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Pharmaceutical and Personal Care Products in Surface Waters from the Inner City of Beijing, China: Influence of Hospitals and Reclaimed Water Irrigation

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Abstract

Surface waters from five districts in the inner city of Beijing were collected for analysis of 43 target compounds of pharmaceuticals and personal care products (PPCPs) to understand the spatial distribution patterns of different groups of PPCPs in the central urban area of a metropolitan city characterized by many hospitals and public parks. The total concentrations of PPCPs showed large spatial variability, ranging from 71.1 to 2400 ng/L. The x-ray contrast medium iopromide was the compound with the highest concentrations. Pharmaceuticals showed similar spatial distributional patterns with large hospitals. Positive correlations between iopromide and pharmaceuticals were observed. In contrast, in general there is no correlation between iopromide and personal care products. The concentrations of PPCPs in the landscape waters were not high but were characterized by high proportions of acidic, nonsteroidal anti-inflammatory drugs with low or even negative removal efficiencies in the WWTP in Beijing, suggesting that the reclaimed water irrigation can be another source of PPCPs in surface waters in the inner city of Beijing.

Pharmaceuticals and personal care products (PPCPs) and endocrine-disrupting compounds (EDCs) are chemicals of emerging concern that are not widely regulated or routinely monitored. PPCPs are substances used by individuals for personal or animal health or cosmetic reason. The use of PPCPs is so frequent and constant that the concentration of some of them in environment showed a phenomenon of "pseudo-persistent pollution" (Daughton 2003). PPCPs have ecological toxicity to plants and microbes (Gagne et al. 2006) and promote the development of drug-resistant microorganisms (Done and Halden 2015; Zhang et al. 2015). EDCs are compounds of natural or synthetic origin, such as natural estrogens (e.g., estrone, 17α-ethenylestriol) and synthetic estrogens (e.g., nonylphenol, bisphenol A, and herbicide atrazine). These chemicals could interfere with the balance of the hormonal system at very low concentrations (ppb to ppt) (Birkett and Lester 2003; Campbell et al. 2006).

China is one of the largest countries for production and consumption of PPCPs in the world (Liu and Wong 2013). The occurrence of PPCPs in waters of rivers flowing in large cities in China, such as Beijing, Tianjin, Shanghai, and Guangzhou, have been reported (Richardson et al. 2005; Luo et al. 2011; Xu et al. 2014). The types and contamination levels of PPCPs in the aquatic environment, however, vary among areas and regions, depending on their emission sources, the local people consumption patterns as well as hydrological and meteorological conditions. Although there have been reports on PPCPs in river waters of Beijing's suburban and rural areas (Dai et al. 2015, 2016), at present there is lack of detailed information about the spatial distribution pattern of contamination levels and types of PPCPs in surface waters, including canals, lakes, and ponds, in public parks in the central urban area of Beijing, an ancient city with dense population. The surface water system in Beijing

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is characterized by many landscape gardens in the urban areas, which are now irrigated by reclaimed water, whereas the WWTPs are mostly located in the suburban areas. Beijing has many large hospitals. There are 71 so-called Grade-A hospitals in the five inner city districts of Beijing, which are the highest grade hospitals in China with more than 500 sick beds each and high-level specialized medical and health services. Although x-ray contrast medium can be used as a marker of medical waste water, unfortunately, to date, there is little report on the occurrence of x-ray contrast medium in environmental media in China (Yu et al. 2011) and no report on x-ray contrast medium in the aquatic environment in Beijing.

In this study, five inner city districts of Beijing were selected as the study area. The concentrations of PCCPs in surface water samples were analyzed, and the spatial distribution of concentrations of and composition profiles of PCCPs are discussed. The emphases are put on the influences of hospitals and the reclaimed water irrigation on the spatial distribution of different groups of PPCPs in a typical metropolitan city's central urban areas to provide basic information for the control and prevention of pollution by PCCPs in urban aquatic environment.

Materials and Methods

The rivers in Beijing are originated in the northwestern mountain areas and flow to the southeastern plain areas. The water sampling sites in Beijing are located within the Fifth Ring Road of the central part of the city and are less affected by industries and agriculture. Water samples were collected at 21 sites in the 5 inner-city districts of Beijing, i.e., Fengtai, Haidian, Xicheng, Dongcheng, and Chaoyang Districts (Fig. 1) in March 2017, which is in the typical dry season of North China. Detailed information about each sampling site is summarized in Table S1 in Supplementary Information (SI). Samples were taken from 0.2-m below the water surface using a stainless steel bucket, transferred into a 2-L amber glass bottle, and transported in an insulated cooler box packed with "blue ice." Upon arrival at the laboratory, samples were immediately filtered with 0.45-μm filters with pH adjusted to 2.5 with diluted H_2SO_4, and stored at 4 °C in the dark before extraction. Field blank and travel blank samples (Millipore water) also were taken.

