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As an important group of emerging contaminants, antibiotics have attracted particular attention due to their wide occurrence and potential impacts on aquatic ecosystems. Beijing is one of the largest and most developed cities in China. The surface water in this region would suffer serious pollution by large amounts of antibiotics from treated and untreated wastewater of hospitals, industries, and livestock farming. This paper investigated the occurrence, distribution, and potential risks of 22 antibiotics in the main rivers and lakes in the urban area of Beijing, China. The results would have significant implications to understand the spatial distribution, temporal variation, and risks of antibiotics in surface water, and help to provide efficient strategies for pollution control of antibiotics in this region.

Occurrence, Distribution and Risks of Antibiotics in Urban Surface Water in Beijing, China

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ABSTRACT

The occurrence and distribution of 22 antibiotics, including eight fluoroquinolones, nine sulfonamides and five macrolides, were investigated in the urban surface waters in Beijing, China. A total of 360 surface water samples were collected from the main rivers and lakes in the urban area of Beijing monthly from July 2013 to June 2014 (except the frozen period). Laboratory analyses revealed that antibiotics were widely used and extensively distributed in the surface water of Beijing, and sulfonamides and fluroquinolones were the predominant antibiotics with the average concentrations of 136 and 132 ng L^{-1}, respectively. Significant difference of antibiotic concentrations from different sampling sites was observed, and the southern and eastern regions of Beijing showed higher concentration of antibiotics. Seasonal variation of the antibiotics in the urban surface water was also studied, and the highest level of antibiotics was found in November, which may be due to the low temperature and flow of the rivers during the period of cold weather. Risk assessment showed several antibiotics might pose high ecological risks to aquatic organisms (algae and plants) in the surface water, and more attention should be paid to the risk of antibiotics to the aquatic environment in Beijing.

Keywords: Antibiotics; Urban surface water; Seasonal variation; Risk assessment

1. Introduction

Antibiotics, an emerging group of environmental contaminant, have attracted growing attention due to the emergence and development of antibiotic resistance in environment and undesirable effects on human health and aquatic ecosystems.[1, 2] They are widely used to prevent and treat infectious diseases for both human beings and animals, as well as to promote the growth of animals in livestock production.[3-5] Nevertheless, most antibiotics administrated cannot be completely absorbed or metabolized by humans and animals, and large amounts of them may be introduced into the aquatic environment through various pathways, including effluent of wastewater treatment plant (WWTP), and discharge of wastewaters from households, hospitals, industries, livestock farming, and landfills.[6-8]

In recent years, antibiotics have been widely detected in aquatic environments, such as the Seine River in France,[9] Elbe River in Germany,[10] as well as the Hiahe River,[11] Pearl River,[12] Yellow River,[13] Liao River,[14] and Huangpu River[15] in China, indicating the levels of antibiotics in rivers ranging from ng L^{-1} to μg L^{-1}. Previous studies have demonstrated that human activities played a significant role in the presence and distribution of antibiotics in surface water,[14-16] and levels of antibiotics have been positively correlated with population densities,[17] suggesting more serious contamination of these chemicals in densely populated urban areas.

Beijing is one of the largest and most developed cities in China, with total dimensions of 16410.54 km^2 and a huge population of 20.693 million. Resulting from the large population, the consumption of antibiotics is expected to be massive in this densely populated city. Large quantities of domestic wastewater (3.3 million tons per day) containing antibiotics were generated from residential areas. However, only 83% of wastewater was treated in the WWTPs, and the rest is directly discharged into the surface water.[18] Unfortunately, most antibiotics were only partly eliminated in WWTPs and may reach the aquatic environment with effluents. Therefore, untreated and treated domestic sewage could be a major source of antibiotics in the receiving waters of Beijing. In addition, over 400 hospitals located throughout the Beijing, so the hospital effluents could also be an input source for antibiotics in the receiving environment. Moreover, there are many farms scattering in the suburb of this city, and wastewater from animal farms can then be directly released into the receiving waters. Accordingly, the surface water would suffer serious pollution by antibiotics in this region. However, limited studies have concentrated on the distribution of antibiotics in urban surface waters in Beijing, China.[19, 20] And the very limited published studies were only performed on a single sampling in one or several rivers, making the robustness of their conclusions to be compromised.

In the present study, a total of 360 surface water samples were collected monthly from July 2013 to June 2014 (except December and January in frozen period) from the main rivers and lakes in the urban area of Beijing. Twenty-two antibiotics, including eight fluroquinolones (FQs), nine sulfonamides (SAs) and five macrolides (MCs), were analyzed. The objectives were to understand the occurrence, spatial distribution, and temporal variation of antibiotics in urban surface waters in Beijing, and to evaluate the potential risks of target antibiotics to different aquatic organisms.

2. Materials and Methods

2.1 *Standards and reagents*

Ofloxacin (OFL, 99.9%), norfloxacin (NOR, 99.9%), ciprofloxacin (CIP, 99.9%), sarafloxacin (SAR, 95.0%), fleroxacin (FLE, 99.5%), lomefloxacin (LOM, 98.0%), difloxacin (DIF, 98.0%), enrofloxacin (ENR, 99.9%), sulfadiazine (SDZ, 99.7%), sulfamerazine (SMR, 99.9%), sulfadimethoxine (SDM, 99.4%), sulfisoxazole (SIA, 99.0%), sulfamonomethoxine (SMM, 99.0%), erythromycin (ERY, 99.1%), roxithromycin (ROX, 90.0%), josamycin (JOS, 98.0%), tylosin (TYL, 82.4%), and spiramycin (SPI, 88.9%) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Sulfathiazole (STZ, 99.0%), sulfapyridine (SPD, 99.0%), sulfamethoxazole (SMX, 99.0%), and sulfamethazine (SMZ, 99.0%) were purchased from KaSei Industry Co., Ltd. (Tokyo, Japan).

