

Occurrence, distribution and risk assessment of abused drugs and their metabolites in a typical urban river in north China

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HIGHLIGHTS

- We developed a method for determining 11 abused drugs in water and sediment.
- METH and EPH were the dominant drugs in water and sediment in Beiyunhe River.
- Abuse drugs in Beiyunhe River were mainly from hospitals and sewage effluents.
- Abused drugs in the water would not impair the aquatic ecosystem biologically.

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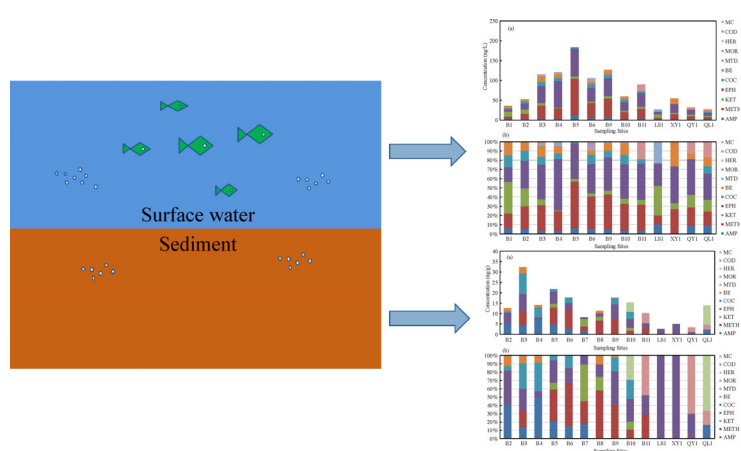
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ABSTRACT

This study investigated the presence of 11 abused drugs and their metabolites, including amphetamine, methamphetamine (METH), ketamine, ephedrine (EPH), cocaine, benzoylecgonine, methadone, morphine, heroin, codeine, and methcathinone in the surface water and sediment samples of Beiyunhe River, a typical urban river flowing through Beijing, Tianjin, and Hebei provinces in North China. An analytical method of determining these abused drugs and their metabolites in water and sediment was developed and validated prior to sample collection in the study area. Results showed that METH and EPH were predominant in water and sediment samples. The total drug concentrations ranged from 26.6 to 183.0 ng/L in water and from 2.6 to 32.4 ng/g dry weight in sediment, and the drugs mainly originated from hospitals and sewage treatment plants. The average field-based sediment water distribution coefficients of abused drugs were calculated between 149.3 and 1214.0 L/kg and corrected by organic carbon. Quotient method was used to assess the risks. The findings revealed that these drugs and their metabolites at determined concentrations in water samples will not impair the aquatic ecosystem biologically, but their potential harmful effect on the function of the ecosystem and human health should not be overlooked.

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1 Introduction

Contamination by pharmaceuticals in the aquatic environment has drawn a widespread concern (Daughton and Ternes, 1999; Pereira et al., 2016; Chen et al., 2018; Huang

et al., 2018). Among various pharmaceuticals, abused drugs are a class of emerging compounds that may pose great challenges to environmentalists due to their trace levels and unknown biological effects to the ecosystem (Chiaia et al., 2008; Zuccato et al., 2008; Pal et al., 2013; Rosi-Marshall et al., 2015; Guo et al., 2017). World Drug Report in 2016 estimated that more than 329 million people worldwide are taking drugs, with thousand tons of consumption of abused drugs per annum (UNODC, 2016).

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Large amounts of abused drugs have been released into the environment during manufacturing, trafficking, and post-consumption, resulting in the wide detection of this kind of emerging compounds worldwide.

The presence of abused drugs with concentrations from pg/L to ng/L has been reported in different aquatic environments, such as lakes, rivers, coastal waters, and other natural waters from Spain (Boleda et al., 2009; Mendoza et al., 2014), Switzerland (Berset et al., 2010), Italy (Zuccato et al., 2008), France (Nefau et al., 2013), US (Bartelt-Hunt et al., 2009), UK (Baker and Kasprzyk-Hordern, 2013), and China (Li et al., 2016; Wang et al., 2016; Yao et al., 2016; Zhang et al., 2017). The major source of abused drugs in the natural environment is the effluents of sewage treatment plants (STPs) (Zhao et al., 2017; Hu et al., 2018; Xu et al., 2018); these wastes contain the raw influents with the original abused drugs or their metabolites via human excretion (McCall et al., 2016). In the STPs, the removal rates of abused drugs vary for every compound. For example, the removal efficiency of cocaine (COC) and amphetamine (AMP) was greater than 90%, whereas that for methamphetamine (METH) or ecstasy was less than 50% (Kasprzyk-Hordern et al., 2009; Boles and Wells, 2010). The majority of these abused drugs can not be completely eliminated in the conventional STPs, and a large number of drugs enter different water bodies with the discharged effluents (Pal et al., 2013).

