, 3, and 4) were higher than those at other sites, which indicates that antibiotics related to human disease control mainly occur in the northern part of Suqian City. This can be further attributed to the higher population density in the area higher than in other areas. Suqian and Huai'an lie close to the northern part of Hongze Lake, where the concentration of quinolone and tetracycline and macrolide are higher. Therefore, Suqian, and Huan'an and other medical institutions should take appropriate measures to strictly control the discharge of quinolone, tetracycline and macrolide into Hongze Lake.

3.4. Analysis of the correlation between antibiotics and physical and chemical factors

A series of biochemical processes such as adsorption, hydrolysis, photolysis and microbial degradation generally follow the introduction of antibiotics into water bodies [45,46]. To further understand the influencing factors of various antibiotics in Hongze Lake, the correlation between the concentration of antibiotics and the main water quality indices of T, pH, Do, ORP, conductivity and DOM were analyzed.

Table 4, shows that quinolone and tetracycline in June and October have a very significant positive correlation (R^2 = 0.955), indicating that the sources of the antibiotics are consistent. Tetracycline and temperature showed a

Table 4
Correlation coefficient between basic parameters of water quality and three classes of antibiotics in the surface water of Hongze Lake

		T	pH	Do	ORP	Conductive	DOM	SM	QNL	TC&MLs
June	T	1								
	pH	0.208	1							
	Do	–0.221	0.299	1						
	ORP	0.033	–0.518	–0.14	1					
	Conductivity	0.421	0.363	0.088	–0.278	1				
	DOM	–0.291	–0.068	0.379	0.424	–0.075	1			
	SM	–0.213	–0.47	–0.396	0.415	–0.727**	–0.053	1		
	QNL	–0.437	0.597*	0.415	–0.589*	0.168	–0.17	–0.35	1	
	TC&MLs	–0.565*	0.518	0.532	–0.488	0.184	–0.004	–0.322	0.955**	1
October	T	1								
	pH	0.208	1							
	Do	–0.221	0.299	1						
	ORP	0.033	–0.518	–0.14	1					
	Conductivity	0.421	0.363	0.088	–0.278	1				
	DOM	–0.291	–0.068	0.379	0.424	–0.075	1			
	SM	–0.22	–0.473	–0.406	0.43	–0.712**	–0.087	1		
	QNL	–0.437	0.597*	0.415	–0.589*	0.168	–0.17	–0.347	1	
	TC&MLs	–0.565*	0.518	0.532	–0.487	0.183	–0.004	–0.309	0.955**	1

significant negative correlation (R^2 = –0.565). The content of tetracycline in Hongze Lake decreased with increases in temperature, mainly because microbe activity increases with temperature, accelerating tetracycline degradation. A positive correlation was found between the degradation efficiency of tetracycline and temperature [47].

Quinolones showed a significant positive correlation with pH (R^2 = 0.597). As OH^- ions increased with increases in pH value, the concentration of quinolones also increased. The hydrolysis of quinolones involves the exchange of organics X^- and OH^- in water, resulting in the degradation of organic matter [48]. The increase of OH^- ions in surface water can promote the decomposition of quinolones. This is speculated to be one of the reasons for quinolones being positively correlated with pH. A significant negative correlation was found between quinolone and ORP (R^2 = –0.589). This could be related to the highly reducing environment that can promote the degradation of quinolone [49].

In this study, only surface water was investigated, and the dissolved organic matter (DOM) in the sediments remained at the bottom; therefore, unlike other studies, no significant correlation could be found between antibiotics in the surface water and DOM [26,50]. In addition, this result may also be due to the perennial large water exchange in the lake, which is not favorable for sediment accumulation. Therefore, DOM content in sediments is less.

3.5. Risk assessment

In general, the ecological risk was higher in June than in October, and SMX posed a higher ecological risk. The RQ values of antibiotics are shown in Fig. 6. SMX is widely used in the aquaculture industry due to its broad spectrum of resistance and bactericidal effects. In June, for green algae, SMX posed a high risk level; CIP and OFL posed moderate risk levels; SDZ, SMZ, TC, and ERY posed low risk levels; and SDM and NOR did not pose any risk. For plants, SMX posed medium risk levels; SDZ, SDM, NOR, CIP, and OFL posed low risk levels; and SCP, ERY, and ROX posed certain risks. In October, for plants WD, ERY posed low risk levels; and SDZ, SMZ, SCP, SDM, and NOR posed no risk. For green algae, SMX posed medium risk levels; SMX, CIP, and OFL also posed medium risk levels; and SCP, NOR, ERY, and ROX posed no risk. For invertebrates, all antibiotics posed risks at different times: SDR, SDM, CIP, and OFL posed low risk levels. SMX, CIP, and OFL should not be overlooked and SMX is particularly serious. Therefore, the use of SMX, CIP, and OFL should be controlled and strictly monitored through measures, such as development of lake water quality protection regulations, strengthening of aquaculture and agricultural source pollution emissions management, and implementation of inter-basin water transfer, to reduce the risk of pollutants such as antibiotics.

