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Occurrence, distribution, and risk assessment of PPCPs in water and sediments of Longgang River in Shenzhen City, south China

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ABSTRACT

Pharmaceuticals and personal care products (PPCPs) contain a diverse range of organic groups that present a serious threat to the ecological environment and human health. However, their actual fate in rivers remains only partially understood. The occurrence, distribution, and risk assessment of PPCPs in aquatic systems have received global research attention. However, few studies have focused on the Longgang River in Shenzhen City, South China. This study was the first to simultaneously identify and quantify five PPCPs residues in the mainstream of Longgang River. All surface water and sediment samples were analyzed by solid-phase extraction (SPE) and high-performance liquid chromatography coupled with tandem mass spectrometry (HPLC-MS/MS). The five assessed PPCPs were all detected in the mainstream of the Longgang River, with sediment concentrations much higher than water concentrations. Fluconazole and Triclosan were the dominant PPCPs in water and sediments, with maximum concentrations of 55.86 ng/L and 19.24 μg/kg, respectively. Others were present at mean concentrations below 40 ng/L in water and 15 μg/kg in sediments. The recovery rates of the five PPCPs ranged from 57.2% to 110.6%, which were within the limits of reliability. These results demonstrate that sewage treatment plants exhibited different degrees of removal effects for the five PPCPs and showed a natural attenuation trend along the Longgang River for all PPCPs except carbamazepine. The trace amounts of individual PPCPs residues in the river posed a low risk to aquatic organisms in the mainstream, although the potential risks created by low dose exposure and bioaccumulation of PPCPs should be considered.

Keywords: Pharmaceuticals and personal care products; Longgang River; Risk assessment; Sediments; Natural attenuation

1. Introduction

In the previous studies, increasing global attention has been paid to the fate of pharmaceuticals and personal care products (PPCPs) in the environment, with their common occurrence attributed to their widespread use worldwide, application in the environment and the advancement of analytical technology [1]. By 2003, the mass of antibiotics detected in the United States reached 50,000 tons, of which 60% were applied, 32% were used as growth promoters, and 8% as veterinary drugs [2]. According to previous reports, about 2 million tons of medicines were produced in 2011 in China [3], accounting for more than 20% of global production. After the antibiotics are ingested by humans or animals, some are metabolized, with most of them finally passed through into urine or feces and therefore, into sewage in the form of metabolites [4]. Since the current sewage treatment processes are not designed for the control of antibiotic substances, some substances cannot be effectively removed by sewage treatment plants, thus being finally discharged into natural water bodies, or adsorbed into activated sludge. Furthermore, due to agricultural production activities such

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as fertilization, PPCPs can directly enter the environment [5,6]. In addition, methods such as solid-phase extraction (SPE) combined with LC-MS and GC-MS have allowed the detection of PPCPs at trace levels (ng/L to μg/L) in complex water environments [7].

PPCPs in urban rivers in China can be released from different sources. The main emission sources of PPCPs in urban rivers remain a highly debatable topic. PPCPs in surface water and municipal wastewater are frequently detected, with concentrations usually between 0.01 and 1.0 μg/L [8]. As PPCPs are continuously introduced into the environment, causing persistence or pseudo-persistence, with many PPCPs being toxic and resistant to biodegradation, there is a realistic potential for bioaccumulation [9]. Simultaneously, when some drugs enter the environment, they exert selective pressure on environmental microorganisms, inducing them to develop or acquire resistance, leading to the improvement of resistance levels, and the generation of super-resistant bacteria [10]. Therefore, PPCPs have gradually become one of the most important indexes to evaluate water quality and ecological security of the water environment [11].

In natural surface water bodies, PPCPs may undergo several environmental processes, mainly adsorption by sediments, biodegradation by microorganisms, and photolysis due to sunlight. Adsorption can be used to remove PPCPs from water. For example, pores of sediments can capture triclosan, while the sediment organic matter can bind triclosan and reduce its solubility [12]. Sediments may also accumulate PPCPs and later release them back into the aquatic environment [13], with a previous study establishing that the pH of the aquatic environment can affect the adsorption process [14]. Photodegradation and biodegradation are both heavily influenced by the molecular structures of xenobiotic compounds. Triclosan undergoes direct degradation by sunlight [15]. Photochemistry is a potentially important transformation pathway for naproxen [16]. Metoprolol (ME), which is the commonly most sold beta-blocker in Uppsala, Sweden, has been shown to undergo biotransformation as well as phototransformation in the environment [17,18]. Carbamazepine (CBZ) has been shown to be highly persistent in wastewater treatment processes and in the aquatic environment due to its low rate of biotransformation and low sorption potential [19–21]. Considering the strong stability of CBZ, it has been proposed as a suitable anthropogenic tracer for PPCPs [22,23].

Shenzhen City is one of the oldest established Special Economic Zones, located in the south of Guangdong Province in China. At present, only a few studies have investigated PPCPs in the Shenzhen drinking water source area and most studies on the ecological risk of pollutants in the water source area have focussed on heavy metals [24]. However, the concentration profiles and distribution patterns of PPCPs in water and sediments of rivers remain unclear. Therefore, this study focused on the occurrence, distribution, attenuation, and ecological hazards of five selected PPCPs in water and sediments from the Longgang River of Shenzhen City, South China.

The major objectives of the present study were (1) to select five widely used PPCPs, representing different groups and analyze their spatial distribution in water and sediments of Longgang River in Shenzhen City; (2) to understand the attenuation process influencing the distribution of PPCPs in water and sediments; and (3) to evaluate the environmental risks from PPCPs residues in Longgang River in Shenzhen City.

2. Materials and methods

2.1. Chemicals and regents

The antibiotic Trimethoprim (TMP), antifungal Fluconazole (FCA), β-blocker ME, anti-bacterial Triclosan (TCS), and anti-epileptic drug CBZ were used for analysis. These commonly occurring PPCPs, represent different chemical groups and applications, which are widely distributed worldwide. These PPCPs were purchased from Toronto Research Chemicals (TRC, Canada) and their physicochemical properties are listed in Table 1.

Five isotopically-labeled internal standards, including TMP-$^{13}C_3$, FCA-d4, ME-d5, Triclosan-d3, and CBZ-d2 were also obtained from TRC (Canada). Individual stock solutions (200 mg L^{-1}) of PPCPs standards with a concentration of 200 mg L^{-1} were prepared and dissolved into methanol. All stock solutions were stored in the dark at –20°C. HPLC-grade methanol, acetone, and acetonitrile were purchased from Fisher (Shanghai, China). Phosphate buffer solution (sodium phosphate monohydrate/phosphoric acid; 0.14 M $NaH_2PO_4·H_2O$/85% H_3PO_4) was prepared using 1.93 g $NaH_2PO_4·H_2O$ in 99 mL reagent water and 1 mL of 85% H_3PO_4. Disodium ethylenediamine tetraacetate (Na_2EDTA), and hydrochloric acid (HCl) were obtained from Aladdin Chemical Reagent (Shanghai, China). Ultrapure water (resistivity 18.3 MΩ cm) was prepared using a Milli-Q water purification system (Millipore, USA).