Surrogate standards ofloxacin-d_3 (OFL-d_3), norfloxacin-d_5 (NOR-d_5) and sarafloxacin-d_8 (SAR-d_8) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Other four surrogate standards, sulfamethazine-d_4 (SMZ-d_4), sulfamethoxazole-d_4

(SMX-d_4), erythromycin-^{13}C, d_3 (ERY-^{13}C, d_3) and spiramycin I-d_3 (SPI I-d_3) were obtained from Toronto Research Chemicals (Oakville, ON, Canada). The physicochemical characteristics of the test antibiotics are listed in Table S1.

HPLC-grade methanol and acetonitrile were purchased from Fisher Scientific (USA). Formic acid (98%) was purchased from Fluka (USA). Ammonium formate (99%) and ammonium hydroxide (v/v, 50%) were purchased from Alfa Aesar (USA). Ultra-pure water (> 18.2 MΩ cm^{-1}) was prepared with the Milli-Q Advantage A10 system (Millipore, USA).

2.2 *Sample collection*

The detailed sampling sites are showed in Fig. 1. Monthly samplings were carried out at 36 sampling sites in the urban of Beijing from July 2013 to June 2014 (except December and January in frozen period). A total of 360 surface water samples were collected. All of the surface water samples were collected in 1-L polypropylene bottles rinsed with water and methanol. Immediately after being transported to the laboratory, the samples were stored at 4 °C and pretreated as soon as possible.

There are complex river network systems in the urban area of Beijing, including many rivers and lakes, which flow through this city from northwest to southeast. Most of them are artificial rivers, where the riverbed was reinforced with concrete and periodically dredged, so only water samples were collected. Sampling for this study was performed at 36 sites in the Beijing River system (Fig. 1). Of which, sites S1, S3-S8, S10 were located in the Kunyu River, S11-S13 were located in the Tonghui River, S19-S22 were located in the Liangshui River, S23-S24 were situated in the Xiaolong River, and S30-S34 were situated in the Qing River and its tributaries. The rest of sampling sites located at Xiaotaihou River (S25), Baijialou Sewer (S26), Liangma River (S27), Xiba River (S28), Beixiao River (S29), Hucheng River (S35), Kunming Lake (S2), Houhai Lake (S9),Yuyuantan Lake (S14), Taoranting Lake (S15), Longtan Lake (S16), Chaoyang Park Lake (S17), Lianhuachi Lake (S18), and Purple Bambo Lake (S36), respectively.

2.3 *Sample preparation and analysis*

Analytical procedures for the 22 antibiotics in the water samples were performed following previously established method with some minor modifications.[19] Firstly, water samples were filtered through nylon film (0.45 μm) to remove particles. Then, the SPE procedure was performed on an AutoTrace SPE 280 system (Dionex, USA) with Oasis HLB cartridge (6 cc, 200 mg; Waters Corp. Milford, USA). A total of 0.2 g Na_2EDTA and 20 ng surrogate standards (NOR-d_5, OFL-d_3, SAR-d_8, SMX-d_4, SPI I-d_3, SMZ-d_4 and ERY-^{13}C, d_3) were added to 200 mL water sample before the mixture were extracted. The HLB cartridges were conditioned with 5 mL of methanol and 5 mL of pure water. After loaded with samples, cartridges were washed with 10 mL of pure water, and then dried under a nitrogen stream for 20 min. Finally, the analytes were eluted with 6 mL of methanol containing 5% ammonium hydroxide. The eluate was concentrated to 1 mL with a stream of nitrogen at 35°C, and an aliquot (15 μL) of this solution was injected into the high-performance liquid chromatography-electrospray ionization tandem mass spectrometry (HPLC-ESI MS/MS) system for analysis.

The antibiotics were analyzed by a LC-MS/MS system, which consisted of an Ultimate 3000 HPLC (Dionex, Sunnyvale, CA, USA) and a triple-quadrupole mass spectrometer (API 3200; Applied Biosystems/MDS SCIEX, US). The separation of the analytes was carried out on a XTerra MS C_{18} column (2.1 mm × 100 mm i.d., 3.5 μm) (Waters Corp., USA) at a flow rate of 0.2 mL min^{-1}. Methanol-acetonitrile (1:1, v/v) was used as mobile phase A, and 0.3% formic acid in water (containing 0.1% ammonium formate, v/v, pH = 2.9) was used as mobile phase B. The gradient program was as follows: the mobile phase starting conditions were 10% of A for 2.0 min, and A was increased to 70% in 10.0 min before being increased to 100% in 4.0 min; 100% of A for 3.0 min, followed by returning to the initial composition in 0.1 min, which was maintained for 13.9 min. The total run time was 33.0 min.

Mass spectrometric analysis was performed in a positive ion mode with multiple reaction monitoring (MRM). The MS/MS parameters were optimized as follows: curtain gas pressure, 0.14 MPa; collision gas pressure, 0.02 MPa; ion spray voltage, 5,000 V; temperature, 600°C; gas 1, 0.38 MPa; and gas 2, 0.45 MPa. Other parameters of MS/MS and ion pair are listed in Table S2.

