

Analysis of pollution levels of 7 antibiotics in the Wenyu river water of Beiyun River water system in Beijing after the pollution control: a preliminary study

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Abstract. An analytical method was developed for the determination of sulfonamides and quinolones and tetracyclines antibiotics in black-odor river by SPE-HPLC-DAD/FLD. Water sample was purified and concentrated by HLB cartridge, sediment sample was purified in tandem. In the analysis of water sample from the Wenyu river in Beijing contents by this method, antibiotic concentration of water was between 0.02~17.4µg/L. The results showed that antibiotic concentration in black and odorous water higher than those of surface water. The pollution by wastewater discharge and sediment release were the main ways that 7 target antibiotics entered the Wenyu River.

1. Introduction

Beijing is one of the largest and most developed cities in China, with total dimensions of 16 million km² and a huge population of 2200 million. Resulting from the large population, the consumption of water is expected to be massive in this densely populated city. Presently, most of the ground water in China gradually tends to be malodorous black river due to the deteriorating pollution. According to statistics of year 2015, 110 strips are up to black and odorous water. Subsequently, Beijing city government was carried out for the pollution control work. At the end of 2017, furthermore work is in progress. The investigation results of environment indicated that the residents holds that the drinking water existing problems, and has correlation between drinking water and these river water. PPCPs pollution becomes the bottle-neck of environmental treatment, which restrain the development of social economy sustainable development. Reclaimed water from wastewater treatment plants (WWTPs) is regarded as one of the important sources of antibiotics residues in the aquatic environment. The treatment efficiency of antibiotics seemed to be inefficient in most WWTPs, because only included traditional primary and secondary treatment processes in these plants ^[1-2].

Wenyu river located in the northeastern of Beijing, flows through whole city from northwest to southeast, is permennial river and only originated from domestic investors Beijing. The rate of wastewater treatment lack 61% in the Wunyu river basin at 2005 and 2006 year. Because of the facility of WWTPs construction lags behind and construction of the sewage network management which is behind construction of WWTPs, lead to the wastewater direct discharged into Wenyu river^[3].

In the recent years, antibiotics and resistance gene was detected constantly in the Beijing area ^[4-7]. Correlative analysis showed that there was a positive correlation between quantity of many



drug-resistant bacteria and the corresponding concentration of antibiotics^[8]. Therefore, Investigation and tracing of the concentration of antibiotics cannot be ignored in this kind of the river.

There are a lot of analysis methods that could be applied to qualitative and quantitative analysis of antibiotics, which includes the microbiological method, TLC, capillary electrophoresis, gas chromatography mass spectrometry, high-Performance liquid chromatography (HPLC) and High Performance Liquid Chromatography/Mass Spectrometry/Mass Spectrometry (LC/MS/MS)^[9-10]. The LC/MS/MS sensor has favorable sensitivity and resolution, but LC/MS/MS system is complex and the cost is high, such problems as the complex methods, the overdue time, the high cost exist. Detection Limit of antibiotics fall on the linear response range of HPLC system because of the enrichment by the sewage and sediments^[11]. The gradient elution technique of HPLC was used to isolate and analyses the complicated component, shows great advantage in complex matrix in HPLC system.

This work will study 7 target antibiotics of the water samples in Wenyu River, Beijing. These achievements will provide scientific support for the selection of technologies in Received WWTPs and surface water management concerning use of reclaimed water. To the best of our knowledge, this is the first paper to concentration antibiotics in rivers of reclaimed water in Beijing.

2. Materials and Methods

2.1. Sample collection

Monthly samplings were carried out at 36 sampling sites in the urban area of Beijing from July to December 2017. In the target area the east longitude is 40°4'33"~39°55'12" and the south latitude is 116°29'56"~116°38'54". A total of 36 surface water samples were collected. All of the surface water samples were collected in 3L 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 Wenyu river in 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.

2.2 Sample preparation and analysis

Analytical procedures for the 7 antibiotics in the water samples were performed following the previously established method. Firstly, water samples were filtered through a nylon film (0.45 mm) to remove particles. Then, the SPE procedure was performed on an Auto Trace SPE system (Dionex, USA) with an Oasis HLB cartridge (6ml, 200 mg; Waters Corp. Milford, USA). A total of 0.6 g Na₂EDTA and 20 ng surrogate standards were added to 1000 mL water sample before the mixture was extracted. The HLB cartridges were conditioned with 5 mL of methanol and 5 mL of pure water. After being loaded with samples, cartridges were washed with 10 mL of pure water, and then dried under a nitrogen stream for 10 min. Finally, the analytes were eluted with 10 mL of methanol. The eluate was concentrated to 1 mL with a stream of nitrogen at 35 °C, and an aliquot (10 µL) of this solution was injected into a high-performance liquid chromatography (HPLC-DAD/FLD) system for analysis.

The antibiotics were analyzed using a LC-DAD/FLDS system, which consisted of an Agilent 1260 HPLC (Agilent Technologies, CA, USA). The separation of the analytes was carried out on an Agilent ZORBAX SB-C18 (4.6 mm*150 mm, 5 µm) (Agilent Technologies, USA) at a flow rate of 1.0 mL/min. Acetonitrile was used as mobile phase B, and 0.1% phosphoric acid in water was used as mobile phase A. The gradient program of SMX, SMZ, TCN and SDZ was as follows: the mobile phase starting conditions were 90% of A for 1.0 min, and A was increased to 85% in 1.0 min, was increased to 70% in 5.0 min, and A was increased to 60% in 5 min before being increased to 90% in 2.0 min, followed by returning to the initial composition in 0.1 min, which was maintained for 14 min. The total run time was 14.0 min.