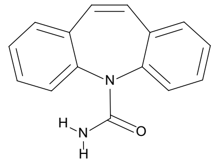
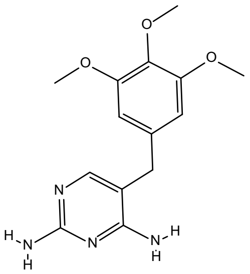
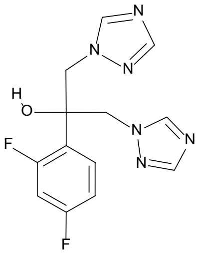
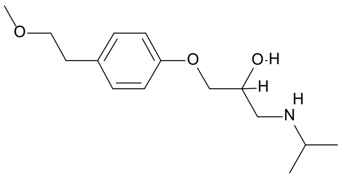
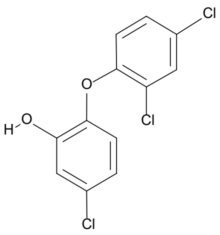
2.2. Sample collection

Water and sediment samples were collected in November 2017, from four sampling sites (P1–P4) along the Longgang River in Shenzhen City, South China (Fig. 1). The wastewater treatment plant (WWTP) was located between sampling sites P1 and P2, with a rubber dam about 200 m from the upstream reach used to intercept the sewage, preventing untreated sewage from being discharged directly into the downstream reach. Water samples were all collected and stored in brown glass bottles to prevent the photolysis of analytes. The riverbed sediment samples were collected using a stainless steel grab sampler, ensuring a wet weight of about 10 g. Three parallel samples were taken at each sampling site and all samples were stored in a PU heating insulation box with ice bags to maintain a cool temperature and all samples were immediately transferred to the laboratory in a cooler. Additional water and sediment samples were collected for physicochemical parameter analyses. Water samples were stored at 4°C while sediment samples were stored at –20°C.

2.3. Sample extraction

Extraction of PPCPs from the water and sediment samples was performed according to the Environment Protection Agency (EPA) method 1694. The pretreatment procedure is shown in Fig. 2.

Table 1
Physicochemical properties of the target compounds

Compounds	Function	Molecular formula	Structure	LogK_{ow}	K_d (L/kg)	pKa
CBZ	Anti-convulsion	$C_{15}H_{12}N_2O$		2.45	35.4	13.9
TMP	Sulfonamide Antibiotics	$C_{14}H_{18}N_4O_3$		0.91	N.A.	7.12
FCA	Antifungal	$C_{13}H_{12}F_2N_6O$		0.25	N.A.	11.65
ME	β-blockers	$C_{15}H_{25}NO_3$		1.88	1.0	14.06
TCS	Anti-bacterial	$C_{12}H_7Cl_3O_2$		4.76	10,000	7.9

N.A., Not Available.

2.3.1. Water samples

Triplicate 1.0 L water samples were used for PPCPs analysis, with samples first filtered through glass fiber filters (GF/F 0.7 μm, Whatman, UK). Following this, the internal standards solution (1 ng of each internal standard) were immediately spiked into the filtrate. Next, the liquid samples were adjusted to pH 3.0 using 1 mol/L HCl, followed by the addition of 500 mg Na$_2$EDTA to each sample to prevent the chelation of antibiotics with metal cations. Water samples were enriched by SPE using Oasis hydrophilic-lipophilic balance (HLB) cartridges (500 mg, 6 mL, Waters, USA), which were preconditioned sequentially with 20 mL of methanol and 6 mL of Milli-Q water at a slow flow rate of 5–10 mL/min. The flow rate of water sample loading onto the HLB cartridges was controlled to 6.0 mL/min, followed by rinsing with 6 mL acidified ultrapure water (pH 3.0) and 10 mL Milli-Q water to remove impurities. The HLB cartridge was then vacuum-dried for 20 min. Subsequently, each HLB cartridge was eluted with 12 mL methanol, additional elution with 6 mL acetone/methanol (V/V = 1/1) was performed for the analysis of triclosan and the eluates were evaporated to dryness in a

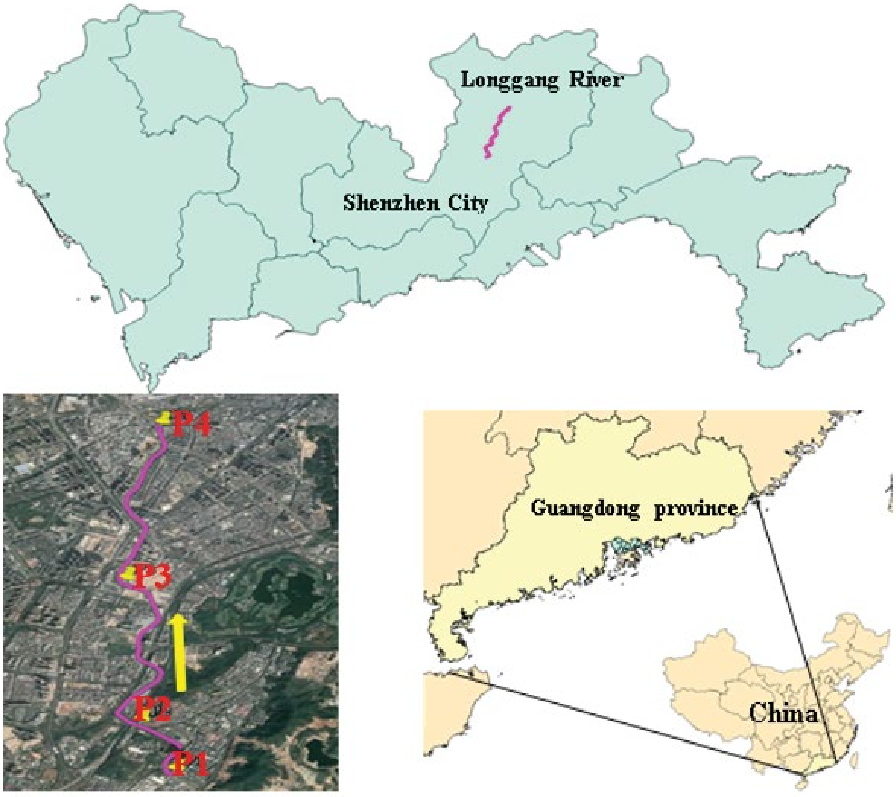


Fig. 1. Map of sampling sites in Longgang River.