Forty-three PPCP target compounds in the water samples were analyzed with high-performance liquid chromatography (HPLC) coupled with tandem mass spectrometry (MS/MS), including 20 antibiotics, 14 nonantibiotic drugs, 8 PCPs, and x-ray contrast medium iopromide (Table S2). Standards of individual PPCPs were purchased from Sigma-Aldrich and AccuStandard (USA). The mass-labeled standards of ofloxacin-D8, sulfamethoxazole-D4, ibuprofen-^{13}C,

Fig. 1 Map of the surface water sampling sites in urban areas of Beijing in March 2017

ciprofloxacin-^{13}C, and erythromycin-^{13}C-D3 were purchased from Wako, Japan. Methanol and acetonitrile were HPLC grade obtained from Merck, Germany. Formic acid, ammonium acetate, and Na_2-EDTA were purchased from Fluka, Inc., USA. All of the water used in the experiment was Milli-Q water.

To facilitate sample collection and storage, shorten the pretreatment time, and prevent degradation of target compounds during sample pretreatment, a sample size of 250 mL was selected. Before the sample pretreatment, 5 mL of freshly prepared 5% (mass fraction) Na_2-EDTA solution were added to the samples (including transportation blank samples) to prevent the chelated reaction of the target PPCPs, such as tetracycline and ciprofloxacin with metal ions (Llorens-Blanch et al. 2015). Then, 100 μL of the mixed isotope-labeled standard solution was added to the sample and was passed through membrane filtration apparatus to filter out the suspended particles and planktons in the samples.

The hydrophilic-lipophilic balance cartridge was used in this study because of its good recovery and reproducibility for polar and nonpolar compounds and suitability for a wide range of pH (pH 0–14). The Oasis HLB column (500 mg, 6 cc, Waters, USA) was used for extraction and enrichment of the target PPCPs. Before loading the samples, the HLB cartridges were first cleaned and preconditioned by the following procedures: 5 mL of methanol containing 1% ammonia (volume fraction), 5 mL of methanol, and 5 mL of Milli-Q water were passed in sequence through the HLB cartridge. The flow rate was adjusted by using a vacuum pump and controlled at 5–10 mL/min when loading the samples. After all the samples had passed, 5 mL of Milli-Q water was

used to leach the HLB column, and then the column was centrifuged at 4000 r/min for 10 min to remove the residual water. The eluents were then concentrated to 1 mL under a gentle stream of nitrogen.

All of the target compounds were analyzed using a liquid chromatography (Agilent 1200) coupled with tandem mass spectrometer (Sciex API4000) in a positive or a negative electrospray mode. Due to the different properties of the target compounds, two kinds of electrospray ionization source mode (the positive and negative ionization modes) were used. XBridge C18 column (3.5 μm, 4.6 mm × 150 mm; Waters company, USA) equipped with a guard column was used for both positive and negative modes. In the positive mode (ESI+), the gradient elution was performed with 2 mM of ammonium acetate solution containing 0.1% formic acid as solvent A and methanol-acetonitrile (1:1, *v*/*v*) solution as solvent B. The gradient profile was as follows: initially 90% of A and 10% of B, maintaining for 0.5 min, then linearly to 95% of B and 5% of A in 13 min and maintaining 7 min, finally with the initial mobile phase ratio 90% of A and 10% of B rebalancing for 7 min. In the negative mode (ESI-), 2 mM of ammonium acetate solution and methanol-acetonitrile (1:1, *v*/*v*) solution were chosen as solvent A and solvent B. The gradient elution procedures were: initially 5% of B to maintain 1 min, then linearly up to 95% (B) in 12 min and maintaining 8 min, and then with the initial mobile phase ratio 95% of A and 5% of B maintaining 7 min. For both positive and negative modes, the sample injection volume was 10 μL. The sample injection rate was 200 μL/min, and the flow phase rate was 400 μL/min. The column temperature was 40 °C.

The MS conditions were as follows. In positive mode, the collision gas pressure was 34.5 kPa with the air curtain gas pressure (CUR) setting at 69 kPa. The pressure of ion source gas 1 (GS1) and Ion source gas 2 (GS2) were 241 and 103 kPa respectively. The spray voltage (IS) was 5000 kV. The ion source temperature was 550 °C. In the negative mode, the collision gas pressure was 34.5 kPa, and the air curtain gas pressure was 69 kPa. The atomizing air pressure was 276 kPa. The auxiliary heating pressure of 138 kPa (IS) and the spray voltage of −4500 kV were applied. The ion source temperature was 450 °C. The multiple reaction monitoring (MRM) mode was applied for both the two ion source modes.

The recovery test was performed using both mass-labeled and native standard chemicals. Quantitative responses were evaluated according to the amount of standards added. Concentrations of analytes were calculated using an external calibration curve. The accuracy evaluation was performed by recovery tests with actual environmental water samples and Milli-Q water. When the peak area was greater than the procedure blank and the signal-to-noise ratio (S/N) was ≥ 10, the lowest concentration of the target analyte was defined as limits of detection (LODs). Table 1 presents the MRM procedural blanks, recoveries, LODs, and standard deviations (SDs) for individual PPCP compounds.