2.4. Quantification and quality control

The calibration curve was prepared within a wide range of concentrations (0.05-500 μgL^{-1}) to reveal strong linearity (r^2 >0.99). The method detection limits (MDLs) for antibiotics, defined as the lowest concentration producing a signal-to-noise ratio (S/N) of 3, were 0.01-0.25 ng L^{-1} for water samples. The relative recovery rates ranged from 72.4-121% for the spiked antibiotics in surface water samples. To correct the losses of analytes during analysis procedure, NOR-d_5 was used as surrogate standard for NOR and CIP, OFL-d_3 for, OFL, DIF, ENR, FLE and LOM, SAR-d_8 for SAR, SMX-d_4 for SMX, STZ and SIA, SMZ-d_4 for SMZ, SPD, SDM, SDZ, SMR and SMM, ERY-^{13}C,d_3 for ERY, SPI I-d_3 for SPI, JOS, TYL and ROX. For each set of samples, at least one procedure blank and one independent check standard were run in sequence to check for background contamination and system performance. Detailed information on correlation coefficients and limits of detection of the 22 antibiotics are listed in Table S3.

2.5. Statistical analysis

Statistical analyses were carried out using the IBM PASW Statistics 18.0 (SPSS Inc., 1993-2007). The Kruskale-Wallis nonparametric test was used to identify if there was a significant difference between the levels of antibiotics in different sampling sites, and Friedman's test was carried out to determine differences in levels of antibiotics between different months. The significant difference was considered at $p < 0.05$.

2.6. Risk characterization

To evaluate the environmental risk of antibiotics, hazard quotients (HQs) were calculated using the following formula:

$$HQ = MEC/PNEC \qquad (1)$$

where MEC represents the maximum measured environmental concentration, and PNEC represents the predicted no effect concentration in water. PNEC was calculated following the formula:

$$PNEC = (EC_{50} \text{ or } LC_{50})/AF \qquad (2)$$

where EC_{50} or LC_{50} is the lowest median effective concentration value obtained from available literature, and AF is an appropriate safety factor of 1000 and 100 for acute and chronic toxicity, respectively.[21, 22] Generally, HQ above 1 indicates a high ecological risk to aquatic organisms, 0.1< HQ <1 reveals a medium risk, and HQ below 0.1 represents a low risk.[23]

3. Results and Discussion

3.1 Occurrence of antibiotics in urban surface water

The concentrations and detection frequencies of target antibiotics in urban surface water of Beijing are summarized in Table 1. A total of 22 antibiotics were found with various detection rates in river and lake water samples, indicating their ubiquitous occurrence in Beijing urban rivers. Among antibiotic families, SAs and FQs are the predominant antibiotics with the average concentrations of 132 and 136 ng L^{-1}, respectively, which is proximately one order of magnitude higher than those of MCs (average: 49.3 ng L^{-1}). As illustrated in Fig.S1, the concentration-percent composition of antibiotics in surface water also indicates SAs and FQs are the most abundant antibiotics, and accounted in average for 42.8% and 41.6% of the total antibiotics, respectively. These results agree well with our previous studies that considerable concentrations of FQs and SAs were frequently detected in WWTP effluents in Beijing.[21, 24, 25]

FQs are one group of the most widely used antibiotics for humans and animals. In this study, OFL was the most abundant compound with the highest average concentration of 93.5 ng L^{-1}, followed by NOR and CIP with average concentrations of 27.6 and 9.87 ng L^{-1}, respectively. This result is consistent with that OFL, NOR, and CIP are the most popular FQs consumed by humans in China (Table S4).[26] The other five FQs, including DIF, ENR, FLE, LOM and SAR, were present at low concentrations (0.01-0.56 ng L^{-1}) and detection rates (1-19%). The levels of NOR, OFL and CIP in urban surface water in Beijing were similar to those detected in Peral River (OFL: ND–439 ng L^{-1}; CIP: ND–459 ng L^{-1}), and Haihe River (OFL: 8.2–112 ng L^{-1}; NOR: ND–129 ng L^{-1}; CIP: ND–59 ng L^{-1})[11], China, but higher than those found in Jialingjiang River (OFL: 6–7 ng L^{-1}; NOR: < 5 ng L^{-1}; CIP: < 5 ng L^{-1}),[27] Zhujiang River (NOR: 1.8–16.4 ng L^{-1}),[28] Qiantang River (OFL: 45.7–51.6 ng L^{-1}; NOR: 7–12.9 ng L^{-1}; CIP: 9.3–11 ng L^{-1}),[29] China, indicating that the levels of FQs in Beijing were relatively high.

Among the nine SAs studied, SMX was detected most frequently (99%) with the highest average concentration of 56.9 ng L^{-1}, followed by SDZ (89%) and SPD (83%) with the average concentrations of 37.2 and 37.5 ng L^{-1}, respectively. SMZ and SMM were present in surface water samples at detection rates of 79% and 53% and at low average concentrations of 3.50 and 0.84 ng L^{-1}, respectively. The detection rates of other four SAs, STZ, SDM, SMR, and SIA, were lower than 5% with average concentrations close to the MDLs in all samples. This may be explained by the fact that these SAs were only occasionally used in Beijing, which have been gradually replaced by FQs and MCs in China over the past 10 years due to their low therapeutic effect.[30] SMX is one of the most frequently detected SAs in surface water, which is widely administered to both humans and animals.[31] In addition, relatively low, or even negative, removal rates were observed for this compound in several WWTPs in previous investigations, leading to high levels of SMX in the receiving rivers.[32, 33] The concentrations of SMX detected in this study were comparable to those previously reported in Pearl River (20–350 ng L^{-1}),[34] Shijing River (12.1–616 ng L^{-1}),[28] and Yangtze Estuary (4.2–765 ng L^{-1}),[35] China. However, the level of SMX was at least one order of magnitude higher than that in Dafeng River (0.65–1.8 ng L^{-1}),[32] and Yangtze River (5–23 ng L^{-1}).[27]