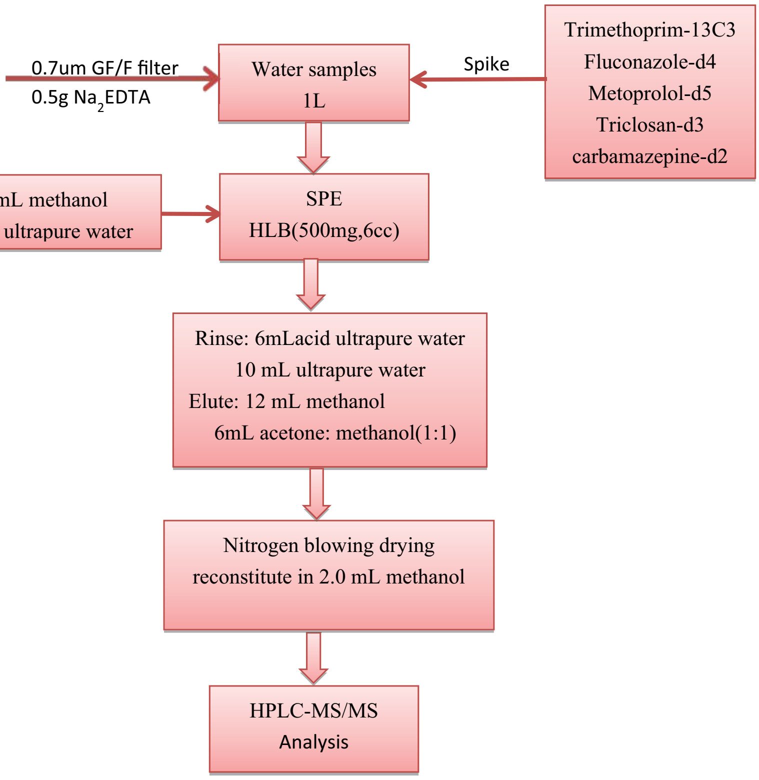


Fig. 2. Sample analysis process.

water bath under a gentle nitrogen stream at 45°C. Finally, the sample was reconstituted in 2.0 mL methanol and stored at −20°C until analysis.

2.3.2. Sediment samples

Upon return of sediment samples to the laboratory, they were first freeze-dried in the dark for 24 h and homogenized through a 2 mm screen. For extraction, 4.0 g of sediment sample was weighed into a 50 mL polytetrafluoroethylene centrifuge tube and spiked with 1 ng internal standards mixture, then immediately vortexed for 1 min. Fifteen milliliters of phosphate buffer solution (pH 3.0) and 20 ml of acetonitrile were added to each tube. The tubes were then ultrasonicated for 30 min and centrifuged at 3,000 rpm for 5 min, with the supernatant from each tube then transferred to a 250 ml glass vial. The extraction process was repeated three times, with only 15 ml added on the final extraction, with all supernatants then combined. Next, the combined extracts were concentrated to a final volume of 20–30 mL by rotary evaporation at 50°C, to remove acetonitrile and prevent it from carrying out target analysis during the SPE treatment. Then, the concentrate was diluted to 250 ml with ultrapure water and before SPE, 0.5 g Na_2EDTA was added to the extract to chelate metal cations. The SPE procedures were performed in the same manner as described for water samples. Finally, the sample was reconstituted in 2.0 mL methanol and stored at −20°C until analysis, which was also consistent with the water sample treatment handling method.

2.4. Analytical methods

Water temperature (T, °C), dissolved oxygen (DO, mg/L), pH, and conductivity were measured in situ at the sampling sites (Table 2). Based on the chemical properties, environmental issues and the dominant anthropogenic activities surrounding the river, seven conventional anions F^-, Cl^-, NO_2^-, SO_4^{2-}, PO_4^{3-}, Br^-, and NO_3^- were determined by ion chromatography and twelve elements, including Na, Mg, K, Ca, Li, Al, Cr, Mn, Fe, Cu, Zn, and As were detected in water samples by ICP-MS. Before analysis, 5 ml of each water sample was acidified with 3–5 drops of nitric acid (95%). As shown in Fig. 3, the concentrations of Cl^-, NO_3^-, SO_4^{2-}, Na, and K in river water were higher than others, while Cl^- was the highest with concentrations reaching 100 mg/L at site P1. As trace metal elements, the concentrations of Al, Cr, Fe, Cu, and Zn were at a low level of a few μg/L. The concentration of most ions reduced along the river mainstream, from site P2 onwards.

The target PPCPs were analyzed by high-performance liquid chromatography-tandem mass spectrometry (HPLC–MS/MS) equipped with an electrospray ionization (ESI) source in multiple reaction monitoring (MRM) mode. Chromatographic separation was carried out using a Waters Xtera C18 (2.1 × 100 mm; 3.5 μm) column. The mobile phases were Milli-Q water with 0.3% formic acid and 0.1% ammonium formate (A) and acetonitrile: methanol at a 1:1 V:V ratio (B). The gradient program started at 5% B and was maintained for 2 min, then a linear gradient was maintained, reaching 100% B in 3 min, which was then maintained for 3 min. Finally, 5% B was restored in 0.5 min and maintained for 6.5 min. The flow was maintained at a constant level of 0.3 mL min^{-1}, the column temperature was fixed at 30°C and the injection volume was 10 μL. Triclosan was injected separately in negative ionization mode. The chromatography conditions were kept the same, except for mobile phase A being Milli-Q water with 0.1% acetic acid and 0.1% ammonium acetate. The gradient program started at 40% B for 0.5 min, followed by a linear gradient until 100% B was achieved in 6.5 min, then the conditions were maintained for 5.5 min. Finally, the initial conditions of 40% B were restored in 0.2 min and maintained for 2.3 min. The gradient elution processes, injection volume, and MS operational parameters are presented in Tables 3 and 4.

Table 2
Situ measurements of sampling sites

Sites	P1	P2	P3	P4
T (°C)	23.6	24.7	25.6	24.8
DO (mg/L; %)	7.78	8.15	8.00	7.58
pH	7.54	7.46	7.67	7.87
Conductivity (μs/cm)	721	707	711	739

2.5. Quality analysis and control

The targets concentrations were quantified using the internal standard method to improve analytical stability.