Results and Discussion

The concentrations of the individual compounds in antibiotics, nonantibiotic pharmaceuticals, and personal care products and EDCs in surface waters at 21 sampling sites in the inner city of Beijing are listed in Tables S2, S3, and S4 in SI, respectively. The maximum concentrations, means, and detection frequencies of each target analytes are summarized in Table S5 in SI. Eleven compounds of the 43 target PPCPs were detected with detection frequencies greater than 50%. Among them 8 compounds (erythromycin, clarith, triclosan, triclocarban, bisphenol A (BPA), DEET (N, N-diethyl-m-toluamide), and atrazine (ATZ) were detected with detection frequencies of 100%. The total concentrations of PPCPs in the water samples showed large spatial variability, ranging from 71.1 to 2400 ng/L, with an average value of 600 ng/L and the maximum at the sampling site 3. Figure 2 shows the spatial distribution of three groups of PPCPs and iopromide in the five districts of Beijing. The total concentration of antibiotics was in the range from 3.88 to 494 ng/L (the average: 95.8 ng/L), with the maximum at Site 2. The total concentration of nonantibiotic drugs (excluding iopromide) was in the range from 4.4 to 548 ng/L, the average value was 108.8 ng/L, and the maximum was at Site 2. The total concentration range of personal care products was 37.1–333 ng/L, the average value was 84.7 ng/L, and the maximum was at Site 5. The concentration range of atrazine ranged from 1.6 to 22.4 ng/L, with an average of 7.4 ng/L and the maximum at Site 21.

The iodinated x-ray contrast medium iopromide was the compound with the highest concentrations, with the maximum concentration up to 1956 ng/L (Site 3) and the mean 296.3 ng/L. Paracetamol was the compound with the second highest average concentration (32.7 ng/L), followed by > DEET (30.8 ng/L) > doxycycline hyclate (29.0 ng/L) > BPA (13.8 ng/L) > erythromycin, (12.1 ng/L) > ketoprofen (11.0 ng/L). All other PPCPs had relatively lower concentrations (< 10 ng/L). The concentrations of sulfamerazine, ceftiofur, ciprofloxacin, minocycline, thiamphenicol, β-lactam, and dexamethasone were below the LODs at any sampling site. Compared with the previously reported PPCPs in river waters of the Beijing's suburban and rural areas, our results showed different contamination levels and compositions. Dai et al. (2015, 2016) reported that except for caffeine (not measured in our study), DEET was the compound with the highest concentrations among all 15 analytes in river waters of the Beijing's suburban and rural area, followed

Table 1 MRM transitions, limits of detections, procedural blanks, and procedural recoveries of each PPCP compound in water samples

