Occurrence, Seasonal Variation and Risk Assessment of Antibiotics in the Surface Water of North China

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Abstract

In this study, the occurrence, seasonal, and spatial variations of four classes antibiotics were investigated in the surface water of North China. Water samples were taken from 24 sampling sites along rivers in May and August and antibiotics in water samples were detected by SPE-UPLC-MS/MS. The occurrence of all antibiotics except for FLO in May were higher than in August. The mean concentrations of four classes antibiotics detected in May and August were in the following order respectively: quinolones (421.23 ng/L) > tetracyclines (28.37 ng/L) > amphenicols (20.38 ng/L) > sulfonamides (5.79 ng/L) and amphenicols (284.36 ng/L) > quinolones (15.74 ng/L) > tetracyclines (3.05 ng/L) > sulfonamides (0.20 ng/L). The results showed that quinolones and amphenicols were dominant antibiotics among four classes antibiotics. To explore the source of antibiotics from the fish ponds nearby, antibiotic concentration data, which was investigated in the sediment, fish feed and fish revealed a direct relationship between the main antibiotics and fish farms along the rivers. Risk assessment data indicated enrofloxacin and florfenicol could cause higher safety risks to aquatic organisms compared to other antibiotics.

Antibiotics are highly effective bactericidal drug for human and livestock disease control (Hu et al. 2010). In China, 30–90% of total usage of antibiotics was excreted into the environment (Hu et al. 2010). The phenomenon of antibiotic abuse was widespread in different parts of China (Zhang et al. 2015). However, it is a pity that there are no related codes to limit the use of antibiotics in farms and control the discharge of antibiotics-containing livestock wastewater in China (Lei et al. 2009). With an increasing number of antibiotics were used to cure human and veterinary illness, these antimicrobially active chemical compound were found and detected in different rivers, lakes, underground water, and soil (Batt et al. 2006; Gros et al. 2006). Moreover, residues

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of antibiotics showed different behaviors under different environmental conditions (Managaki et al. 2007), which could induce bacterial resistance even at low concentrations (Hernández et al. 2007). Antibiotics were excreted from animal bodies in stable forms (prototypes or metabolites) (Wiuff et al. 2002), so that it can enter the environment by manure spreading or via sludge storage (Martínez-Carballo et al. 2007). Research had shown that residues of antibiotics in the environment may lead to fearful impact on humans and the environment (Tello et al. 2012).

It had been reported that water was an important reservoir for antibiotics, and the surface water bodies were more easily contaminated by aquaculture wastewater, pharmaceutical industries, and agricultural activities (Anthony et al. 2018). For instance, the levels of veterinary antibiotics in effluents from pharmaceutical industries range from low mg/L to approximately 200 mg/L (Bielen et al. 2017). The total concentrations of the detected antibiotics can reach up to 3.91×10^3 ng/L in the Hai River system (Chen et al. 2018). Only a few articles have been reported about antibiotics in the river of North China. Yet, little information is known on distribution of veterinary antibiotics in the watery environment of Beijing-Tianjin-Hebei region. According to Hu et al. (2010), the range of SMZ was 7.2–9.5 ng/L, the range of TC was 5.2 ng/L in the groundwater of northern China, and CAP and CIP also were detected. Few reports have analyzed the

source of antibiotics and evaluated the potential ecological risks of antibiotics in aquatic environment of Beijing-Tianjin-Hebei region. There is the need for better measurements, comprehensive investigation, and traceability to achieve the purpose of governance.

This study not only characterizes the concentrations and spatial distribution patterns of 15 antibiotics residues, kinds of sulfonamides (SAs), quinolones (QNs), tetracyclines (TCs), and amphenicols (AMs) in rivers from the North China region but also proves that most of the antibiotics in the river are attributed to the wastewater discharged from the fish farms near the river. The distribution of multiple antibiotics pollution in the river of North China and risk assessment of local water environment will provide beneficial information for the control and improvement of antibiotics contamination in the study area.

Materials and Methods

Chemical and Reagents

The targeted antibiotics in this study were chosen according to their application frequency in aquaculture in China. Including four classes of antibiotics, i.e., tetracyclines (TCs), quinolones (QNs), sulfonamides (SAs), and amphenicols (AMs). Four TCs included tetracycline (TC), doxycycline (DC), oxytetracycline (OTC), and chlorotetracycline (CTC). Four QNs included ofloxacin (OFL), ciprofloxacin (CIP), norfloxacin (NOR), and enrofloxacin (ENR). Four SAs included sulfamethazine (SMM), sulfamethoxazole (SMZ),