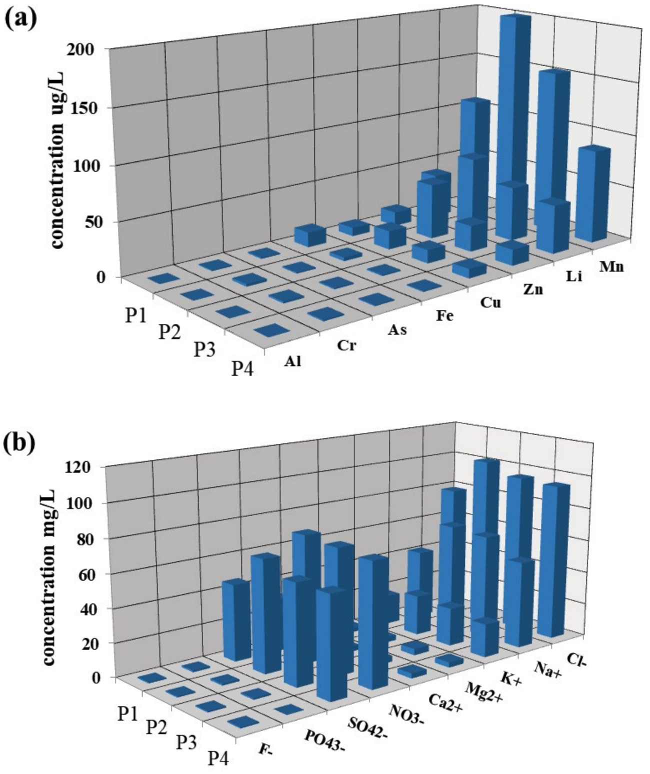
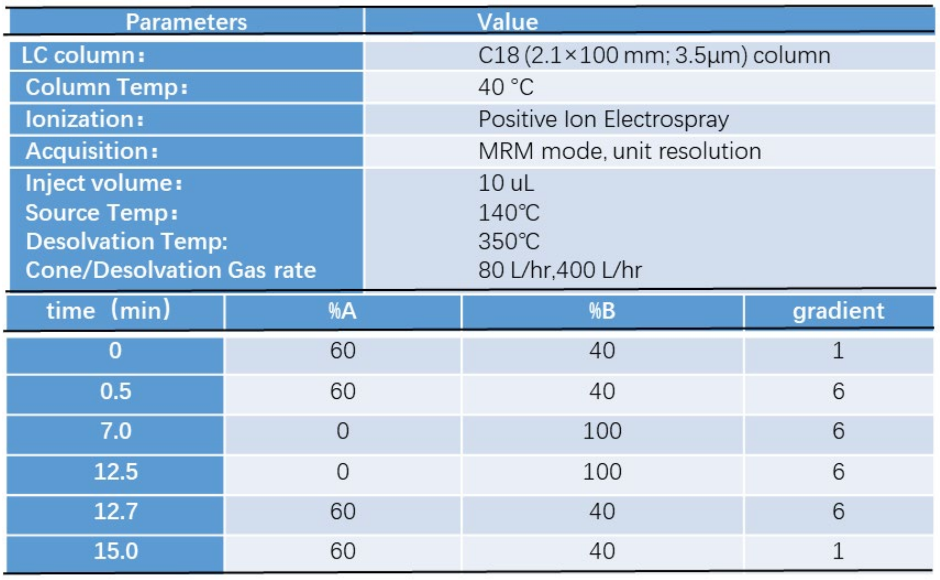


Fig. 3. Monitoring data for anions and cations in water from sites P1, P2, P3, and P4. (a) Low level concentrations and (b) high level concentrations.

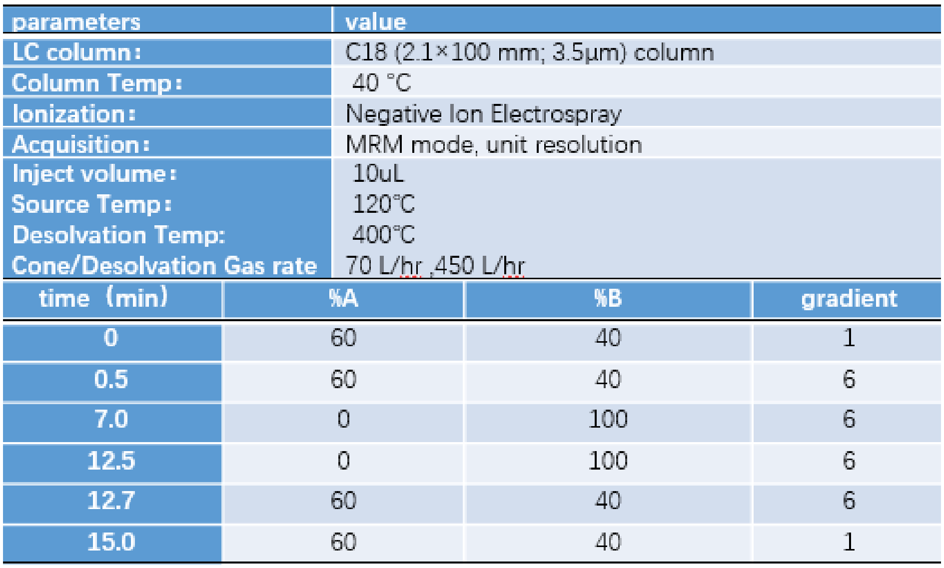
Table 3
Analytical conditions for the detection and quantification of TMP, FCA, ME, and CBZ by liquid chromatography and Electrospray-tandem mass spectrometry



Parameters	Value
LC column:	C18 (2.1×100 mm; 3.5μm) column
Column Temp:	40 °C
Ionization:	Positive Ion Electrospray
Acquisition:	MRM mode, unit resolution
Inject volume:	10 uL
Source Temp:	140℃
Desolvation Temp:	350℃
Cone/Desolvation Gas rate	80 L/hr,400 L/hr

time（min)	%A	%B	gradient
0	60	40	1
0.5	60	40	6
7.0	0	100	6
12.5	0	100	6
12.7	60	40	6
15.0	60	40	1

Table 4
Analytical conditions for the detection and quantification of Triclosan by liquid chromatography and Electrospray-tandem mass spectrometry



parameters	value
LC column:	C18 (2.1×100 mm; 3.5μm) column
Column Temp:	40 °C
Ionization:	Negative Ion Electrospray
Acquisition:	MRM mode, unit resolution
Inject volume:	10uL
Source Temp:	120℃
Desolvation Temp:	400℃
Cone/Desolvation Gas rate	70 L/hr ,450 L/hr

time（min)	%A	%B	gradient
0	60	40	1
0.5	60	40	6
7.0	0	100	6
12.5	0	100	6
12.7	60	40	6
15.0	60	40	1

Seven concentration levels (5 ng/L–50 μg/L) of the target PPCPs standard mixtures were used to establish calibration curves ($r^2 > 0.99$), which were prepared on the same day as analysis, to avoid degradation. Equal concentrations of isotope internal standards were added to all samples to monitor the accuracy of full-range analysis. The recovery rates (RAs) of the five PPCPs spiked in the surface water and sediment samples at a concentration of 1 ng/L ranged from 57.2% to 110.6% and from 63.6% to 106.5%, respectively. The blank samples spiked with the same concentration were applied as the control group, with the RA ranging from 62.5% to 86.8%. The absolute RA of the method was calculated as:

$$R_A = \frac{\left(A_{\text{spiked samples}} - A_{\text{non-spiked samples}}\right)}{A_{\text{solvent}}} \times \% \qquad (1)$$

where $A_{\text{spiked samples}}$, $A_{\text{non-spiked samples}}$, and A_{solvent} refer to the peak areas of the compound in the spiked samples, non-spiked samples, and pure standard solvent samples, respectively.