In most cities worldwide, discharged effluents are an important water resource to supplement urban rivers. The areas in North China are short of water resources, and effluents from STPs are discharged directly into urban rivers, such as Beiyunhe River. Beiyunhe River flows through Beijing, Tianjin, and Hebei provinces and is heavily polluted by anthropogenic activities. Xu et al. (2016) reported antibiotic contamination in seven urban rivers in Beijing, including Beiyunhe River, with sulfonamide and tetracycline concentrations ranging $1.3 \times 10^{-1.5} \times 10^3$ ng/L and $3.9 \times 10^{-5.4} \times 10^4$ ng/L, respectively. The concentration of 15 selected pharmaceutically active compounds in the surface water of Beiyunhe River were typically in the ng/L level (Dai et al., 2015). As a class of PPCPs, the contamination of abused drugs in Beiyunhe River is expected; however, minimal information is available on its occurrence and distribution in the aquatic environment.

In this study, 11 abused drugs including AMP, METH, ketamine (KET), ephedrine (EPH), COC, benzoylcegonine (BE), methadone (MTD), morphine (MOR), heroin (HER), codeine (COD), and methcathinone (MC) were investigated in the surface water and sediment of Beiyunhe River. Seasonally variable studies indicated that the levels of abused drugs in rivers in winter and spring are relatively high (Mendoza et al., 2014; Zhang et al., 2017). Sampling was conducted in spring to avoid the difficulties caused by freezing in winter, and the setting of sampling points was fully considered to make them generally representative.

Mixed water samples around each point were collected, and experiments were conducted repeatedly to ensure accuracy of results. Thirteen water and 14 sediment samples were collected from 15 sites along the river covering rural, suburban, and urban areas. The surface water samples were extracted by solid-phase extraction and quantified by liquid chromatography tandem mass spectrometry (LC-MS/MS). Only few studies reported the method of extraction and quantification of abused drugs in solid matrices (Table S1) (Álvarez-Ruiz et al., 2015). Hence, for the sediment samples, an ultrasonic-assisted solid-liquid extraction method was developed and validated in this study. The partitioning behavior of these drugs between water and sediment was investigated, and their potential sources and environmental risks were also analyzed. The results help us understand the occurrence, sources, fate, and potential risks of abused drugs in the urban river environment.

2 Materials and methods

2.1 Reagents and materials

Standards of abused drugs and their deuterated internal standards (AMP-d8, KET-d4, METH-d8, EPH-d8, COC-d3, BE-d3, MTD-d5, MOR-d3, HER-d9, COD-d6, and MC-d8) were obtained from Cerilliant Corporation (Round Rock, TX, USA), and detailed information is given in Table S2 in supplementary materials. Deionized water was acquired from Milli-Q purification system (Millipore, MA, USA), and other solvents and chemicals were received from Sigma-Aldrich. McIlvaine buffer used as sediment extraction solvent was prepared by mixing Na_2HPO_4 with citric acid and diluted to 1 L with deionized water (Álvarez-Ruiz et al., 2015).

The filters (GF/CTM glass microfiber filters, Whatman Corporation, UK) with a pore size of 2.5 μm and diameter of 47 mm, Oasis MCX SPE cartridges (60 mg, 3 mL, Waters Corporation, USA), and a SPE Vacuum Manifold (Supelco VisiprepTM) were used for water pretreatment.

2.2 Sample collection and processing

Surface water and sediment samples were obtained from 15 locations from Beiyunhe River in April 2017. Beiyunhe River is 145 km-long with drainage area of 6166 km² (Dai et al., 2015). Eleven of the sites (B1–B11) were located in the main stream, and the other four were from Liangshui River (LS1), Xiaoyoufa Canal (XY1), Qinying Canal (QY1), and Qinglong Bay (QL1). The water samples were obtained using a stainless steel bucket and then stored in 1 L polypropylene container. Sediment samples were collected by using Peterson's grab sampler. After collection, all samples were placed in the iced vessel and then brought back to the laboratory for further treatment. Some

physicochemical properties of the sediment samples are listed in Table S3.