sulfadiazine (SDZ), and trimethoprim (TMP). Three AMs included chloramphenicol (CAP), thiamphenicol (THI), and florfenicol (FLO). The standards were purchased from Dr. Ehrenstorfer Ltd., Germany. Acetonitrile, formic acid, and methanol (HPLC grade) were obtained from Thermo Fisher Scientific (China) Co., Ltd. Oasis HLB Cartridge were obtained from Waters Technology (Shanghai) Co., Ltd. Hydrochloric acid used for adjustment pH were obtained from Beijing Chemical Plant. Water was purified by Milli-Q system.
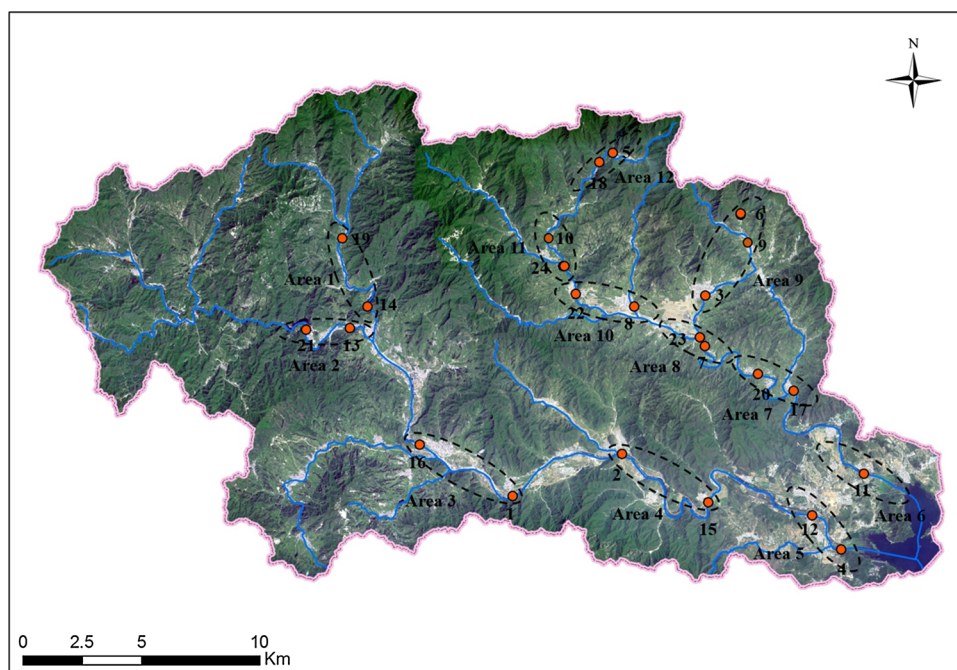
Sample Collection

There are many rivers in the suburbs of the Beijing-Tianjin-Hebei region. Along the rivers, most local residents live on fish farming. To assess the water quality impact of fish farming, 48 water samples were collected twice from two major rivers in the plentiful water season and the withered water season in 2017. The area of this region is 530 km^2. Detailed information about the sampling location is shown in Fig. 1. Two sediment samples were collected from the bottom of a fish pond, two feed samples for sturgeon and rainbow trout respectively were collected from a local fish farm, and two fish samples were caught in the fish pond.

Sample Preparation

Water Samples

The method of purification and enrichment for antibiotics in water was modified according to the preceding report (Lei

Fig. 1 Spatial distributions of 24 sampling location and 12 areas

et al. 2009). First, all water samples were collected from 24 sites along two rivers. Two sampling campaigns were conducted in May 2017 and August 2017 (May: high flow; August: low flow). Water samples were stored in 2.5-L amber glass bottles at 4 degrees and were filtered immediately through the glass fiber filter. All filtration covered 1 day.

The pH of 500-mL volume, filtered water samples was adjusted to 4 with hydrochloric acid. By adding 0.5 g of ethylenediaminetetraacetic acid disodium (Na_2EDTA), the interference of various metal ions was removed. Water samples were enriched and cleaned by HLB solid-phase extraction column. Six milliliters of methanol and 6 mL of hydrochloric acid at pH 4.0 were precondition for the cartridges. Then, the samples were introduced to the cartridges at flow rate of 3 mL/min. The cartridges were washed with 6 mL of deionized water after sample loading and vacuum-dried. At last, all cartridges were eluted with 4 mL of methanol and 4 mL of 0.1% acidified methanol. The extracts were concentrated to near dryness by nitrogen gas and dissolved again with 1 mL of methanol. Syringe filters (0.45 μm) were used to filter the final analytes before detection on UPLC system.

Fish Feed, Fish, and Sediment Samples

A simple extraction process was applied to sediment samples, feed samples, and fish samples. Two grams of sample was extracted by using 5 mL of methanol and was treated ultrasonically for 30 min in 10-mL centrifuge tube. The sample was centrifuged at 8000 rpm for 10 min. The methanol was poured out and the extraction was repeated once, and combined with the methanol of twice extraction. Afterwards, the extracts were concentrated to near dryness by nitrogen gas and dissolved again with 1 mL of deionized water. Five milliliters of n-hexane was used to remove lipid compounds and the extraction was repeated once. Finally, 1 mL of deionized water was filtered through syringe filters (0.45 μm) before detection on UPLC system.

Instrumental Analysis Using UPLC-MS/MS

The analytes of the 15 antibiotics were separated on the Acquity UPLC C18 reversed phase column (2.1 mm × 100 mm, 1.7 μm) using Acquity UPLC- tandem mass spectrometry system with multiperiod multireaction monitoring ion mode (MRM) (Waters). Eluent A was methanol and eluent B was 0.1% formic acid (water solution) at a flow rate of 0.35 mL/min. The temperature of column was stable at 40 °C, and the sample aliquots of 2 μL were injected into the system. The detection of AMs was conducted with ESI$^-$ mode and others were detected with ESI$^+$ mode. Table S1 shows supported detailed information.