2.6. PPCPs attenuation model

When PPCPs enter rivers from pollution sources, during the process of water migration, they interact with a variety of water environment indicators and are attenuated through hydrolysis, adsorption, sedimentation, photolysis, and biodegradation. In a study on the migration of 12 antibiotics in the Haihe River Basin [25], it was found that the attenuation behavior of pharmaceuticals in the aquatic environment follows first-order kinetics and the calculation method for the attenuation coefficient (k) uses the following formula as defined by Eq. (2):

$$K = \left(\frac{V}{L}\right)\ln\left(\frac{C_1}{C_2}\right) \tag{2}$$

where L is the distance from site 1 to site 2; C_1 and C_2 are the PPCPs concentrations at sites 1 and 2, respectively; and V is the average river velocity between the two sites. K determination did not use the conservative tracer required for quantitative dilution. Thus, the value of k represents the overall attenuation coefficient, which provides insight into both the relative persistence and potential range of each PPCPs, rather than the specific attenuation coefficient used to predict fate and transport models. As shown in Fig. 6, the first-order attenuation hypothesis was tested by the goodness of fit of the evaluation data to the exponential decay model [$C = C_0e^{-KL/V}$]. This model is only applicable to segments containing a single source of contamination, usually located within a tributary.

2.7. Environmental risk assessment

The probability of adverse environmental impacts on aquatic organisms due to pollutant exposure was assessed by calculating the risk factor (RQ). In the current risk assessment research method, a common standard for interpreting RQ values was also applied, and different risk levels were established. An RQ value of more than 1.0 indicates high risk, while RQ values from 0.1 to 1 and 0.01 to 0.1 indicate a medium risk and a low risk to aquatic organisms, respectively [26]. RQ was calculated according to Eq. (3) as follows:

$$\text{RQ} = \frac{\text{MEC}}{\text{PNEC}} \tag{3}$$

In this expression, the MEC is the measured environmental concentration, which is the actual measured environmental concentration and the PNEC is the predicted unaffected concentration value, calculated according to Eq. (4) as follows:

$$\text{PNEC} = \frac{\text{NOCE}}{\text{AF}} \tag{4}$$

where NOEC is the no observed effect concentration for the most sensitive species. This can be estimated using the chronic toxicity value obtained from an Ecological Structure Activity Relationships (ECOSAR) model (US EPA 2012). AF is an evaluation factor and in this study, an AF value of 100 was selected [26,27]. Three different trophic levels of aquatic organisms were selected as ECOSAR models: fish, daphnid, and green algae.

3. Results and discussion

3.1. Occurrence of PPCPs in water and sediments

Table 5 shows concentrations and detection frequencies of five PPCPs in water and surface sediments from Shenzhen City. All target compounds were detected in both water and sediment samples, indicating the widespread use of PPCPs in this region [28]. In water samples, CBZ and triclosan were detected in all samples with a high detection frequency of above 90%. FCA was detected at the highest concentration in river water samples while the residue concentrations of triclosan were the highest in sediments, reaching about 3 μg/kg.

Pharmaceuticals were detected with an average concentration ranging from low ng/L to low μg/kg. The average concentration of compounds detected in sediments was generally 10–10^3-fold higher than in river water. As shown in Table 6, target PPCPs from site P1 were detected at a higher concentration than the other three sampling sites, which may be attributed to the release of raw untreated water from the WWTP. The concentration of four PPCPs (ME, FCA, TMP, and TCS) in river water, exhibited an obvious decrease downstream from site P2, indicating natural attenuation with the downstream flow of river water.

3.2. Removal efficiency of PPCPs by the wastewater treatment plant

Generally, CBZ is very stable with negligible degradation occurring in the aquatic environment. Therefore, this concept was applied to estimate the elimination of pharmaceutical residues along the river stretch by normalizing their concentration to the relative concentration change of CBZ. This method is only completely errorless if the discharge doesn't change with time or if the concentrations of CBZ and the compound of interest at the four sampling sites are perfectly positively correlated. Site P1 is located in the upper reaches of the Longgang River, which contained source water, with the sewage treatment plant between sites P1 and P2, while the treated tailwater was discharged downstream.

As shown in Fig. 4a, the concentration of CBZ in river water and sediment maintained at a stable level, almost unchanged with river flow. This not only proved the stability of CBZ but also indicated that no external pollutants were discharged into the river reach of the study area. In addition to CBZ, the concentration of the other four substances in site P2 decreased significantly compared to site P1. The reduction rate between P1 and P2 for these four PPCPs in both water and sediment were calculated in this study (Fig. 4b). The observed attenuation can be attributed to the contribution of the WWTP. PPCPs can be removed in STPs mainly through two processes, biodegradation and adsorption. Many studies have shown that some PPCPs can be partly or even completely removed through sewage treatment plant processes [29,30]. ME appeared to be removed effectively by the sewage treatment plant with the highest removal rate of

Table 5
Concentrations of five target PPCPs in water and sediment at the four sampling sites P1, P2, P3, and P4

PPCPs	P1		P2		P3		P4	
	Water (ng/L)	Sediment (μg/kg)	Water (ng/L)	Sediment (μg/kg)	Water (ng/L)	Sediment (μg/kg)	Water (ng/L)	Sediment (μg/kg))
CBZ	32.64	0.48	30.09	0.46	28.76	0.50	27.84	0.44
ME	37.45	0.50	5.14	0.10	4.98	0.14	4.70	0.50
FCA	51.56	4.77	44.34	2.01	40.24	1.13	38.11	0.96
TMP	23.25	0.56	23.55	0.14	12.13	0.09	8.12	0.09
TCS	36.32	15.35	19.95	0.63	9.28	0.73	7.92	2.90