In the group of MCs, ROX and ERY were the most frequently detected compounds with detection rates of 98% at average concentrations of 26.7 and 20.8 ng L^{-1}, respectively. As the commonly prescribed drugs for humans and animals,[26] they are widely used in Beijing. In contrast, SPI, TYL and JOS were only detected in 56%, 18% and 14% of the surface water samples, with average concentrations of 1.51, 0.19 and 0.06 ng L^{-1}, respectively. The levels of ROX and ERY detected in surface water in Beijing were greater than those detected in Haihe River (ERY: 15–90 ng L^{-1}; ROX: ND–12 ng L^{-1}),[33] Jialingjiang River (ERY: 12–23 ng L^{-1}; ROX: 5–39 ng L^{-1}),[27] and

Huangpu River (ROX: ND–9.9 ng L^{-1}),[15] China.

It is should be noted that the three veterinary drugs, DIF, ENR and TYL, which are widely used for animals, were detected with very low frequencies and concentrations in this study (Table 1). This may be due to the fact that the study area is a highly urbanized area, where livestock breeding is prohibited within the 5th Ring Road of Beijing, and few farms located in this region.[36] Therefore, livestock farming accounted for minor contribution to the antibiotics in the receiving waters of urban Beijing. To some extent, the influence of livestock farming on the total antibiotics can be ignored.

3.2 Spatial distribution of antibiotics in urban surface water

The concentrations of antibiotics in 14 rivers and 8 lakes from Beijing are summarized in Table 2. Statistical analysis revealed that there were significant differences (Kruskale-Wallis test, $p < 0.05$) in concentrations of antibiotics between the lakes and rivers. In general, the total antibiotic concentrations in rivers (mean 400 ng L^{-1}) were 15-fold higher than those in urban lakes (mean 25.9 ng L^{-1}), most of which were located in urban parks far from major sources of pollution such as municipal sewage and industrial wastewater.

Significant differences were also observed for the antibiotic levels among the 14 rivers from different regions of this city ($p < 0.05$) (Fig.2). Geographically, the levels of antibiotics in the rivers situated in the eastern and southern urban of Beijing are substantially higher than those in other rivers. The highest level of antibiotics was found in Xiaotaihou River (S25, 1604 ng L^{-1}), one of the most polluted rivers in the south of Beijing, whose water quality isn't able to achieve the secondary standards of "Standard for Discharge of Pollutants from Sewage Treatment Works in Towns and Cities" (GB18918-2002).[37] Likewise, high concentrations of antibiotics were also found in other two southern rivers, Liangshui River (S19-S22, 699 ng L^{-1}), and Xiaolong River (S23-S24, 1056 ng L^{-1}) as well as in the eastern rivers, including Baijialou Sewer (S26, 1341 ng L^{-1}), Liangma River (S27, 714 ng L^{-1}), Xiba River (S28, 453 ng L^{-1}), Tonghui River (S11-S13, 279 ng L^{-1}), and Beixiao River (S29, 274 ng L^{-1}).

The rivers located in the east urban flow through densely populated area in Beijing (over 7500 people per square kilometer),[38] where three major WWTPs (B, C and D) are located. Previous study has shown that the antibiotics cannot be eliminated completely in these WWTP, and a considerable proportion of these compounds were discharged into the nearby rivers.[39] Accordingly, these rivers are heavily impacted by large amounts of domestic sewage and WWTP effluents in this area. As for the southern rivers, they are mainly close to the suburban area of Beijing, where the domestic sewage collection rate is very low (< 50%).[18] Thus, a large amount of untreated wastewater along the river was directly discharged into the water body, resulting in high levels of antibiotics in these rivers. Additionally, there are also three WWTPs (E, G and F) situated in the upper reaches of the southern rivers, so the receiving waters may suffer heavy antibiotic pollution because a considerable amount of effluents containing antibiotics is released into these rivers. Moreover, relative high levels of veterinary antibiotics, SDM and TYL, were only found in the south sampling sites, indicting livestock wastewater from the nearby Dahongmen Farm could also be an input source for antibiotics in this area (Fig.S2).

Compared to the eastern and southern rivers, lower levels of antibiotics were detected in the western rivers and the Qing River system situated in the north district. The western rivers, Kunyu River and Hucheng River, are important recreation watercourse where the point sources of pollution along the river were strictly controlled,[19] even the upstream of Kunyu River is an important drinking water source for Beijing residents that has been protected from any human activities by the fence. In addition, the Qing River (S31, 264 ng L^{-1}) together with its three main tributaries, Yangshan River (S30, 76.8 ng L^{-1}), Xiaoyue River (S32-S33, 130 ng L^{-1}) and Wanquan River (S34, 125 ng L^{-1}) flows through the less densely populated area with about 6000 people per square kilometer.[38] These rivers were mainly used as irrigation and landscape water, receiving large quantities of effluent from WWTP A. Our previous study has reported that this WWTP, a wastewater reclamation plant coupled with an ultrafiltration and ozone oxidation system, could remove most of antibiotics in the tertiary effluent,[18] which may make a limited contribution of antibiotic input to the north rivers.