Quality Control

The external standard method that created standard curves by a series of different concentrations of antibiotic standard solutions was used to calculate concentrations in the samples based on peak area. Standard solutions ranging from 30 to 50 μg/L in five points were prepared by spiking blank surface water with 15 targeted antibiotics. The calibration curves of the 15 antibiotics showed good linearity. The correlation coefficient was better than 0.990, and the limit of quantity (LOQ) was 0.01–0.3 ng/L ($S/N > 10$). The recoveries of the blank matrix were 49.0–102.3%, and the relative standard deviations ($n = 3$) were 4.6–14.0%. Table S2 showed detailed information of four kinds of matrix.

Results and Discussion

Concentrations of Antibiotic in Water Samples

All of the selected 15 antibiotics were detected in water samples from two sampling campaigns, and the dissolved concentrations of almost antibiotics were in the ng/L level, whereas the concentrations of selected antibiotics in some points was more than 1000 ng/L to μg/L level, illustrating abuse of antibiotics in this region with potential ecological risk. Table S3 and Table 1 show detailed information of concentrations of 15 antibiotics in 48 water samples. One AMs (CAP) and one TCs (DC) were the highest frequently detected compounds among the selected antibiotics. The detection rate was 100%, indicating that CAP and DC existed in the surface water environment widely. At same time, the concentrations of CAP and DC were relatively low and evenly distributed in this region, suggesting that CAP and DC were not used for treating disease in fish farms. AMs and QNs were cardinal antibiotics among the four classes antibiotics, leading to 85–98% antibiotic burden in this region.

As for three AMs antibiotics (CAP, THI, and FLO), the detection frequency of THI and FLO in August was higher than in May, indicating that THI and FLO may be used more often in August, especially for FLO. The highest concentrations of AMs were observed in August, including 5.5 ng/L of CAP, 13.1 ng/L of THI, and 1784.7 ng/L of FLO, respectively. The mean concentrations of FLO were much higher than those of CAP and THI, and the mean concentrations of FLO in August were higher than in May. Because of its low cost, AMs had been used extensively for the treatment of animals and humans all over the world (Kehrenberg and Schwarz 2006). But with its serious toxic effects in humans, AMs had been banned for use in food-producing animals in many countries (Dionysiou et al. 2004; Chantziaras et al. 2013). Most sample sites where relatively high concentration

Table 1 Summary of antibiotic concentrations in North China from May 2017 to August 2017 (ng/L)

Class	AMs			SAs				QNs				TCs			
Compound	CAP	THI	FLO	SDZ	SMZ	SMM	TMP	NOR	CIP	ENR	OFL	TC	DC	OTC	CTC
2017-05															
Freq. (%)	100	37.5	79.2	100	100	87.5	100	95.8	58.3	70.8	54.2	4.2	100	54.2	12.5
Max.	5.8	6.4	233.4	4.7	11.6	3.8	5.4	1893.2	641.3	5681.9	11.2	31.4	43.3	51.5	49.3
Min.	0.8	nd	nd	0.1	0.2	nd	1.2	nd	nd	nd	nd	nd	3.6	nd	nd
Mean	2.55	0.8	20.47	1.01	2.43	0.60	1.75	103.39	62.04	243.30	0.70	1.31	20.34	4.60	2.12
2017-08															
Freq. (%)	100	70.8	100	29.2	8.3	62.5	29.2	100	20.8	54.2	12.5	0	100	45.8	0
Max.	5.5	13.1	1784.7	0.3	0.3	<LOQ	0.8	15.4	26.6	141.3	4	nd	2.6	4.2	nd
Min.	0.6	nd	0.4	nd	nd	nd	nd	3.5	nd	nd	nd	nd	0.7	nd	nd
Mean	1.12	2.3	280.94	0.06	0.02	0	0.12	4.86	2.12	8.28	0.48	0	1.87	1.18	0

nd not detected; *<LOQ* below LOD

of FLO was detected from adjoining fish ponds, from this speculation, FLO was most likely to be used for fish treatment in China. In this study, the concentrations of FLO in some sample sites of northern region outclassed those in southern China (Yan et al. 2013).

For SAs, the detection frequency of SDZ, SMZ, and TMP was 100% at all sites, whereas SMM was up to 87.5% in May with low concentrations, showing that surface water sources have been contaminated with sulfa antibiotics in this region. But the mean detection frequencies became low from 96.9% in May to 32.3% in August for the four kinds of SAs, possibly due to dilution of antibiotic concentration during the wet season. The mean concentrations of SAs ranged from 0.60 to 2.43 ng/L in May, whereas from 0 to 0.12 ng/L in August. The concentrations of the individual compounds detected were commonly less than 1 ng/L according to the previous report (Campagnolo et al. 2002). In addition, the concentrations of these antibiotics were approximately the same at all sample sites along the river, which reflected that SAs were not used for treatment of aquatic products in this region. At the same time, it was confirmed that SAs had wide usage in China and were detected continually in surface aquatic environment coupled with other researches (Yan et al. 2013; Sun et al. 2017).