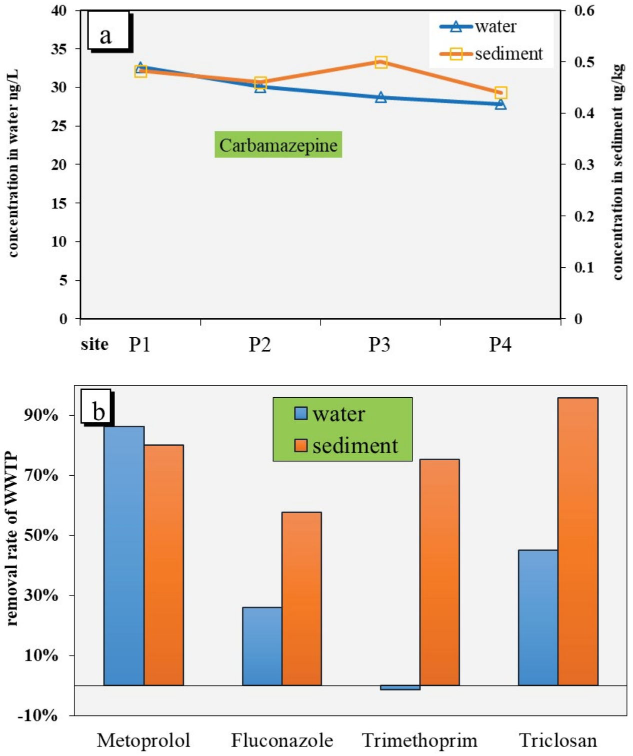


Fig. 4. Changes in CBZ concentration and attenuation rates (a) Concentration of CBZ in water and sediment at the four assessed sites and (b) Attenuation rates of the other four PPCPs at site P2 relative to P1.

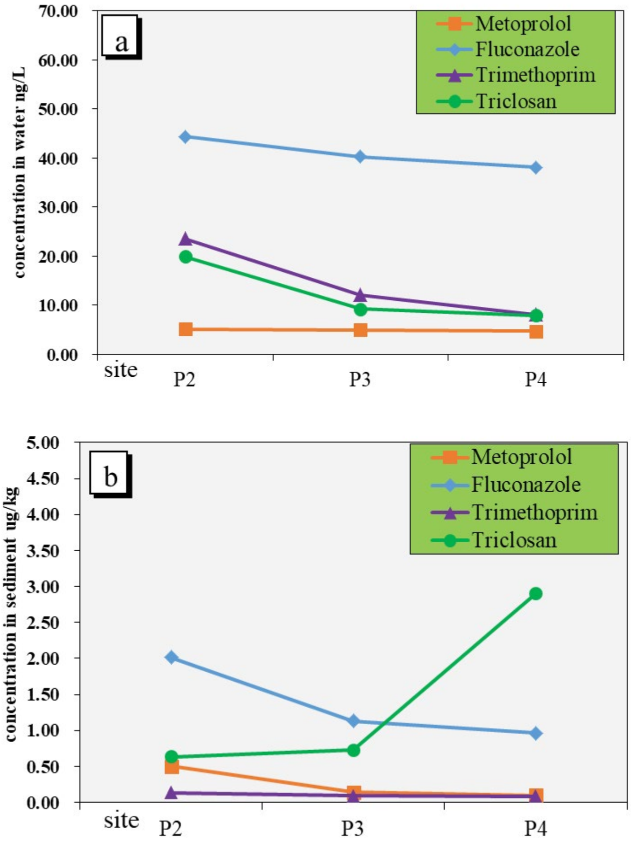


Fig. 5. Elimination of pharmaceuticals at three sampling sites along the river stretch (a) Concentrations in water and (b) concentrations in sediments.

up to 70%–90%. In addition, the concentration of triclosan in sediments at site P2 was 90% lower than at site P1. The concentration was slightly increased for TMP, showing that this compound was not effectively removed by WWTP processes and may be produced during the removal process.

3.3. Elimination of pharmaceuticals along the river stretch

The transformation of these five PPCPs was observed along the river. The changes of concentration for the target pharmaceuticals from site P2 to site P1 were attributed to the sewage treatment plant removal effect. However, the attenuation observed after site P2 likely relates to natural processes for pharmaceuticals, including photolysis, biodegradation, and adsorption processes. Except for CBZ, the other four substances showed an obvious elimination trend progressing downstream along the river stretch in Fig. 5a. In sediments, concentrations of TMP, FCA, and ME decreased gradually with the direction of current flow, while triclosan showed the opposite trend, rising constantly along the river in Fig. 5b, which may be related to the strong adsorption capacity of soil for triclosan with its high K_d value of 10,000.

The mainstream of Longgang River investigated in this study contains the section where discharge water is released from the sewage treatment plant, which is the PPCPs pollution source. Therefore, the test data meet the requirements of a single pollution source. Five kinds of PPCPs were fitted according to Eq. (2) as shown in Fig. 6. It was found that the attenuation behavior of all detected PPCPs conformed to the first-order kinetic equation, with the attenuation coefficients of all five PPCPs ranging from 0.008 to 0.11 h^{-1}. TMP had the highest attenuation coefficient and the fastest attenuation rate, while CBZ had the lowest attenuation coefficient and the slowest attenuation rate in the assessed environment.

3.4. Risk assessment of PPCPs in the mainstream of the Longgang River

In previous studies, RQ has been used to assess the ecological risks of PPCPs to aquatic organisms [26,31]. The estimated RQ values for the five PPCPs are shown in Fig. 6. Overall, the ecological risk created by triclosan was the highest among the five assessed PPCPs.

To better illustrate the level of risk generated by PPCPS, the calculated RQ was divided into four risk levels: <0.01 represents an insignificant risk; 0.01–0.1 a low risk; 0.1–1 a medium risk; and >1 a high risk [32]. As shown in Fig. 7, the calculated risk value of CBZ and TMP varied between 10^{-4}–10^{-3} and 10^{-6}–10^{-3}, respectively. The risk value of FCA was within 10^{-5}–10^{-3}, while for ME the risk level was 10^{-4}. Therefore, the ecological risks of triclosan for these three organisms were distinctly different from each other, ranging from 10^{-3} to 10^{-1}. The maximum RQ value of TCS for daphnids exceeded 0.01, indicating a low risk. The minimum RQ value of TMP was under 0.01 for green algae, showing an insignificant risk. Though there were larger differences in RQ values within the different selected models for TMP and FCA, all RQ values were below 0.01, indicating the overall risk was not significant.