Compounds	Abbreviations	MRM transition 1 (m/z)	MRM transition 2* (m/z)	LOD (ng/L)	Blank (ng/L)	Recovery (%)	RSD (%)
Sulfadiazine	SD	251.1/156.1	251.1/108.1	0.20	< 0.20	107	5.8
Sulfamethoxazole	SMX	254.1/156.1	254.1/108.1	0.20	< 0.20	99.6	8.2
Sulfamerazine	SMZ	265.2/156.1	265.2/108.1	0.05	< 0.05	94.6	8.4
Trimethoprim	TMP	291.0/230.0	291.0/123.0	0.10	< 0.10	97	7.3
Nalidixic Acid	NA	233.0/215.0	233.0/187.0	0.10	< 0.10	104	7.8
Norfloxacin	NOR	320.2/302.1	320.2/276.2	0.10	< 0.10	84.7	6.7
Enrofloxacin	ENR	360.2/316.3	360.2/342.3	0.20	< 0.20	90	10.0
Ofloxacin	OFL	362.2/318.2	362.2/261.2	0.05	< 0.05	111	12.3
Ciprofloxacin	CIP	332.0/230.9	332.0/313.9	0.05	< 0.05	68.4	5.6
Doxycycline	DC	445.2/428.2	445.2/410.0	0.50	< 0.50	114	11.2
Tetracycline	TC	445.2/154.0	445.2/426.9	0.50	< 0.50	107	11
Oxytetracycline	OTC	461.1/443.2	461.1/425.9	1.00	< 1.00	110	17.9
Minocycline	MC	458.1/441.2	458.1/283.0	2.00	< 2.00	112	7.8
Erythromycin	ERY	734.6/158.2	734.6/576.2	0.10	< 0.10	84.5	4.6
Clarithromycin	CLA	748.4/590.5	748.4/158.2	0.10	< 0.10	98	11.4
Chloramphenicol	CAP	320.9/256.9	320.9/193.8	0.10	< 0.10	108	6.2
Thiamphenicol	TAP	353.9/289.8	353.9/184.8	0.10	< 0.10	102	7.1
Ampicillin	AMP	350.1/160.1	350.1/114.0	0.50	< 0.50	101	10.2
Aztreonam	ATM	436.0/313.0	436.0/356.0	0.50	< 0.50	112	10.9
Ceftiofur	CTF	523.9/240.9	523.9/209.8	1.00	< 1.00	111	5.5
Paracetamol	APAP	152.1/110.0	152.1/64.9	0.50	< 0.50	84.2	10.1
Ibuprofen	IBU	204.9/160.9	204.9/158.9	0.10	< 0.10	106	7.3
Naproxen	NAP	228.9/169.9	228.9/184.9	0.50	< 0.50	95.6	8.7
Ketoprofen	KTP	253.0/209.0	253.0/197.0	0.10	< 0.10	105	5.4
Diclofenac acid	DIC	293.8/249.8	293.8/213.9	0.10	< 0.10	95.5	3.1
Carbamazepine	CBZ	237.1/194.2	237.1/192.0	0.10	< 0.10	108	6.5
Diphenhydramine	DHM	256.3/167.1	256.3/152.2	0.10	< 0.10	91.8	12.4
Fluoxetine	FXT	310.3/44.1	310.3/148.2	0.10	< 0.10	102	11.5
Diltiazem	DTZ	415.2/178.1	415.2/370.2	0.10	< 0.10	107	13.4
Metoprolol	MPL	268.2/116.2	268.2/191.1	0.10	< 0.10	86.5	11.1
Atorvastatin	ATO	559.4/440.3	559.4/488.2	0.10	< 0.10	62	8.7
Gemfibrozil	GEM	249.0/120.9	249.0/126.9	0.10	< 0.10	107	7.8
Bezafibrate	BZF	360.1/274.0	360.1/154.0	0.10	< 0.10	100	6.1
Iopromide	IPM	792.0/573.1	792.0/559.0	0.50	< 0.50	97.1	8.7
Dexamethasone	DEX	393.1/355.3		0.50	< 0.50	106	12.7
Bisphenol A	BPA	226.9/211.8	226.9/132.8	0.10	< 0.10	95.7	8.1
Diethylstilbestrol	DES	267.0/251.0	267.0/236.9	0.40	< 0.40	84.6	7.0
Estrone	E1	269.0/145.0	269.0/158.9	0.40	< 0.40	93.7	3.3
17α-Ethinylestradiol	EE2	295.3/144.8	295.3/158.8	2.00	< 2.00	90.7	8.1
Triclosan	TCS	286.6/35.0	286.6/268.8	0.10	< 0.10	71.8	3.0
Triclocarban	TCC	312.9/159.7	312.9/125.9	0.05	< 0.05	76	5.4
Diethyltoluamide	DEET	192.1/119.1	192.1/91.1	0.05	< 0.05	105	7.8
Atrazine	ATZ	216.0/174.1	216.0/96.0	0.10	< 0.10	110	7.3
Mass-labeled	SMX-D_4	258.0/159.9	258.0/112.1	0.10	< 0.10	99.5	6.6
Standards	OFX-D_8	370.1/326.0	370.1/265.0	0.10	< 0.10	95.3	10.2
	CIP-^{13}C	336.0/318.0	336.0/248.0	0.10	< 0.10	71.1	4.8
	ERY-^{13}C-D_3	738.3/580.3	738.3/162.1	0.10	< 0.10	102	12.8
	IBU-^{13}C	208.0/163.1	208.0/161.0	0.10	< 0.10	91	4.4
	ATZ-D_5	221.2/179.2	221.2/69.1	0.10	< 0.10	102	11.9

*MRM transition 2 were not used for quantification

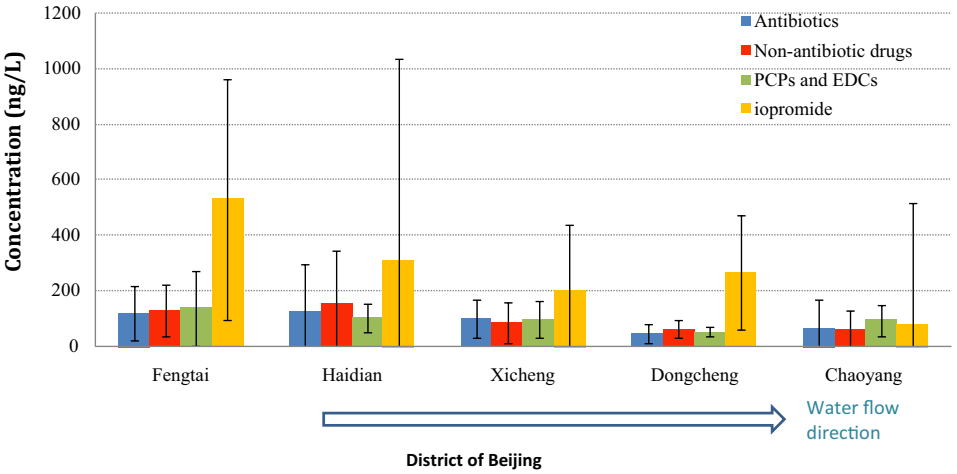

Fig. 2 The average concentrations of three groups PPCPs and iopromide in the surface water samples from the inner city of Beijing (the error bars denote standard deviations)

by metoprolol, ketoprofen, diclofenac, trimethoprim, and carbamazepine with the mean concentrations above 50 ng/L.