The detection frequencies ranged from 12.5 to 100% for the four kinds of QNs (NOR, CIP, ENR, and OFL). The detection frequency of NOR, which was the dominant antibiotic among four QNs, was far higher than other three QNs in environmental water samples. But the maximum concentration detected at all sample sites was 5681.9 ng/L (ENR) in May amidst 15 commonly used veterinary antibiotics. Simultaneously, the concentrations of NOR and CIP were relatively high at some sample sites with 1893.2 ng/L and 641.3 ng/L, respectively, revealing that NOR, CIP, and ENR were used extensively in fish farms and discharged into the river. The detection frequencies of four QNs except NOR decreased from May to August. The mean concentrations of QNs ranged from 0.48 to 243.3 ng/L, and the level of QNs in this study was higher than the concentration detected in surface water from Pearl River and Huangpu River (Jiang et al. 2011; Yang et al. 2011), although QNs were unstable and had faster degradation rate in aquatic environment (Xu et al. 2007); therefore, more attention for QNs in water of this region was necessary.

Four TCs (TC, DC, OTC, and CTC) were seldom detected at 48 sample sites of two campaigns, except for DC and OTC. The detection frequencies of OTC ranged from 54.2% in May to 45.8% in August, the same as CAP, whereas DC was detected at all water samples. In May, the detection frequency of CTC was 12.5%, followed by TC (4.2%). In August, the detection frequency of CTC was 0, as well as TC. OTC showed the highest concentration among TCs (maximum, 51.5 ng/L), whereas the mean concentration of DC was the highest among TCs, which was up to 20.3 ng/L in May. In August, the mean concentrations of four TCs were all below 2 ng/L, which were lower than data reported in foreign rivers (Matsui et al. 2008). Due to replacement of TCs by other antibiotics, such as β-lactam, TCs that we detected in this region showed low concentrations and detection frequencies (Zou et al. 2011).

The data revealed that the detection frequencies of CAP and DC were 100% associated with their high stability and strong persistence in water (Chen et al. 2009). Conversely, according to the statistical analysis of 15 selected antibiotics, the concentrations of AMs, SAs, QNs, and TCs were significantly different in rivers. The concentration of some antibiotics, such as FLO, NOR, CIP, ENR, and OTC, varied greatly in different areas of the river. These results clearly manifested that FLO, NOR, CIP, ENR, and OTC were used frequently and discharged into river directly. The reason for the abnormally high concentration of antibiotics at these points requires further testing of data.

Concentrations of Antibiotic in Fish Feed, Fish, and Sediment

To clarify the source of abnormal points where the concentrations of antibiotics were relatively high, we further investigated the concentrations of antibiotics in fish feed, fish, and sediment in fish ponds near rivers. Three AMs (CAP, FLO, and THI), two QNs (ENR and NOR), two TCs (OTC and DC), and one SAs (SDZ) were detected in the solid samples (Table 2). The detection frequencies of eight antibiotics decreased in the following order: ENR (100%) > CAP (83.0%) = FLO (83.0%) > DC (33.3%) = NOR (33.3%) > SDZ (16.7%) = THI (16.7%) = OTC (16.7%).

ENR showed the highest detection frequency in solid samples, indicating that ENR widely existed in the environment and organisms and was adsorbed to solid phase, including sediment, so that it was not easily metabolized or degraded in the organisms (Pena et al. 2010). Similarly, CAP and FLO showed similar properties to ENR. Due to long-term accumulation and enrichment, the concentrations of antibiotics in sediment and fish were generally higher than in water. CAP, FLO, THI, ENR, NOR, and SDZ were detected in the two feeds of rainbow trout and sturgeon, declaring that various antibiotics was indeed illegally added in fish feed for the treatment of fish diseases to increase the output of fish farms in the absence of legal supervision. The

Table 2 Concentrations (μg/kg) of antibiotics in the solid samples in North China