In conclusion, the maximum RQ values for all target PPCPs were <0.1, indicating that the five PPCPs present in the mainstream of the Longgang River did not reach a high-risk level for the assessed organisms. However, triclosan posed a low risk, suggesting that this ecological risk should not be completely ignored. Triclosan is contained and widely used in daily cleaning products and these results may provide a reference guideline for its rational use. Additionally, the presence of PPCPs in the freshwater environment may proliferate and develop ARGs in pathogenic and environmental microorganisms, which may directly affect human health [33].

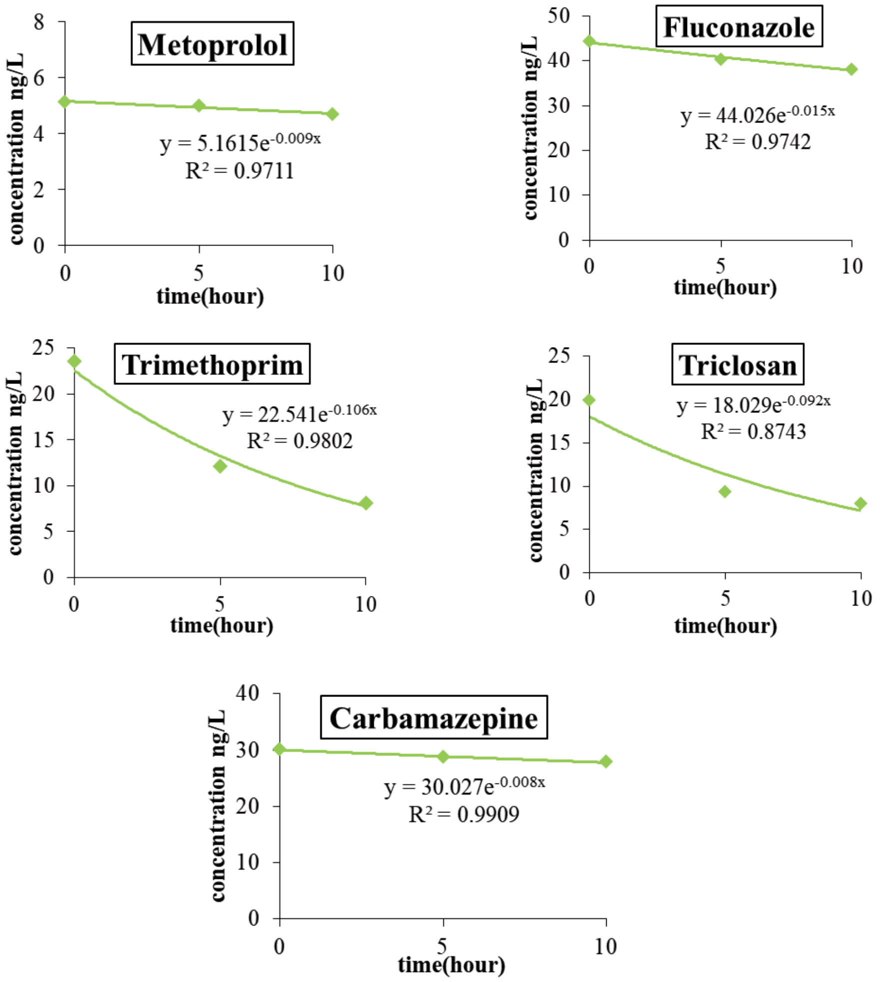


Fig. 6. Fitting model of the target PPCPs attenuation downstream in the river.

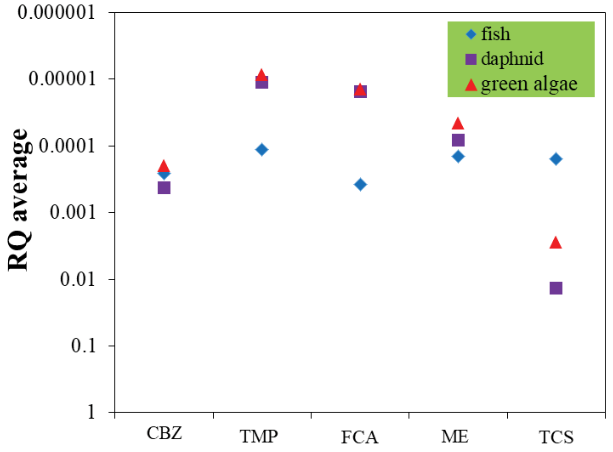


Fig. 7. Risk assessment of PPCPs in the mainstream of Longgang River (The different symbols represent the average RQ values for the three different organisms).

4. Conclusions

This study comprehensively investigated the fate of pharmaceutical residues in water and sediments of Longgang River for the first time. All four common pharmaceuticals were detected and attenuated compared to CBZ, which was used as a conservative tracer. In the selected water samples, FCA was detected with the highest average concentration ranging from 38.11 to 51.56 ng/L at all sampling sites. Triclosan was also widely distributed with high concentrations ranging from 2.9 to 15.35 μg/kg and the highest detection frequency of 100% in sediments. The concentrations of PPCPs in water and sediment samples were comparable to or higher than those in surface water, indicating the extensive and long-term use of PPCPs in this area. Triclosan's were mostly prone to accumulation in the sediment due to its high partition coefficients. The concentrations of PPCPs were significantly related to human activities and sewage discharge was likely to be the main source of PPCPs in this area. Furthermore, these results reflect that sewage treatment plants have different degrees of removal effects on target substances. Based on natural environment exposure, the risk assessment showed that CBZ, TMP, FCA, ME, and TCS posed an insignificant or low risk to aquatic organisms in the mainstream of the Longgang River, while the potential risk of PPCPs to the aquatic environment should not be ignored. These results show that some of the target PPCPs can attenuate along the river stretch and may pose a threat to the environment. More information is required on this aspect, with studies of micro-organics transformation.

However, further studies are still required analyzing more kinds of PPCPs and establishing reliable analytical methods to simultaneously determine a variety of substances, to understand the status of these emergent micro-pollutions in Longgang River. Besides, migration and transformation processes of each substance and its natural reduction process along the river should be studied thoroughly to provide a clear picture of the dominance and relevance of individual attenuation processes on organic micro-pollutants.