The spatial distribution of antibiotics, non-antibiotic drugs, personal care products and EDCs, and iopromide are showed in Fig. 3a–d, respectively. In the antibiotic group, sulfonamides and macrolides were found at low levels in most of the samples. Tetracycline-type antibiotics occurred only at some particular sites (1, 2, 10, and 18) with relatively high concentrations, where several veterinary hospitals, such as the Veterinary Research Institute of Beijing, Chinese Academy of Agriculture and Forestry, are located near these sites, suggesting that tetracycline was mainly used for animals in Beijing. It is not difficult to find out that the spatial distribution of antibiotics is closely related to the distribution of the major hospitals in the city by comparing the distribution map of the sampling sites (Fig. 1). Sites 1, 2, and 3 are located near Beijing Tumor Hospital, the General Hospital of Air-force, and other large hospitals. Site 10 is located near the China-Japan Friendship Hospital; and Site 18 is very close to two pet hospitals. The sampling sites 5, 6, and 13 are located in an area where large- and medium-sized hospitals, such as the Capital Medicine Institute and the Navy Hospital, are intensively distributed. Generally the concentration distribution of antibiotics in surface waters in the central urban area of Beijing is basically showing a trend of higher concentrations of antibiotics in the northeast of the city and lower concentrations in the southwest that is in accordance with the density of large hospitals in Beijing.

The concentrations of the non-antibiotic drugs (excluding iopromide) in surface waters in the central urban area of Beijing also varied spatially. The minimum total concentration of nonantibiotic drugs (4.4 ng/L) occurred at Site 7 where the drinking water source of the city is located and the maximum as high as 548 ng/L occurred at Site 2. The detection rates of six groups of the investigated non-antibiotic drugs were in the sequence of analgesic and anti-inflammatory drugs (100%) > anticonvulsant drugs (90.5%) > antidepressant drugs > cardiovascular agent drug (85.7%) > anti-allergy drug (71.4%) > estrogen (52.4%). In most of the sampling sites, ibuprofen and naproxen were not detected. The distribution pattern of nonantibiotic drugs is similar to that of antibiotics. Analgesic and anti-inflammatory drugs contributed a larger proportion of the nonantibiotic drugs. The sampling sites with high concentrations of nonantibiotics also are mostly located in the areas where hospitals are densely distributed. Similar cases were reported; for example, trimethoprim, erythromycin, dihydrate, norfloxacin, ofloxacin, and diclofenac sodium were the most frequently detected pharmaceuticals in hospital effluents in Hangzhou, China (Chen et al. 2012).

The concentrations of iopromide in the surface waters of the central urban area of Beijing had a very obvious characteristic spatial distribution pattern. In the areas along the western Third Ring Road and the southwestern Second Ring Road, there are many Grade-A hospitals (19 in Haidian District alone), such as Beijing Tumor Hospital, Tiantan Hospital, and Capital Medical University Affiliated Hospital. In particular, in the vicinity of Beijing Tumor Hospital (Sites 3 and 5), the concentrations of iopromide can be as high as μg/L level. Iopromide is a nonionic, low osmolar contrast agent mainly used as an x-ray contrast medium and auxiliary developer agent for large diagnostic equipment. Iopromide can be applied in high concentrations by intravenous injection and are rapidly released via urine and faeces (Drewes et al. 2001). On the other hand, iopromide is not easily degraded (Steger-Hartmann et al. 1999). In addition, iopromide was not effectively removed in WWTPs (Miege et al. 2009). Therefore, an alternative scenario might be that iopromide could be from the effluent of the WWTPs in Beijing. However, the WWTPs are mostly located in the western suburban areas of Beijing. The water flow direction is from northeast and east to west, and the occurrence of iopromide was not evenly distributed but mainly distributed near large hospitals in the east part of Beijing City. Therefore, the