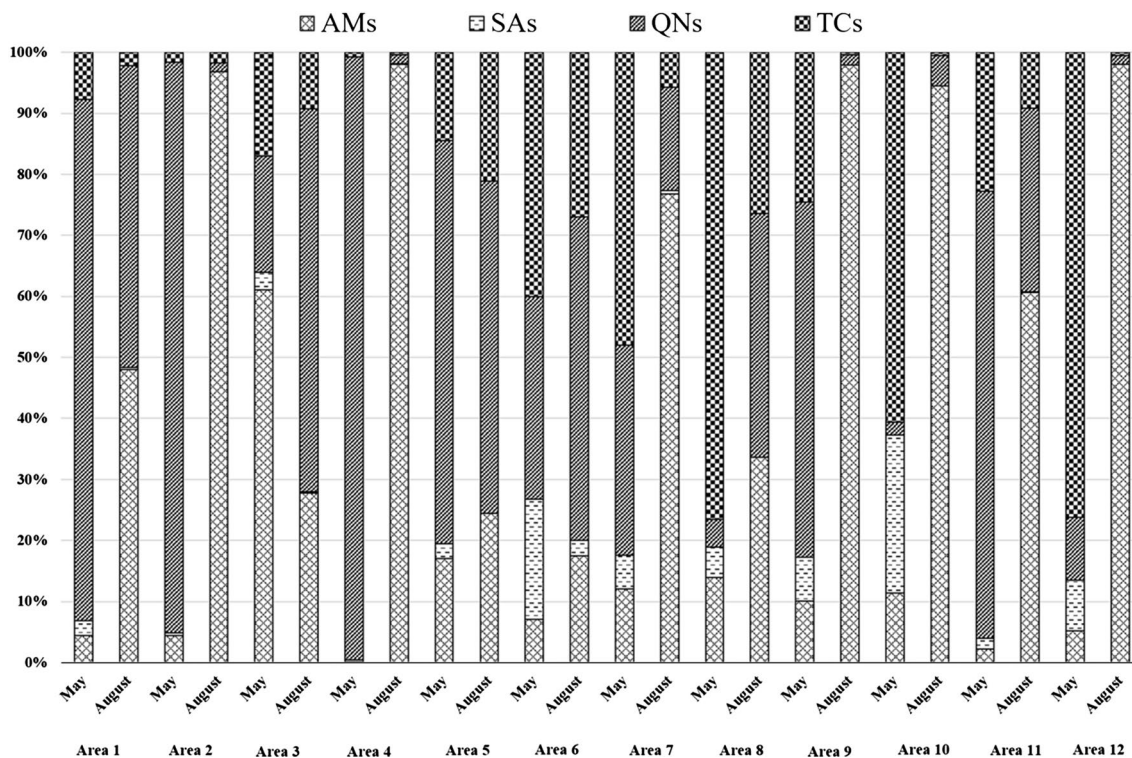| Matrix	Compound							
	CAP	FLO	THI	ENR	OTC	DC	NOR	SDZ
Sediment-1	0.11	0.18	nd	1.24	nd	nd	nd	nd
Sediment-2	0.10	nd	nd	0.72	nd	0.13	nd	nd
Fish-1	0.18	0.24	nd	3.82	nd	nd	nd	nd
Fish-2	0.14	0.50	nd	1.86	0.43	0.21	nd	nd
Rainbow trout feed	nd	24.60	1.60	26.40	nd	nd	451.20	nd
Sturgeon feed	0.80	3.20	nd	22.00	nd	nd	264.00	2.20
Freq. (%)	83.3	83.0	16.7	100.0	16.7	33.3	33.3	16.7

nd not detected

Fig. 2 The proportions of the four types of antibiotics in May and August at 12 areas respectively
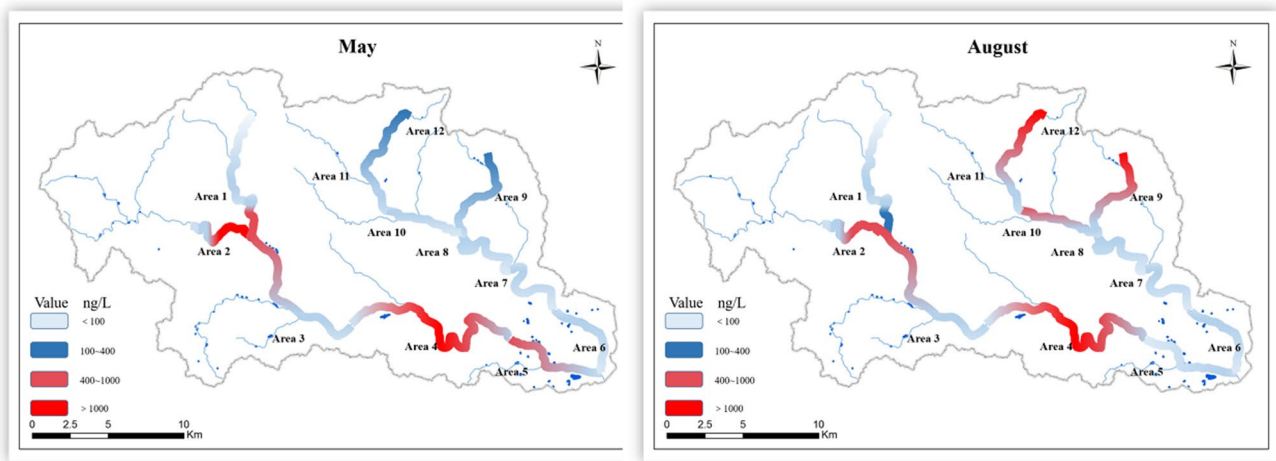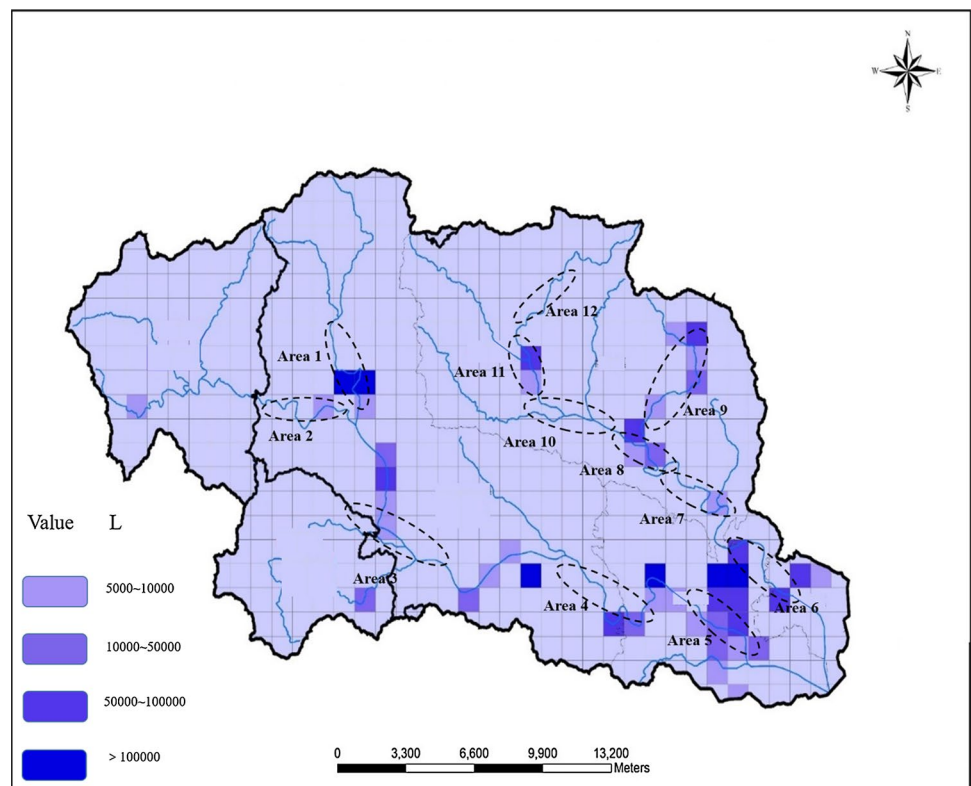
Fig. 3 Spatial distribution of total antibiotics in May and August