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References

[1] C.G. Daughton, T.A. Ternes, Pharmaceuticals and personal care products in the environment: agents of subtle change?, Environ. Health Perspect., 107(Suppl 6) (1999) 907–938.
[2] A.K. Sarmah, M.T. Meyer, A.B.A. Boxall, A global perspective on the use, sales, exposure pathways, occurrence, fate and effects of veterinary antibiotics (VAs) in the environment, Chemosphere, 65 (2006) 725–759.
[3] M. Zhang, Y. Shi, Y. Lu, The relative risk and its distribution of endocrine disrupting chemicals, pharmaceuticals and personal care products to freshwater organisms in the Bohai Rim, China, Sci. Total Environ., 590–591 (2017) 633–642.
[4] D. Tobergte, S. Curtis, Scrutinizing pharmaceuticals and personal care products in wastewater treatment, J. Chem. Inf. Model., 53 (2013) 0–9.
[5] B. Meyer, J.-Y. Pailler, C. Guignard, Concentrations of dissolved herbicides and pharmaceuticals in a small river in Luxembourg, Environ. Monit. Assess., 180 (2011) 127–146.
[6] A. Daneshvar, J. Svanfelt, L. Kronberg, Seasonal variations in the occurrence and fate of basic and neutral pharmaceuticals in a Swedish river–lake system, Chemosphere, 80 (2010) 301–309.
[7] M.Q. Cai, R. Wang, L. Feng, Determination of selected pharmaceuticals in tap water and drinking water treatment plant by high-performance liquid chromatography-triple quadrupole mass spectrometer in Beijing, China, Environ. Sci. Pollut. Res. Int., 22 (2015) 1854–1867.
[8] G.L. Page, L. Gunnarsson, J. Snape, Integrating human and environmental health in antibiotic risk assessment: a critical analysis of protection goals, species sensitivity and antimicrobial resistance, Environ. Int., 109 (2017) 155–169.
[9] Q. Bu, B. Wang, J. Huang, Pharmaceuticals and personal care products in the aquatic environment in China: a review, J. Hazard. Mater., 262 (2013) 189–211.
[10] T.R. Walsh, J. Weeks, D.M. Livermore, Dissemination of NDM-1 positive bacteria in the New Delhi environment and its implications for human health: an environmental point prevalence study, Lancet Infect. Dis., 11 (2011) 355–362.
[11] L. Li, B. Zhu, Y. Bai, Mechanisms and efficiencies of removal of PPCPs by pilot river water bypass treatment process, Environ. Sci., 39 (2018) 1637–1644.
[12] J.L. Liu, M.H. Wong, Pharmaceuticals and personal care products (PPCPs): a review on environmental contamination in China, Environ. Int., 59 (2013) 208–224.
[13] J.L. Zhao, G.-G. Ying, Y.-S. Liu, Occurrence and risks of triclosan and triclocarban in the Pearl River system, South China: from source to the receiving environment, J. Hazard. Mater., 179 (2010) 215–222.
[14] H. Lin, Y.Y. Hu, X.Y. Zhang, Sorption of triclosan onto sediments and its distribution behavior in sediment–water–rhamnolipid systems, Environ. Toxicol. Chem., 30 (2011) 2416–2422.
[15] M. Lv, Q. Sun, H. Xu, Occurrence and fate of triclosan and triclocarban in a subtropical river and its estuary, Mar. Pollut. Bull., 88 (2014) 383–388.
[16] J.C. Durán-Álvarez, B. Prado, D. González, Environmental fate of naproxen, carbamazepine and triclosan in wastewater, surface water and wastewater irrigated soil — results of laboratory scale experiments, Sci. Total Environ., 538 (2015) 350–362.
[17] L.J. Fono, E.P. Kolodziej, D.L. Sedlak, Attenuation of wastewater-derived contaminants in an effluent-dominated river, Environ. Sci. Technol., 40 (2006) 7257–7262.

[18] Q.-T. Liu, H.E. Williams, Kinetics and degradation products for direct photolysis of β-blockers in water, Environ. Sci. Technol., 41 (2007) 803–810.

[19] S. Castiglioni, R. Bagnati, R. Fanelli, Removal of pharmaceuticals in sewage treatment plants in Italy, Environ. Sci. Technol., 40 (2006) 357–363.

[20] V. Matamoros, A. Duhec, J. Albaigés, Photodegradation of carbamazepine, ibuprofen, ketoprofen and 17α-ethinylestradiol in fresh and seawater, Water Air Soil Pollut., 196 (2009) 161–168.

[21] T. Scheytt, P. Mersmann, R. Lindstädt, Determination of sorption coefficients of pharmaceutically active substances carbamazepine, diclofenac, and ibuprofen, in sandy sediments, Chemosphere, 60 (2005) 245–253.

[22] M. Clara, B. Strenn, N. Kreuzinger, Carbamazepine as a possible anthropogenic marker in the aquatic environment: investigations on the behaviour of Carbamazepine in wastewater treatment and during groundwater infiltration, Water Res., 38 (2004) 947–954.

[23] U. Kunkel, M. Radke, Fate of pharmaceuticals in rivers: deriving a benchmark dataset at favorable attenuation conditions, Water Res., 46 (2012) 5551–5565.

[24] T. Zhu, B. Duan, Z. Song, Pollution characteristics and ecological risk assessment of antibiotics in Tiegang Reservoir in Shenzhen, Ecol. Environ. Sci., 23 (2014) 1175–1180.

[25] Y. Luo, L. Xu, M. Rysz, Occurrence and transport of tetracycline, sulfonamide, quinolone, and macrolide antibiotics in the Haihe River basin, China, Environ. Sci. Technol., 45 (2011) 1827–1833.

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

[27] H. Zhou, T. Ying, X. Wang, Occurrence and preliminarily environmental risk assessment of selected pharmaceuticals in the urban rivers, China, Sci. Rep., 6 (2016) 34928.

[28] R. Dong, G. Yu, Y. Guan, Occurrence and discharge of pharmaceuticals and personal care products in dewatered sludge from WWTPs in Beijing and Shenzhen, Emerging Contam., 2 (2016) 1–6.

[29] Y. Yu, Q. Huang, Z. Wang, Occurrence and behavior of pharmaceuticals, steroid hormones, and endocrine-disrupting personal care products in wastewater and the recipient river water of the Pearl River Delta, South China, J. Environ. Monit., 13 (2011) 871–878.

[30] X. Peng, Q. Huang, K. Zhang, Distribution, behavior and fate of azole antifungals during mechanical, biological, and chemical treatments in sewage treatment plants in China, Sci. Total Environ., 426 (2012) 311–317.

[31] X.L. Wu, L. Xiang, Q.-Y. Yan, Distribution and risk assessment of quinolone antibiotics in the soils from organic vegetable farms of a subtropical city, Southern China, Sci. Total Environ., 487 (2014) 399–406.

[32] N. Li, X. Zhang, W. Wu, Occurrence, seasonal variation and risk assessment of antibiotics in the reservoirs in North China, Chemosphere, 111 (2014) 327–335.

[33] Q. Wen, L. Yang, R. Duan, Monitoring and evaluation of antibiotic resistance genes in four municipal wastewater treatment plants in Harbin, Northeast China, Environ. Pollut., 212 (2016) 34–40.