Microfiber filter was used to filter 500 mL of water to eliminate suspended particulate matters, and the pH of the solution was adjusted to 2 with 3 mol/L HCl. Water samples were loaded onto the SPE cartridge, which was pre-conditioned with 5 mL of MeOH and 5 mL of deionized water after the addition of deuterated internal standards. Afterward, the cartridge was rinsed with 10 mL of pure water and then dried for 30 min under vacuum to remove excess water. The abused drugs were eluted from SPE cartridge with 6 mL of 5% NH₄OH in ACN at gravity flow. The eluates were evaporated under weak N₂ in water bath (40°C) to less than 1 mL. The volume of residue was brought to 1 mL using ACN for the instrumental analysis. The sediment was freeze-dried and fractioned by a 100 mesh sieve. In brief, 1 g of sediment was placed in a 50 mL falcon tube and added with 5 ng of the internal standards. The sediment was ultrasound-assisted extracted by 10 mL of McIlvain buffer–methanol (1:1, v/v). The samples were then homogenized, sonicated for 10 min, and centrifuged at 1200 r/min for 15 min. The supernatants were transferred to 250 mL flasks, diluted with deionized water, pH-adjusted to 2 using 3 mol/L HCl, and subjected to the following procedures for water samples.

2.3 Instrumentation

The target analytes were quantified by LC-MS/MS. The Acquity UPLC separation module, which is equipped with an Acquity UPLC BEH HILIC column (2.1 mm × 100 mm, 1.7 μm) (Waters, Milford, MA, USA), was used for LC separation. During sample analysis, the column was maintained at 30°C. Mobile phase A was the ultra-pure water containing 10 mmol/L ammonium formate and 0.2% formic acid, and mobile phase B was the acetonitrile–water (9:1, v/v) containing 10 mmol/L ammonium formate and 0.2% formic acid. The gradient began with 0% of A for

0.1 min, followed by decreasing of B to 70% for 4.8 min and then to 50% for 0.1 min. Afterward, 50% of A was kept for 1.0 min, then decreased to 0% for 0.1 min, and finally maintained for 2.9 min. The entire run time was 9.0 min, the flow rate was at 0.4 mL/min, and the injection volume was 1 μL.

MS determination of the target analytes was conducted on triple quadrupole 6500 (AB SCIEX, USA), which is equipped with an ESI source in the positive ionization mode. The multiple responses monitoring mode was used to identify the analytes. The collision gas pressure was 9.0 Psi, the curtain gas pressure was 35.0 Psi, and the ion spray voltage was 5.5 kV. The pressures of ion source gases were both 50 Psi, and the source temperature was 550°C. The general optimal quantification conditions are summarized in Table S4.

Chiral ephedrine and pseudoephedrine were quantified as a whole EPH because they have the same ionization and fragmentation patterns (Postigo et al., 2010; Senta et al., 2015).

2.4 Quantification and quality control

The performance of the proposed method was evaluated by testing the linearity, recovery, precision, and matrix effect. The 7-point calibration curve was constructed with a correlation coefficient value greater than 0.99. The matrix spike recoveries ranged from 76% to 94% in tap water, 72% to 92% in surface water, and 68% to 101% in sediment (Table S5). The recoveries at other spiking concentrations in surface water and sediment shown in Table S6 ranged from 68% to 110%, with RSD below 10% for each compound. Limit of quantification (LOQ) and limit of detection (LOD) were calculated from the experimental analysis of water and sediment samples with the analyte concentrations generating signal-to-noise ratios of 3 and 10, respectively (Table 1). For each compound, the LODs ranged from 0.20 to 1.20 ng/L in

Table 1 Parameters for method validation

Analytes	r^2	Surface water				Sediment			
		LOD (ng/L)	LOQ (ng/L)	Precision (%RSD)		LOD (ng/g)	LOQ (ng/g)	Precision (%RSD)	
				10 ng/L ($n = 5$)	100 ng/L ($n = 5$)			10 ng/g ($n = 5$)	100 ng/g ($n = 5$)
AMP	0.9985	0.2	0.8	7.32	8.41	0.5	1.5	2.56	4.99
METH	0.9986	0.6	2.0	4.60	5.63	1.0	2.0	3.56	5.25
KET	0.9990	0.3	1.0	5.02	8.65	0.2	0.8	2.45	4.84
EPH	0.9987	0.3	1.0	0.86	3.56	0.9	1.5	5.65	5.23
COC	0.9969	0.5	5.0	2.48	5.66	0.5	5.4	6.32	3.25
BE	0.9982	1.2	5.0	10.25	7.65	0.6	4.8	5.69	4.43
MTD	0.9943	0.9	2.0	7.52	3.91	1.2	3.4	2.34	5.96
MOR	0.9980	0.5	1.5	8.20	6.33	0.8	2.5	2.45	6.15
HER	0.9941	0.8	2.0	6.25	4.36	1.5	5.0	1.96	4.67
COD	0.9961	0.8	2.5	2.36	3.23	1.2	4.6	4.87	2.35
MC	0.9987	1.0	5.0	2.42	4.55	1.0	5.0	6.74	5.12