As mentioned above, the treated or untreated wastewater discharges were one of the important factors responsible for the relatively high levels of antibiotics in the eastern and southern rivers of Beijing. In addition, the eastern and southern areas of Beijing are not only very densely populated, but also highly industrialized, leading to large amounts of untreated household wastes, urban sewage and industrial wastewaters containing antibiotic residues discharged into the rivers. Above all, the concentrations of antibiotics in the surface water in northern and western urban were significantly lower than those detected in the southern and eastern areas in Beijing.

3.3 Temporal variation of antibiotics in urban surface water

Monthly variations of antibiotic concentrations were observed in surface water samples in Beijing (Friedman's test, $p < 0.05$). As illustrated in Fig. 3, it was obvious that the total amounts of antibiotics were highest in November (411 ng L^{-1}), while the lowest in June (260 ng L^{-1}). This result agree well with our previous study showing higher antibiotic concentrations in winter and spring than those in summer and fall in wastewater.[20] This may be due to the higher consumption of antibiotics in the winter than that in the summer, leading to large quantities of input of these compounds from wastewater to surface water during periods of cold weather.[19] Additionally, the average water temperature during November 2013 is 5℃, whereas the river temperature increased to 27℃ during June 2013. Compared with warmer periods, microbial activity was inhibited during cold periods, which means that the biodegradation of antibiotics in rivers would be decreased during periods of cold weather.[40] Moreover, as the most important degradation pathway for various drugs in natural waters, photodegradation of antibiotics may be faster in summer due to exposure to intense ultraviolet radiation.[22, 41] Furthermore, rainfall may also affect the level of antibiotics in the aquatic environment. It is reported that the average annual rainfall in Beijing is 640 millimeters, with approximately 72.5% of the total precipitation concentrated in the wet season (June to August).[42-44] Thus, the stronger dilution by heavy rainfall and stronger surface runoff was another explanation for lower concentration of antibiotics in the rivers during the wet season.[39] The river runoff in Beijing can often change dramatically from one season to the next, which may influence the temporal variation of antibiotics. Taking the Tonghui River as an example, the concentrations of antibiotics in October (755 ng/L) are higher than that in June (390 ng/L), July (335 ng/L), August (222 ng/L) and September (449 ng/L), while lower flow rate of Tonghui River was found in October (0.8 m^3/s) than that in June to September (2.61-4.21 m^3/s), which indicates that the different monthly flows was one of important factors contributing to the temporal variation of antibiotics. Therefore, a combination of factors including high consumption of drugs, low river temperature and flows might enhance the persistence of antibiotics in the surface water during the dry season.

3.4 Environmental risk assessment

Previous studies have demonstrated that antibiotics in the aquatic environment may cause adverse effects on wild organisms.[45] As a consequence, hazard quotients (HQs) were calculated to evaluate the ecological risk of these antibiotics in surface water on organisms in the present study.

According to the most sensitive values of EC_{50} (Table S5 and S6), the highest HQs of antibiotics for various aquatic organisms (algae, plant, invertebrate and fish) are listed in Table 3. Obviously, invertebrate and fish are not likely at risk, because all their HQs are far lower than 1. However, algae and plant are relatively susceptible to antibiotics in the aquatic environment. [46] Significantly high HQ values of OFL (47.1), CIP (24.3), SMX (21.7), ERY (18.6), SDZ (3.86), and SMZ (1.19) were found for algae, and high HQ values of OFL (8.18), SDZ (7.43), CIP (2.04) and SPD (1.11) were also found for plants, indicting fairly high ecological risks to algae and plant in the surface water of Beijing.

Additionally, in different sampling sites, the HQs of antibiotics for the most sensitive aquatic species (algae or plant) varied obviously. As illustrated in Fig.4, the proportions of the samples causing high risk (HQ > 1) by OFL, SMX, ERY, and CIP were 67%, 56%, 56%, and 36%, respectively, suggesting significantly high risks of the four antibiotics in most surface water systems, especially in the rivers located in the south and east of Beijing (Fig. S3). For the other 8 antibiotics (NOR, ENR, LOM, SDZ, SMZ, SDM, SPD and ROX), they only posed a medium (0.1 < HQ < 1) or low risk (HQ < 0.1) to the aquatic organism in most of the sampling sites. It should be noted the selected antibiotics in most of the sampling sites could pose ecological risks to aquatic organisms in the surface waters. Therefore, more attention should be paid to the risk of antibiotics to the aquatic environment in Beijing, especially the eastern and southern river waters. Moreover, the development and spread of antibiotic resistance gens (ARGs) is a more serious threat to the ecosystem and human health. Many studies have illustrated the occurrence of ARGs in wastewater, reclaimed water and river water [47, 48]. Therefore, with the high level of antibiotics in the urban surface water of Beijing, it needs more concerns on the levels, transfer and health risks of ARGs in this region in the future.

4. Conclusions

In the present study, totally 22 target antibiotics were detected in the urban surface water samples in Beijing. The concentration was similar to or higher than those in other regions, implying a serious antibiotic pollution in surface water in Beijing. Significant differences were observed between the total concentrations of antibiotics in rivers and lakes. The south and east regions of Beijing showed higher concentration of antibiotics in the surface water, which may be mainly attributed to the wastewater discharge of WWTPs. Seasonal variation of the antibiotics in the urban surface water was also studied, and the greatest level of antibiotics was found in November, which may be due to the low temperature and flow of the rivers during the period of cold weather. Risk assessment showed that the risks of several antibiotics to algae and plants in the surface water of Beijing are very high.