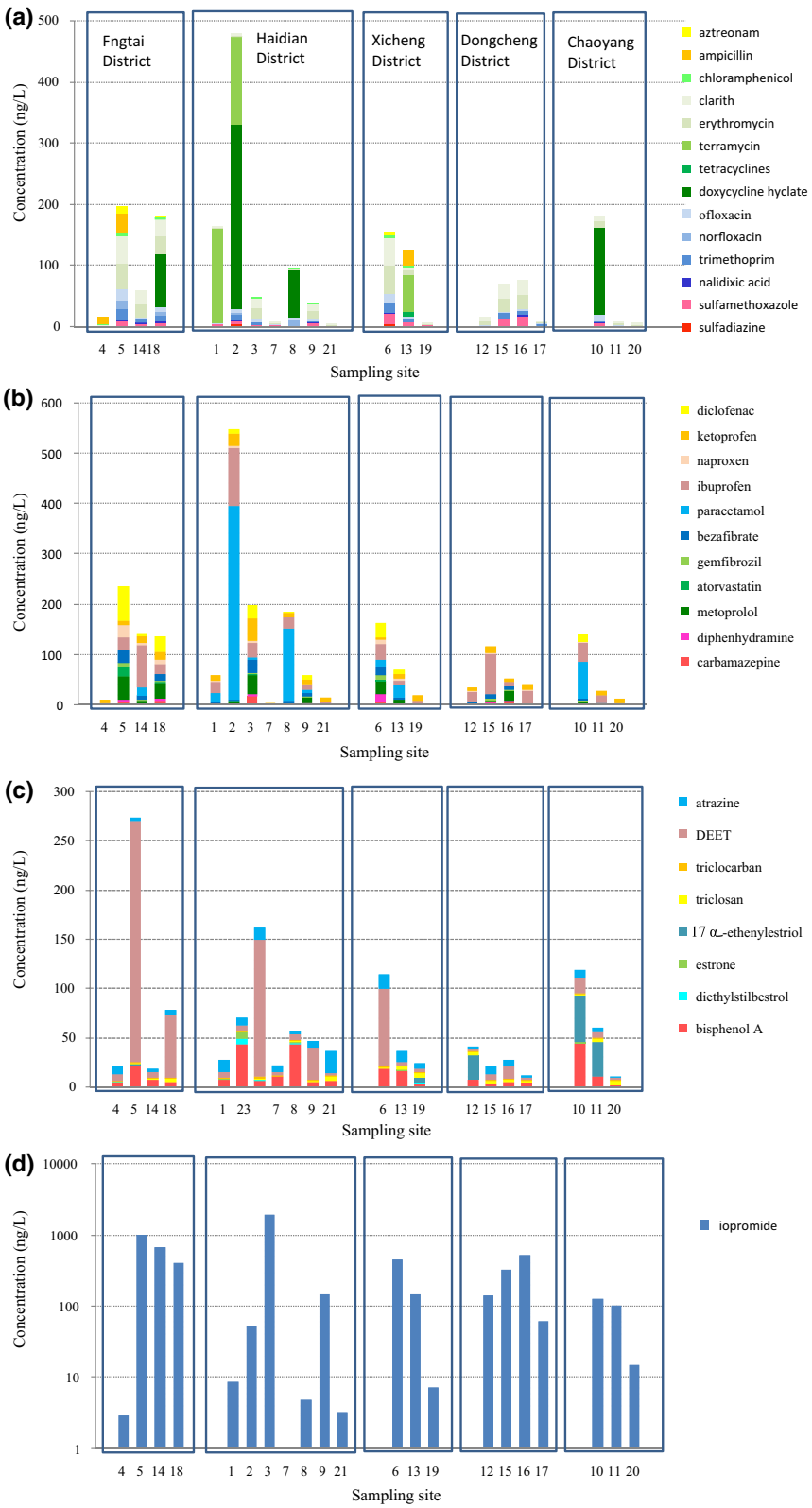

Fig. 3 The concentrations of **a** antibiotics, **b** nonantibiotic drugs, **c** personal care products, and **d** iopromide (in logarithm scale) in surface waters in the inner city of Beijing

possibility that iopromide could be from the effluent of the WWTPs in Beijing or reclaimed water irrigation could be ruled out. There were weak positive correlations between iopromide and antibiotics, nonantibiotic drugs, and personal care products/EDCs, whereas iopromide showed no correlations with atrazine and bisphenol A (Fig. 4a).

Estrogenic drugs diethylstilbestrol, estrone (E1), and 17α-ethenylestriol (EE2) also has obvious spatial distributional characteristics, which were mainly distributed in the eastern and northeastern Third Ring Road area of Chaoyang District. There are a few maternity hospitals near the sampling sites 10, 11, and 12. Such specialized hospitals for gynaecology and obstetrics will use a large amount of estrogen drugs, so the estrogenic concentrations in the surface waters in these areas were higher than those in other areas.

The concentration of bisphenol A (BPA) were in the range from 2.6 to 46.0 ng/L, averaging 13.8 ng/L. BPA is a building block chemical used in making fragrances, surfactants, thermoplastic elastomers, antioxidants, adhesives, coatings, carbonless copy paper, and high performance rubber paper (Huang et al. 2012; Oketola and Fagbemigun 2013). The potential emission sources of BPA could be from both industrial and domestic sewage discharge (USEPA 2014). It has been reported that the total removal rates of BPA in a Chinese WWTP were 79.5% (Zheng et al. 2011). The concentrations of BPA both showed evenly spatial distribution patterns without unusually high values, demonstrating that they were likely from the domestic sewage due to the fact that there is no industrial point source in the central urban area of Beijing.

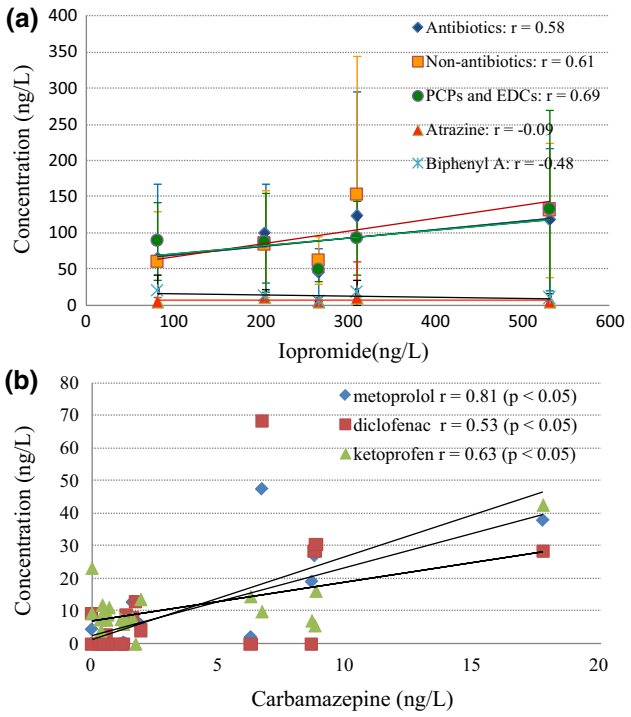

Fig. 4 **a** Correlations between the average concentrations of iopromide in the five inner city districts with those of antibiotics, nonantibiotic drugs, personal care products/EDCs, and atrazine ($p < 0.1$; the error bars denote standard deviations); **b** correlations of the concentrations of carbamazepine with those of diclofenac, ketoprofen, and metoprolol at the 21 sampling sites (r denotes Pearson correlation coefficient and p is the significance level)