water and 0.20–1.50 ng/g in sediment, whereas the LOQs ranged from 0.80 to 5.00 ng/L in water and 1.96–6.74 ng/g in sediment.

2.5 Risk assessment

The toxicological risk level of each compound was assessed by risk quotient (RQ) method. RQs are the ratio of the potential exposure to the pollutant and the concentration that does not produce any adverse effect (US EPA, 1997a, 1997b). These values were calculated as the ratio of measured environmental concentration (MEC) to the predicted no effect concentration (PNEC). The PNEC was obtained from the aquatic toxicity data using the pertinent assessment factors (AFs) according to the EU, the US EPA, and the OECD protocols (US EPA, 1998; OECD, 2002; EU, 2003, 2011).

$$RQ = \frac{MEC}{PNEC}, \quad (1)$$

$$PNEC = \frac{\text{Toxicity benchmark}}{AF}. \quad (2)$$

In general, RQ below 0.1 reveals that the risk to aquatic organism is low, $0.1 < RQ < 1$ indicates that the risk is medium, and RQ above 1 shows that the risk is high. This study aims a region-specific screening level risk assessment, and the measured concentration of the pollutant at every sampling point was employed as MEC in the calculation. For maximum protection, if the pollutant level at a certain sampling point is lower than either the LOD or LOQ, then the value of the corresponding limit is indicated as the MEC.

The exhaustive toxicity data of fish, algae, and cladocerans for the target contaminants were collected from literature and the Ecological Structure Activity

Relationships (ECOSAR, US EPA). For algae, cladocerans, and fish, their LC50 or EC50 values for target compounds were used for RQ calculation. The AF value was set at 1000 and was used to all obtained data according to the ECOSAR and literature.

3 Results and discussion

3.1 Abused drugs in surface water and sediment

Table 2 shows the levels and detection frequencies of 11 abused drugs in the surface water and sediment in Beiyunhe River. MC and HER were not detected in any sampling site. The concentrations of 9 abused drugs in surface water ranged from below the detection limit to 92.2 ng/L, and the detection frequencies of drugs with concentrations greater than their LOQs in surface water ranged from 15.38% to 100%. METH, KET, and EPH were the most frequently detected drugs (100%) with average concentrations of 25.0, 5.7, and 29.7 ng/L respectively. The highest concentration of 92.2 ng/L was determined for METH in surface water samples from site B5. The drugs COD and MTD were less frequently detected in the surface water in Beiyunhe River with detection frequencies of 15.38% and 30.77%, respectively. Among the 11 drugs, 6 were identified with detection frequency higher than 75%, followed by 46.15% for MOR.

The results indicated that METH had high detection frequencies and concentrations, which agree with the report of Chinese authorities stating that KET and METH are the major synthetic abused drugs in China (Office of China National Narcotic Control Commission, 2017). KET had the highest detection frequency in the surface water of Beiyunhe River but was not present at high concentrations; this finding is in line with the reported KET concentrations

Table 2 Frequency of detection, median, mean and concentration range of the 11 target drugs in surface water and sediment

Analytes	Surface water				Sediment			
	Freq (%) <i>n</i> = 13	Median (ng/L)	Mean (ng/L)	Range (ng/L)	Freq (%) <i>n</i> = 14	Median (ng/g dw)	Mean (ng/g dw)	Range (ng/g dw)
AMP	92.31	2.8	3.6	nd ^{a)} –11.3	50.00	< LOQ	2.0	nd–6.9
METH	100	17.4	25.0	2.6–92.2	57.14	5.0	3.2	nd–9.1
KET	100	4.8	5.7	1.5–12.3	28.57	nd	< LOQ	nd–3.6
EPH	100	22.2	29.7	5.6–70.4	92.86	2.9	3.5	< LOQ–8.4
COC	76.92	4.6	4.9	nd–10.7	50.00	< LOQ	< LOQ	nd–10.0
BE	76.92	5.1	5.8	nd–14.6	35.71	nd	< LOQ	nd–3.1
MTD	30.77	nd	< LOQ	nd–6.3	0.00	nd	nd	nd
MOR	46.15	nd	1.78	nd–6.1	21.43	nd	< LOQ	nd–4.9
HER	0	nd	nd	nd	nd	nd	nd	nd
COD	15.38	nd	< LOQ	nd–5.6	0.00	nd	nd	nd
MC	0	nd	nd	nd	0.00	nd	nd	nd