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481 Table 1 Concentrations of targeted antibiotics in urban surface water samples (ng/L)

Analytes	Maximum	Minimum	Mean	Median	Frequency（%）
NOR	403	0.87	27.6	7.65	100
CIP	414	n.d.	9.87	2.23	89
DIF	1.23	n.d.	0.01	n.d.	1
ENR	28.8	n.d.	0.31	n.d.	8
FLE	1.94	n.d.	0.02	n.d.	3
OFL	990	0.34	93.5	11.1	100
LOM	4.71	n.d.	0.02	n.d.	1
SAR	30.8	n.d.	0.56	n.d.	19
STZ	4.91	n.d.	0.04	n.d.	3
SMX	650	n.d.	56.9	13.5	99
SIA	1.56	n.d.	0.01	n.d.	1
SPD	510	n.d.	37.5	1.65	83
SDM	2.34	n.d.	0.03	n.d.	4
SMZ	123	n.d.	3.50	0.31	79
SDZ	520	n.d.	37.2	2.40	89
SMR	2.61	n.d.	0.01	n.d.	1
SMM	27.8	n.d.	0.84	0.18	53
SPI	45.1	n.d.	1.51	0.29	56
JOS	2.24	n.d.	0.06	n.d.	14
TYL	35.2	n.d.	0.19	n.d.	18
ROX	352	n.d.	26.7	3.83	98
ERY	372	n.d.	20.8	4.60	98

482 n.d.= not detected

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Table 2 Concentrations of antibiotics in river and lake waters of Beijing (ng/L)

Sampling sites	FQs			SAs			MCs			Total		
	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max
Rivers (n=28)	165	3.06	1357	173	0.38	1437	62.6	0.17	530	400	4.32	2681
Kun-Tong River System												
Kunyu River (S1, S3-S8, S10)	14.4	3.06	80.9	8.46	0.38	43.0	2.96	0.17	28.0	25.9	4.32	100
Tonghui River (S11-S13)	109	10.8	520	118	2.96	497	51.8	1.43	325	279	16.5	1342
Liangshui River System												
Liangshui River (S19-S22)	261	4.08	1357	327	14.2	1011	111	1.74	516	699	25.2	2681
Xiaolong River (S23-S24)	415	249	559	508	40.4	1399	133	17.5	258	1056	412	1854
Qing river system												
Yangshan River (S30)	28.2	4.47	125	28.3	10.8	80.8	20.4	1.43	67.7	76.8	25.7	161
Qing River (S31)	113	36.7	286	104	11.3	284	47.9	7.94	138	264	59.7	631
Xiaoyue River (S32-S33)	71.9	9.25	726	34.5	1.13	218	23.2	2.14	153	130	30.3	1097
Wanquan River (S34)	65.1	8.52	453	42.1	3.05	132	17.6	3.45	48.3	125	18.5	579
Other rivers												
Xiaotaihou River (S25)	668	464	943	689	116	1437	247	103	460	1604	923	2339
Baijialou Sewer (S26)	596	315	1181	508	214	1041	237	124	530	1341	847	1994
Liangma River (S27)	281	39.2	596	352	131	677	80.5	42.0	127	714	238	1309
Xiba River (S28)	227	79.6	600	134	21.6	292	91.9	21.2	208	453	173	1101
Beixiao River (S29)	114	34.2	408	106	25.5	182	53.3	22.0	209	274	117	782
Hucheng (S35)	60.2	7.73	155	66.4	11.9	229	22.9	5.23	63.5	150	26.5	404
Lakes (n=8)	16.6	2.19	102	6.77	0.00	59.2	2.52	0.00	31.7	25.9	7.13	127
Kunming Lake (S2)	14.6	4.03	38.4	4.46	0.90	13.6	0.94	0.54	1.56	20.0	7.13	49.7
Houhai Lake (S9)	20.1	2.19	102	6.26	1.71	14.3	3.20	0.50	17.6	29.5	8.25	127
Yuyuantan Lake (S14)	15.2	4.15	78.2	6.57	3.13	14.1	2.92	0.94	6.34	24.7	12.5	94.6
Taoranting Lake (S15)	8.07	3.94	18.8	10.4	1.88	19.1	3.08	0.00	10.8	21.5	7.80	41.9
Longtan Lake (S16)	13.7	5.44	50.5	4.78	0.88	8.42	1.86	0.00	5.78	20.3	10.7	56.0
Chaoyang Park Lake (S17)	18.4	6.45	37.8	8.15	1.72	45.0	2.09	0.53	4.40	28.6	11.1	63.5
Lianhuachi Lake (S18)	27.2	11.9	49.1	2.10	0.00	6.39	0.87	0.21	1.76	30.2	12.4	51.3
Purple Bambo Lake (S36)	16.0	3.73	92.3	11.5	1.06	59.2	5.22	0.20	31.7	32.6	9.18	112

Table 3

Hazard quotients (HQs) for the aquatic organisms as calculated from measured environmental concentrations (MECs) and predicted no effect concentrations (PNECs)