The concentration level and variation range of herbicide atrazine were low but were detected in all samples. As a herbicide, it is a good indication of agricultural sources. However, as the sampling sites are all located in the urban area (within the Fifth Ring Road of the city), farms are extremely rare and therefore the occurrence of atrazine was less affected by agricultural activities in the urban area of Beijing. The possible source is the application of atrazine as a herbicide in the urban green belts, as proved by its evenly spatial distributional pattern. There were no correlations between atrazine and other PPCP compounds, which could be explained because atrazine is directly sprayed in the gardens in the form of solution of technical products with no other sources.

Except for DEET, the concentrations of the investigated individual personal care products showed no correlation with iopromide. DEET had a large spatial variation of concentration, with the lowest concentration of 2.0 ng/L and the highest up to 245 ng/L. Abnormally high concentrations of DEET occurred at three sampling sites (Site 3, 5, and 6), and it is presumed that they might have the same kind of source. DEET occurred at comparable or higher concentrations in the central urban Beijing than in some of other regions and countries. For example, a concentration range of 3–57 ng was reported in waters of the Pearl River in the southern China (Yang et al., 2013). DEET has been detected at low concentrations in water of the Danube River, Germany (<LOQ—81 ng/L, mean: 13 ng/L) (Loos et al. 2017). As a common active ingredient in insect repellents, DEET is intended to be applied to the skin or clothing and provides protection against mosquitoes and many other biting insects usually as a component of nonhospital prescription commercial products.

The sampling sites 4, 9, 16, 19, and 20 are ornamental waters in Fengtai Garden (a public park), Yuan Dynasty Ruins Park, Longtan Park, Beihai Park, and the Olympic Park, respectively. These landscape water bodies in the parks are less disturbed by external water bodies and far away from the sewage pipes due to the control of the water quality of the parks by municipal management departments. The PPCPs concentrations in the landscape waters were not high but characterized by high proportions of diclofenac, ketoprofen, metoprolol, and carbamazepine that belong to the class of acidic nonsteroidal anti-inflammatory drugs (NSAIDs). Reclaimed water is practically used for irrigation purpose in Beijing central urban area. For example, the consumption of reclaimed water in the city was 860 million cubic meters in 2014. To date, there are already 16 reclamation plants in Beijing. The composition of PPCPs in the effluents from different WWTPs may be different. Gao et al. (2016) reported that negative removal efficiencies in a WWTP in

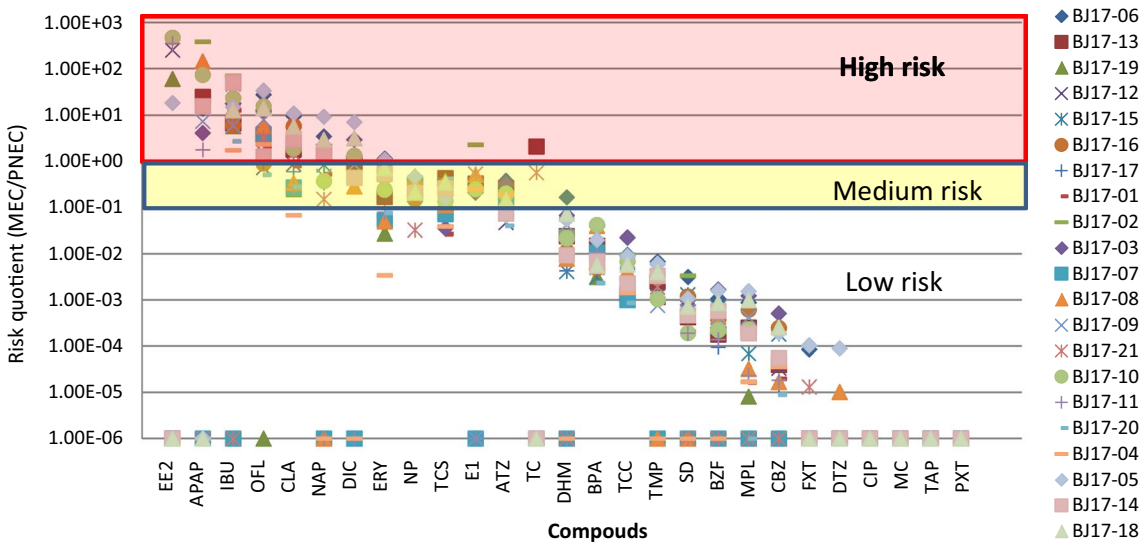

Fig. 5 Environmental risk quotients of pharmaceuticals and personal care products in Beijing inner-city surface waters

Chaoyang District of Beijing were obtained for metoprolol and carbamazepine. Low removal rates for diclofenac (0–24%) and ketoprofen (0–50%) in WWTPs in Spain were reported (Camacho-Muñoz et al. 2012). At this stage, no data about the removal rates of diclofenac and ketoprofen in WWTPs in Beijing available.