Fig. 4 Emission load of fish pond wastewaters

concentrations of FLO, ENR, and NOR exceeded 20.0 μg/kg. What's more, the concentration of NOR even was up to 451.2 μg/kg. The high concentrations of FLO, ENR, and NOR in fish feed precisely explained why their concentrations suddenly increased in some sample sites of the nearby fish pond. When fish from fish farms ate feed containing antibiotics, antibiotics that are not easily metabolized will be enriched in fish. At the same time, aquatic organisms in this region also suffered from residual antibiotics.

Seasonal Variation and Spatial Distribution of Antibiotic

To further verify the relationship between fish ponds and abnormal points, the distribution and discharge of fish ponds

were investigated. Twenty-four sample sites were divided to 12 areas according to location. Figure 2 shows the proportions of the four types of antibiotics in May and August at 12 areas, respectively. The detection frequencies of about half of antibiotics exceeded 85% in May, but the ratio decreased to 26.7% of all in August. The detection frequencies of four types of antibiotics declined in August compared with May, except for AMs (THI and FLO). The detection frequencies of CAP and THI increased by 20.8% and 33.3%, respectively.

Changes were particularly evident that the proportion of four types of antibiotics was different with seasonal variation. QNs was the dominant antibiotic in May, and AMs was the dominant antibiotic in August in Areas 4, 9, 10, and 12 compared with other areas. Figure 3 shows the highest concentrations (6287.9 ng/L) of the total 15 antibiotics in Area 4 among 12 areas. The high antibiotic contamination occurred in both Area 2 and Area 4 in May or August, but the main antibiotics were QNs (represented by ENR) in May and AMs (represented by FLO) in August. The concentration ranges of total antibiotics in Area 9 and Area 12 changed from 100 to 500 ng/L in May to more than 1000 ng/L (AMs accounted for 98%) in August, whereas there were no significant changes in antibiotic concentrations in other areas, suggesting that antibiotics used in fishery culture could be directly discharged into surface water. Figure 4 showed the discharge of fish pond wastewaters and different levels of emission at different areas. Especially, a large number of fish pond wastewaters were found to be discharged directly into nearby rivers in Areas 1, 2, 3, 4, 5, 6, 7, 8, 9, and 11. Although Areas 5 and 6 contributed to the highest emissions in all areas, the discharge of these wastewaters was farther away from the river's main roads, and the river flow in Areas 5 and 6 was larger. The mean concentrations of antibiotics did not become very high compared with other areas. Correlation analysis illustrated that the discharge of wastewater emitting by fish pond was positively correlated with the mean concentrations of antibiotics in rivers ($P < 0.01$).