Overall, the ecological risk in June was generally higher than in October, mainly due to the high production activities and high population density in June, leading to increased aquaculture wastewater, agricultural non-point source pollution, and domestic sewage. The average water level in June is approximately 0.5 m lower than in October, and the dilution and degradation rates of antibiotics in Hongze Lake are reduced. However, as a complex mixed contaminant, the toxicological risk to aquatic organisms may increasecompared to that of the individual chemicals. Therefore, there is an urgent need for further monitoring and detailed investigation of the ecological risks of these antibiotics.

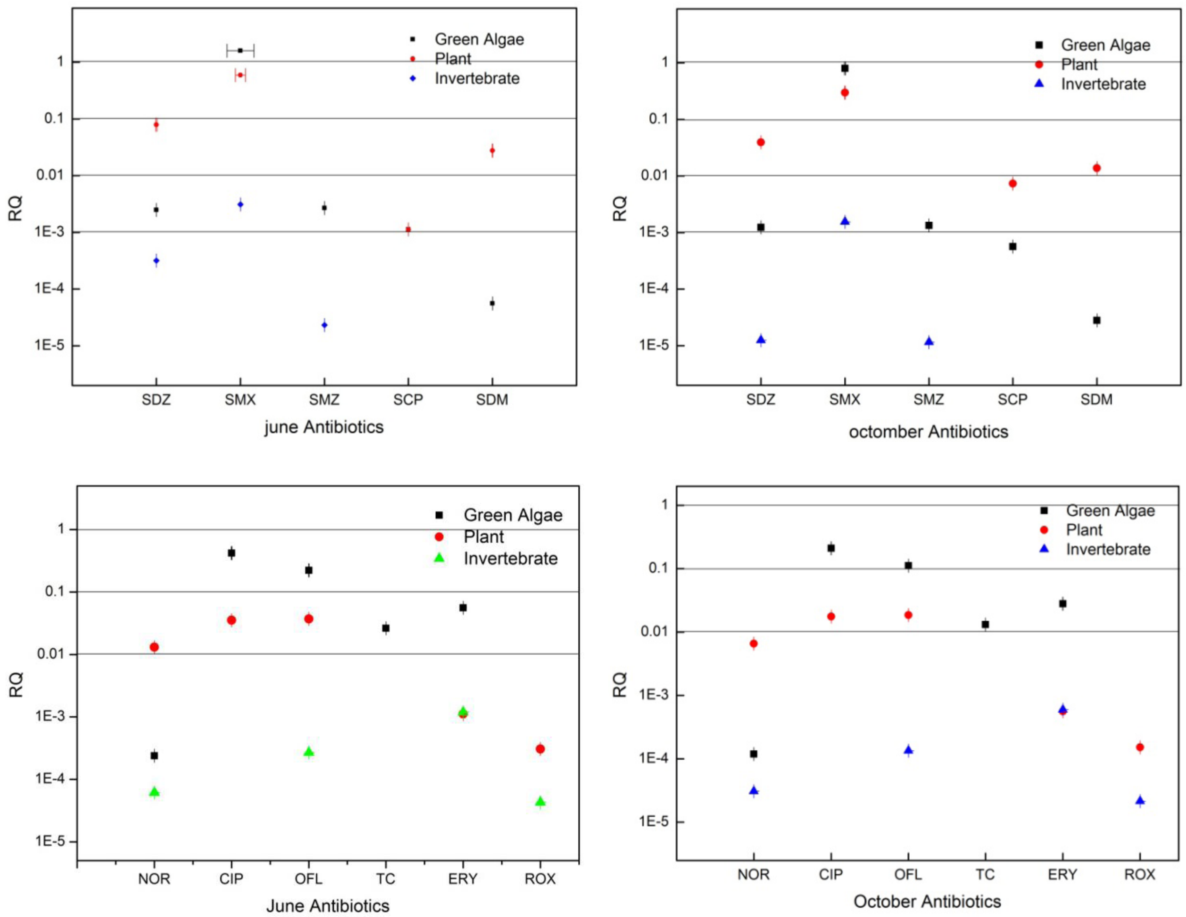

Fig. 6. Risk values of antibiotics in Hongze Lake.

4. Conclusions

A study on the concentration of 16 antibiotics in the surface water of Hongze Lake was conducted for describing their occurrence and distribution. The overall antibiotic content in June was higher than in October, likely due to the active local aquaculture industry, especially lobster farming in June. Sulfonamides are the main antibiotic pollutants in Hongze Lake, and sulfamethoxazole had the highest concentration. Sulfonamide concentration was generally higher in the eastern water transfer area than in the western area. Quinolones and tetracyclic and macrolide concentrations were higher in the northern area than in other areas. The overall risk of antibiotics in Hongze Lake on sensitive aquatic organisms was low. However, SMX in algae posed a high risk at individual sampling points. In addition, the toxicological risk of complex mixtures of such contaminants to aquatic organisms may be higher compared with that of individual chemicals. Therefore, further monitoring and detailed investigations of the ecological risks of compound antibiotics in aquatic bodies are important topics for future research. Furthermore, formulation of more efficient practices for managing aquaculture drainage and livestock waste prior to discharge is necessary.

Acknowledgments

We are grateful for grants from the National Science Funds for Creative Research Groups of China (No.51421006), the Key Program of National Natural Science Foundation of China(No.41430751), the National Natural Science Foundation of China (No. 51479065),the National Key Plan for Research and Development of China (2016YFC0502203) andthe Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD).

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