Class	Antibiotic	Taxonomic group	EC_{50} (mg/L)	PNEC [a] (ng/L)	MEC[b] (ng/L)	HQ
FQs	NOR	Algae	50.18 (96 h)	50,180	403	0.008
		Plant	0.913 (7 d)	9,130		0.044
		Invertebrate	194.98 (48 h)	194,980		0.002
	CIP	Algae	0.017 (24h)	17	414	24.32
		Plant	0.203 (24h)	203		2.037
	ENR	Algae	0.049 (24h)	49	28.8	0.588
		Plant	0.114 (24h)	114		0.253
		Invertebrate	56.7 (48h)	56,700		0.001
		Fish	>100 (48h)	100,000		0.000
	OFL	Algae	0.021 (24h)	21	990	47.14
		Plant	0.121 (24h)	121		8.182
		Invertebrate	17.41 (48 h)	17,410		0.057
		Fish	>1000 (48h)	1,000,000		0.001
	LOM	Algae	0.186 (24h)	186	4.7	0.025
		Plant	0.106 (7 d)	1,060		0.004
SAs	SMX	Algae	0.03 (96h)	30	650	21.67
		Plant	0.081 (7 d)	810		0.803
		Invertebrate	15.51 (48 h)	15,510		0.042
		Fish	562.5 (96h)	562,500		0.001
	SDZ	Algae	0.135(72h)	135	520	3.852
		Plant	0.07(72h)	70		7.429
		Invertebrate	221 (48h)	221,000		0.002
	SMZ	Algae	0.103 (72h)	103	123	1.189
		Plant	1.277 (7 d)	12,770		0.009
		Invertebrate	110.7 (48h)	110,700		0.001
		Fish	>100 (48h)	100,000		0.001
	SDM	Algae	9.85(24h)	9,850	2.3	0.000
		Plant	0.02(72h)	20		0.117
	SPD	Algae	5.28(24h)	5,280	510	0.097
		Plant	0.46(72h)	460		1.109
MCs	ROX	Plant	>1 (7 d)	10,000	352	0.035
		Invertebrate	7.1 (96 h)	7,100		0.050
		Fish	288.3 (96 h)	288,300		0.001
	ERY	Algae	0.02 (72h)	20	372	18.58
		Plant	>1 (7 d)	10,000		0.037
		Invertebrate	0.94 (48 h)	940		0.395
		Fish	>1000 (48h)	1,000,000		0.000

[a] PNEC= Lowest EC_{50}/ 1000 for acute toxicity or EC_{50}/ 100 for chronic toxicity;

[b] maximum measured concentrations in water.

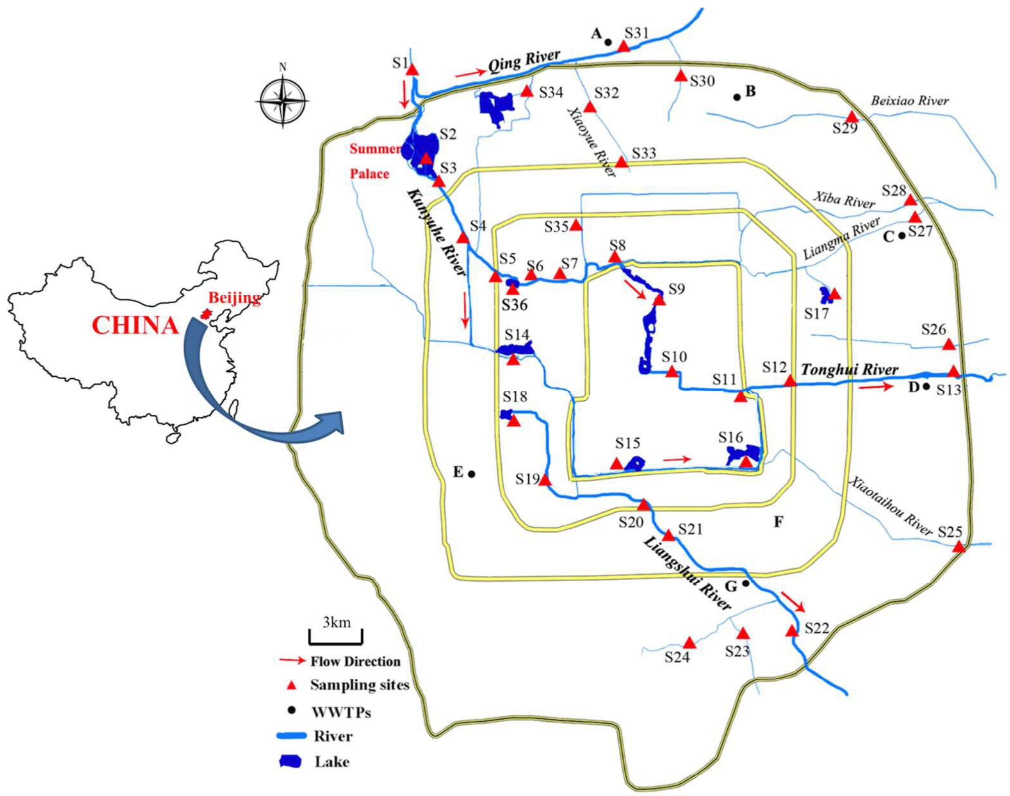

Fig.1. Study areas and sampling sites in the main rivers and lakes in Beijing, China.

Fig.1. Study areas and sampling sites in the main rivers and lakes in Beijing, China.
250x215mm (150 x 150 DPI)