Additionally, a screening library contained 103 pharmaceuticals, including antibiotics and hormones, etc., was established by UNIFI software in our study. Using information, such as retention time, exact mass, characteristic ions, and fracture mechanism in the library, progesterone and bisphenol S were detected by UPLC-Q-TOF MS (Wang et al. 2007). Furthermore, there was a poor linear relationship between the concentration of bisphenol S and total concentration of antibiotics (except for abnormally high concentrations of a few points where close to fish farms) ($P > 0.1$). However, a significant linear relationship between the concentration of progesterone and total concentration of antibiotics (except for abnormally high concentrations of a few points where close to fish farms) was observed by statistical calculation ($R^2 = 0.735$, $P < 0.001$; Fig. 5). In addition, progesterone was a drug that only humans could consume,
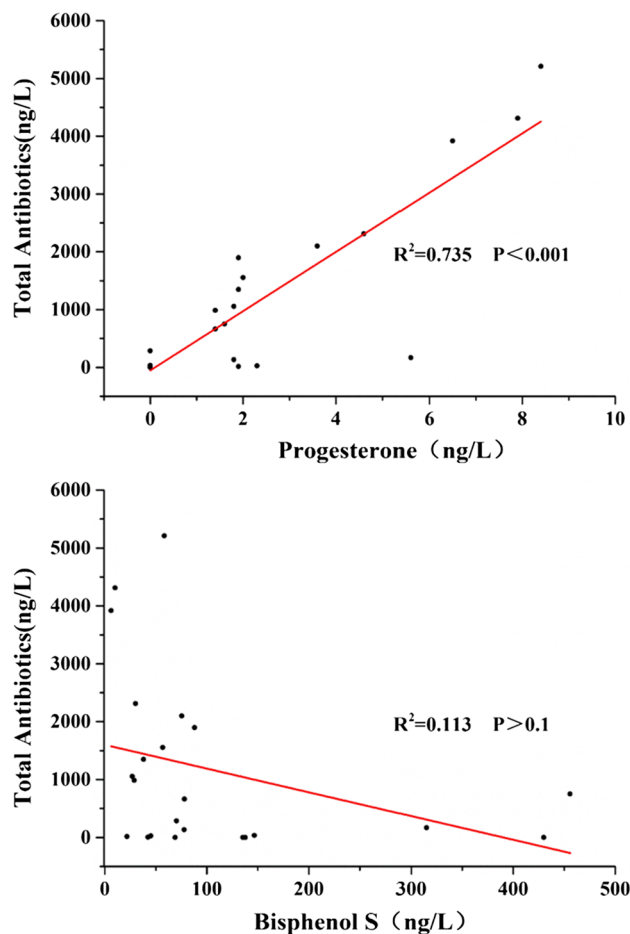

Fig. 5 Relationship between total concentration of antibiotics and concentrations of progesterone, bisphenol S in water

reflecting that domestic sewage containing antibiotics and hormones was discharged into rivers without treatment; therefore, human activities also contributed to antibiotics pollution.

In summary, the fishery culture, resulting the high levels of antibiotics, might contribute to most of the antibiotic pollution on the basis of data that we detected in fish ponds. People's domestic sewage containing various antibiotics and hormones directly discharged into the river also may be one of the causes of antibiotic pollution. Medicinal antibiotics used by residents, veterinary antibiotics used in livestock, poultry breeding, and pesticides used for crops all caused pollution to surface water, soil, and groundwater.

Potential Ecological Risk

Large area of antibiotic pollution would inevitably cause certain harm to aquatic organisms. The risk quotient (RQs) is a basic approach widely accepted by the international community. According to EU legislation context, RQs is a guideline for new or existing substances, including biocides or