Figure 4b shows that there were positive correlations of the concentrations of carbamazepine with other NSAIDs, i.e., diclofenac, ketoprofen, and metoprolol in the surface waters at the 21 sampling sites in the inner city area of Beijing. These compounds may be an index for the reclaimed water irrigation in Beijing. It has been suggested that the acidic drugs, naproxen, ibuprofen, gemfibrozil, can be regarded as an indicator of municipal sewage (Yargeau et al. 2007; Liu et al. 2014; Yang et al. 2017). No correlations of these acidic pharmaceuticals with BPA and DEET were found in our study; therefore, they may represent different modes of sewage discharge (i.e., effluents from WWTPs or reclaimed waters, direct discharge of domestic sewage via municipal rain drainage system, urban road rainwater runoff, leachate of domestic trashes, and illegal discharge).

Pharmaceuticals and EDCs are not included in the water environmental quality standard of China and, hence, not directly regulated. Although it is not common international practice to regulate or provide guidelines for PPCPs in surface waters, a few countries have taken proactive approaches and do provide guideline concentrations for certain pharmaceuticals and EDCs that are applicable to reclaimed water. For example, Australia has put forward the water reuse standard and set up discharge threshold for water reuse for some drugs and EDCs in effluents from sewage treatment plants (NRMMC, 2008). In the United Kingdom, the standard for estrogens in effluent water from WWTPs that the concentration of estrogenic hormones has been recommended (Williams et al. 2008). Our results show that the concentrations of metoprolol, diclofenac, E1, and EE2 at several sampling sites had exceeded the threshold values of these guidelines (metoprolol: ≤ 25 ng/L and diclofenac: ≤ 1.8 ng/L by the Australian standard; $([E1]/3 + [E2] + 10[E2]) \leq 1$ ng/L by the UK standard, where the square brackets denote concentrations).

Although the detection concentration of PPCPs in the aquatic environment is generally very low and does not cause acute toxic effects, the long-term cumulative toxic effects of PPCPs on aquatic organisms exposed to them throughout the life cycle cannot be ignored. In this study, ecological risk associated with PPCPs in surface waters from the inner city area of Beijing was preliminarily assessed based on the risk quotient (RQ) that is defined as the ratio between the measured environmental concentration (MEC) to the predicted no-effect concentration (PNEC) of the PPCPs following the Technical Guidance Document on Risk Assessment from the European Commission (European Commission 2003):

$$RQ = MEC/PNEC$$

$$PNEC = (EC50 \text{ or } LC50)/1000$$

where EC50 and LC50 denote the concentrations required to cause short-term and lethal effects, respectively, on half the organisms of a tested population after a specified exposure time. According to this criterion, $RQ < 0.1$ implies the minimum risk to the organisms, $0.1 \leq RQ \leq 1$ implies medium risk and RQ=1 implies high risk (Hernando et al. 2006). In the present study, the PNEC values for water samples ($PNEC_{water}$) of the detected PPCPs were adopted from the literature when available (Young et al. 2002; Caldwell et al.

2012; Verlicchi et al. 2012a, b). Figure 5 showed the risk assessment for 27 PPCPs in the Beijing urban surface waters using PNEC values for fish species. In this work, surface water samples were collected in the low water season in Beijing and therefore should reflect the upper environmental risks limits.

Among the 27 PPCPs and EDCs being assessed for environmental risk, 10 compounds (EE2, paracetamol, ibuprofen, ofloxacin, diclofenac, clarith, naproxen, E3, tetracycline, and erythromycin) showed the RQ values greater than 1 at certain sampling sites which means an ecological "high risk" is suspected, whereas those of the other PPCPs and EDCs were all below 1. In case of EE2, paracetamol, ibuprofen, and ofloxacin, very high RQ values (> 1) at some particular sites (e.g., Sites 1, 5, 10, 11, and 19 for EE2; Sites 1, 2, 6, 8, and 13 for paracetamol), which warrant high risk against fish. At more than half of the sampling sites, erythromycin, tetracycline, atrazine, and diphenhydramine showed medium risk. These results show that the ecological environment in the surface water system of the inner city of Beijing is seriously affected by some antibiotics (ofloxacin, diclofenac, clarith, tetracycline, and erythromycin), analgesic and anti-inflammatory pharmaceuticals (paracetamol, ibuprofen, naproxen, diclofenac), and EDCs (EE2, E3, and atrazine).

Overall, the high concentrations of iopromide at the sampling sites near hospitals may be an indication of untreated sewage discharge into natural water bodies directly from hospitals or by patients. Reclaimed water irrigation could be another source of PPCPs in surface waters in the inner city of Beijing. This study presents only preliminary results. More detailed investigation is needed with more sampling sites and on the composition of PPCPs in the reclaimed waters used for irrigation purpose in the green belts and public parks in Beijing.

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