Methanol was used as mobile phase B, and 0.1% phosphoric acid in water was used as mobile phase A. The gradient program of NOR, OFL and ENR was as follows: the mobile phase starting

conditions were 80% of A for 3.0 min, and A was increased to 40% in 5.0 min before being increased to 80% in 4.0 min, 80% of A for 2.0 min, followed by returning to the initial composition in 0.1 min, which was maintained for 14 min. The total run time was 14.0 min.

2.3 Quantification and quality control

The calibration curve was prepared within a wide range of concentrations (0.05–500 µg/L) to reveal strong linearity ($r^2 > 0.999$). The method detection limits (MDLs) for antibiotics, defined as the lowest concentration producing a signal-to-noise ratio (S/N) of 3, were 5–16 ng/L for water samples. The relative recovery rates ranged from 35.1–66.1% for the spiked antibiotics in surface water samples. For each set of samples, at least one procedural blank and one independent check standard were run in sequence to check for background contamination and system performance.

3. Results and discussion

The concentrations of target antibiotics in water samples of Wenyu River are summarized in Table 1. A total of 7 antibiotics were found with various detection rates in river water samples, indicating their ubiquitous occurrence in Wenyu River. Among the antibiotic families, TCN is the predominant antibiotics with the average concentrations of 26 µg/L. The concentration-percent composition of antibiotics in surface water also indicates that TCN is the most abundant antibiotics, these results agree well with previous studies that considerable concentrations of TCN was frequently detected in WWTP effluents in Beijing^[12]. Concentration of TCN in the rainy season is higher than those in the usual discharge period and dry season. This shows that the pollution by wastewater discharge is the main ways that TCN enter the Wenyu River.

Likewise, the detection rate of SMZ, SMX, NOR, ENR and SDZ are independent of runoff of rivers, but their concentration in the rainy season higher than those in the usual discharge period and dry season. This shows that the pollution by wastewater discharge is the main ways that SMZ, SMX, NOR, ENR and SDZ enter the Wenyu River.

The detection rate of OFL is independent of runoff of rivers, but its concentration in the dry season higher than those in the rainy season and usual discharge period. This shows that the pollution by sediment release is the main ways that OFL enter the Wenyu River.

Table 1 Concentrations of targeted antibiotics in Wenyu River water samples (µg/L)

No		1	2	3	4	5	6	7	8	9	10	11	12
rainy season	SDZ	-	-	-	-	-	-	5.12	-	-	-	-	-
	SMZ	2.49	1.92	1.66	1.32	1.37	1.32	1.03	0.67	1.4	0.45	0.48	1.15
	TCN	7.22	5.26	7.49	5.62	10.8	9.7	1.03	8	8.06	10.2	6.15	9.02
	SMX	1.34	0.85	1.82	1.14	1.18	0.75	5.7	1.2	0.97	-	-	-
	OFL	-	-	-	-	-	-	1.76	0.99	-	-	-	-
	NOR	1.09	0.6	1.37	1.27	1.31	1.23	1.33	0.13	1.09	1.32	1.43	1.28
	ENR	0.23	0.14	0.53	0.42	0.33	0.28	0.9	1.64	0.16	0.16	0.18	0.16
No		1	2	3	4	5	6	7	8	9	10	11	12
usual discharge period	SDZ	-	-	-	-	-	-	-	-	-	1.34	0.88	1.1
	SMZ	0.73	4.01	1.36	1.47	0.75	1.54	0.96	1.61	1.31	2.86	1.38	0.73
	TCN	8.62	26	8.37	12	16	13.6	12.5	16.4	17.4	11.5	12.9	13.2
	SMX	0.76	0.9	0.75	0.76	0.62	0.75	0.8	0.97	-	0.87	-	-
	OFL	-	0.44	-	-	-	-	-	-	-	2.34	-	-
	NOR	0.35	0.54	0.43	0.43	0.59	0.5	0.43	0.56	0.51	0.99	0.71	0.67
	ENR	0.04	0.37	0.03	0.02	0.23	0.07	0.02	0.06	0.03	1	0.03	-

No		1	2	3	4	5	6	7	8	9	10	11	12
dry season	SDZ	-	-	-	-	2.14	3.17	-	-	-	-	-	-
	SMZ	0.31	0.56	-	1.57	1.44	1.03	1.4	2.02	1.77	1.58	1.23	1.72
	TCN	11.9	2.75	2.69	0.96	4.17	4.47	9.13	10.8	13.9	11.4	11.8	12.1
	SMX	0.74	0.63	0.74	0.6	1.11	0.91	0.4	0.35	0.32	0.52	0.81	0.61
	OFL	-	0.5	0.42	0.56	0.53	0.69	0.23	0.3	0.19	0.22	0.45	0.37
	NOR	0.48	0.46	0.59	0.19	0.73	0.69	0.19	0.17	0.24	0.33	0.77	0.57
	ENR	0.07	0.09	0.24	0.04	0.52	0.53	0.12	0.14	0.18	0.14	0.21	0.09

4. Conclusions

In the present study, totally 7 target antibiotics were detected in the urban surface water samples in Wenyu River, Beijing. The concentration was similar to or higher than those in other regions, implying a serious antibiotic pollution in surface water rivers of reclaimed water in Beijing. Significant differences were observed between the concentrations of antibiotics at different months. The pollution by wastewater discharge and sediment release are the main ways that 7 target antibiotics enter the Wenyu River.

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