Fig. 6 RQs of antibiotics in the surface water of the North China from May 2017 and August 2017. The different symbols represent the mean RQs for the fish, daphnia, and algae, while the bars represent the maximum RQs for those organisms
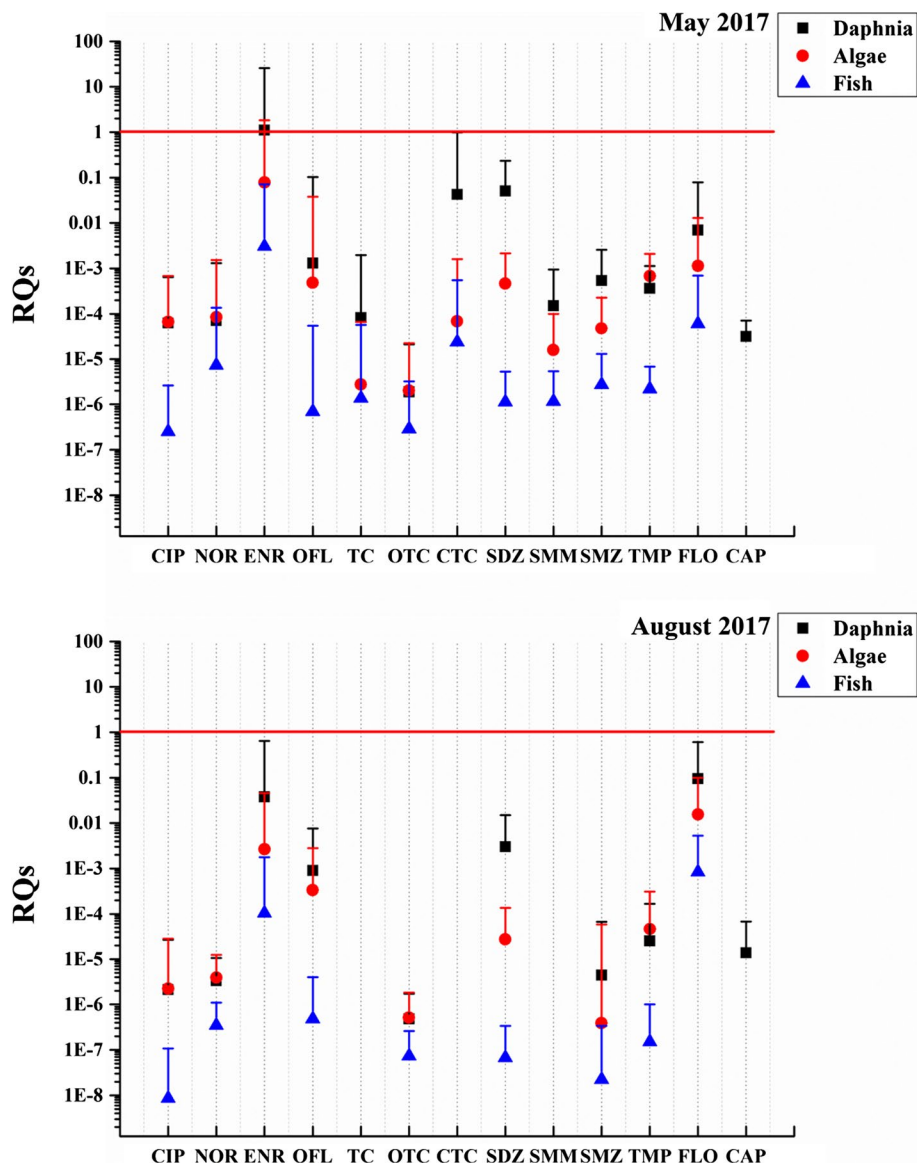
hazard substances (Thomaidi et al. 2017; González-Pleiter et al. 2013). In this study, RQs was based on a comparison of measured environmental concentration (MEC) with the predicted no effect concentration ($PNEC_{water}$) in the aquatic environment. Meanwhile, $PNEC_{water}$ was equal to the quotient between EC_{50} values that acquired from acute toxicity tests and the standard assessment factor (1000) (Hernando et al. 2006). EC_{50} and $PNEC_{water}$ are shown in Table S4. The acute toxicity test data of DC and THI for fish, daphnia, and algae were not reported, and the acute toxicity test data of CAP for fish and algae were not found.

The mean and maximum RQs values of selected 13 antibiotics were calculated and are shown in Fig. 6. Common criteria for RQs was divided into different level: high risk = RQs exceeded 1.0; medium risk = RQs between 0.1 and 1; low risk = RQs between 0.01 and 0.1 (Sánchez-Bayo

et al. 2002; Zhang et al. 2013). According to these results that we calculated, it is overt that the mean and maximum RQs of most antibiotics were less than 0.01, showing that most antibiotics in water had little risk to aquatic organisms, such as daphnia, algae, and fish whether in May or August. ENR posed a high risk to daphnia, medium risk to algae, and low risk to fish, respectively, in May. At the same time, the RQs of CTC and SDZ indicated medium risk to daphnia, and the RQs of OFL and FLO showed low risk to daphnia.

In August, ENR, OFL, and FLO showed relatively high RQs for three aquatic organisms among the all antibiotics. The mean RQs of ENR and FLO were above 0.01 for daphnia, suggesting that ENR and FLO could pose a low risk to daphnia and show a little risk to algae. Moreover, the maximum RQs of ENR and FLO exceeded 0.1 for daphnia, manifesting medium risk to daphnia. Also, ENR and FLO showed

little risk to algae. Because the ecological risk results from the interaction of multiple hazardous substances, the RQ approach cannot fully reflect the potential risk of antibiotics and various factors needs to be further investigated (Chen et al. 2014).

Conclusions

In this study, the occurrence, seasonal variations, and distribution of 15 antibiotics were revealed by analyzing water samples from the surface water in North China. All of four classes antibiotics were detected in this region by UPLC-MS/MS, and the detection frequencies of all antibiotics except for FLO in May were higher than in August. The mean concentrations of four classes antibiotics detected in May were in the following order: QNs (421.23 ng/L) > TCs (28.37 ng/L) > AMs (20.38 ng/L) > SAs (5.79 ng/L). In August the mean concentrations were: AMs (284.36 ng/L) > QNs (15.74 ng/L) > TCs (3.05 ng/L) > SAs (0.20 ng/L). Traceability of antibiotics (ENR, NOR, and FLO) with unusually high concentrations had been found to be related to the use of fish feeds with illegally added antibiotics in fish farms around rivers. The RQ approach was used to assess potential ecological risk of antibiotics. The RQs indicated that FLO and ENR had higher safety risks compared with other antibiotics. Therefore, this study had significant implications for antibiotic prevention and early warning of antibiotic pollution in this region.

Compliance with Ethical Standards

Conflict of interest The authors declared that they have no conflict of interest.

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