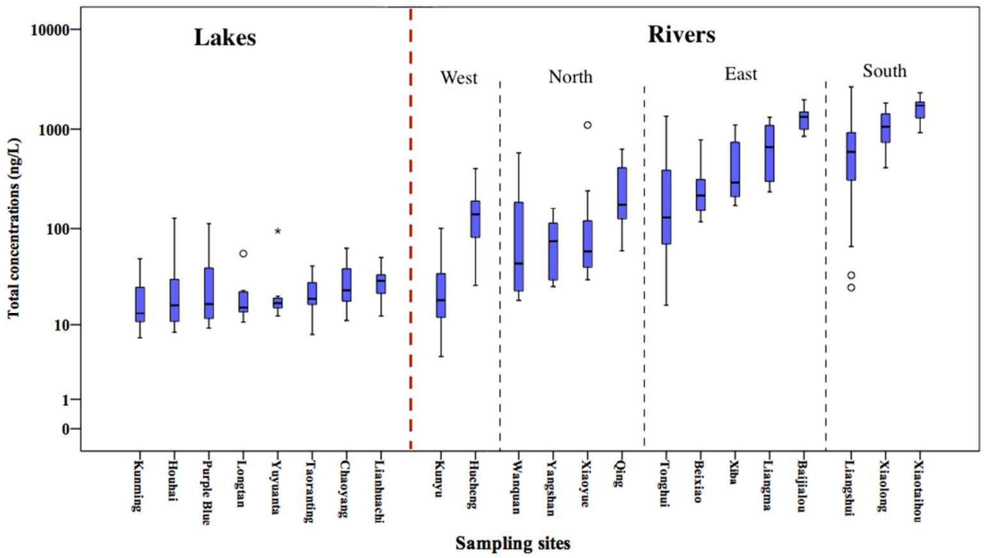

Fig.2. Box-and-whisker plots of the total antibiotic concentrations in different rivers and lakes of Beijing

Box-and-whisker plots of the total antibiotic concentrations in different rivers and lakes of Beijing
359x223mm (72 x 72 DPI)

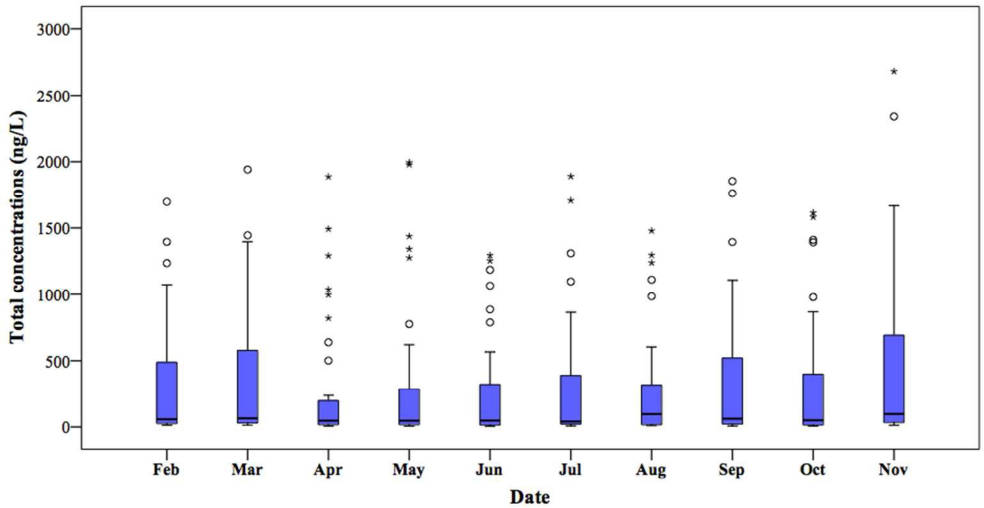

Fig. 3. Box-and-whisker plots of the total antibiotic concentrations in different months

Box-and-whisker plots of the total antibiotic concentrations in different months
339x196mm (72 x 72 DPI)

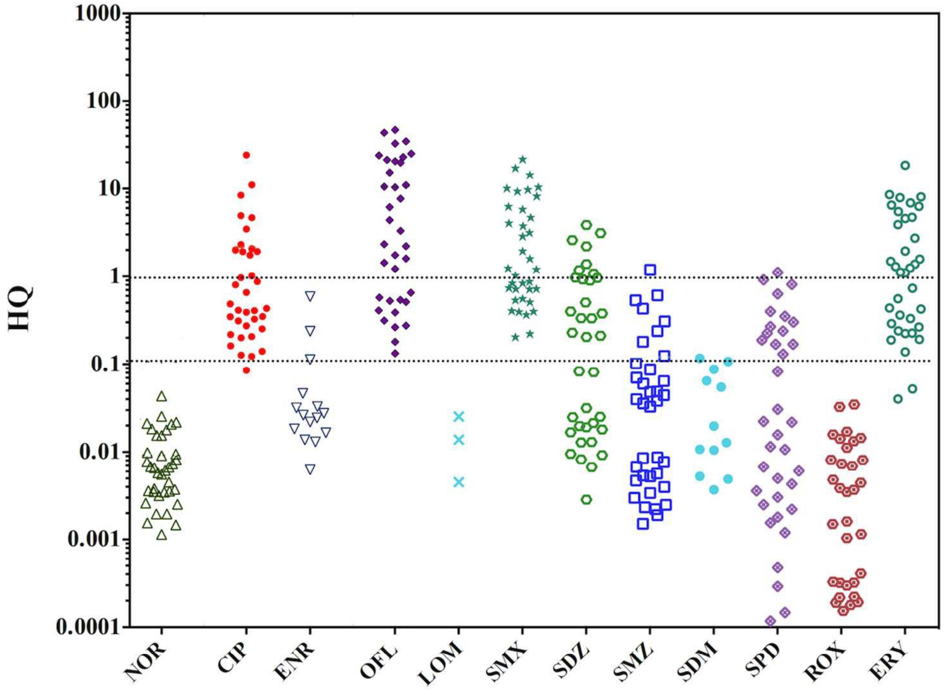

Fig. 4. The hazard quotients (HQs) of 12 antibiotics from 36 sampling sites in Beijing

Fig. 4. The hazard quotients (HQs) of 12 antibiotics from 36 sampling sites in Beijing
130x99mm (300 x 300 DPI)