in the surface water and STP effluents from Beijing (Du et al., 2015; Zhang et al., 2017). EPH was the dominant illicit drug in the surface water and had high concentrations and detection frequencies. EPH can be used as the raw material to synthesize METH and AMP and is also utilized in nasal decongestants and bronchodilators (Baker and Kasprzyk-Hordern, 2011). High detection frequencies and levels of EPH indicated its extensive application in Beijing, Tianjin, and Hebei provinces. The concentrations of target drugs in other areas across the globe are listed in Table S7, which showed that the METH levels (2.6–92.2 ng/L) in Beiyunhe River were greater than those in the rivers in the UK (nd–0.3 ng/L) (Baker and Kasprzyk-Hordern, 2013), Spain (3.1–5.0 ng/L) (Mendoza et al., 2014), and Italy (0.9 ng/L) (Zuccato et al., 2008) but were lower than those in the rivers of Taiwan (nd–917 ng/L) (Jiang et al., 2015). The EPH concentrations in this study (5.6–70.4 ng/L) were lower than those in Madrid, Spain (85.6–206.0 ng/L) (Mendoza et al., 2014), comparable with those in Henares River, Spain (70 ng/L) (Martínez Bueno et al., 2011), and higher than those in UK (nd–12.5 ng/L) (Baker and Kasprzyk-Hordern, 2011, 2013) and Ebro River, Spain (5.4 ng/L) (Postigo et al., 2010). No universal pattern of drug abuse across the world was found in this study. Owing to its large consumption, KET had been detected in several surface waters in China (Li et al., 2016; Zhang et al., 2017) but was rarely detected in other countries.

Table 2 shows the drug concentrations in the sediment. EPH was the most detected compound with frequency of 92.86%, followed by METH, COC, and AMP. Four drugs including MTD, HER, COD, and MC were not detected in all the sediment samples. The results also showed that EPH had the highest sediment concentrations (mean value of 3.5 ng/g dry weight, dw), followed by METH at 3.2 ng/g dw and AMP at 2.0 ng/g dw. To the best of our knowledge, this study is the first attempt to determine the abused drug contamination in the sediments in China river environment. Most studies focused on the detection of abused drugs in sewage sludge. Gago-Ferrero et al. (2015) reported that the maximum concentrations of pharmaceuticals and abused drugs are higher than 100 ng/g dw in different types of sewage sludge from five WWTPs in Santorini Island, Greece. In three Canadian cities, the mean concentrations of COC and BE in sewage sludge are 16.9 and 9.6 ng/g dw, respectively (Metcalf et al., 2010). The concentrations of abused drugs in the sediment in Turia River, East of Spain, are in the range of BDL to 30 ng/g dw (Álvarez-Ruiz et al., 2015), which was higher than the levels in the sediment of Beiyunhe River in the present study.

3.2 Spatial distribution of abused drugs

Spatial distribution of the abused drugs in surface water is shown in Fig. 1. Most drugs were detected in the main

stream of Beiyunhe River. At site B3, 8 out of the 11 target drugs were detected, closely followed by B2 and B4. These sites are located in Beijing urban area, where many amusement centers with highly dense population can be found. Several STPs and hospitals are adjacent to site B5, which showed the highest total illicit drug concentration of 183.0 ng/L as expected. At other sampling sites such as LS1, XY1, QY1, and QL1, few types of abused drugs and low concentrations were detected. For all sampling sites, METH, KET, and EPH were detected most frequently, with METH and EPH at a high concentration. According to sewage epidemiology (Daughton, 2001), METH, KET, and EPH could be the most abused drugs in the study area.

The contamination of these abused drugs in the main stream of Beiyunhe River was heavier than in their tributaries (Fig. 1), which was likely attributed to the inflows of several urban rivers in Beijing, including Ba River, Beixiao River, Tonghui River, and Qing River, which received domestic wastewater and STP effluents. For instance, Tonghui River and Ba River are located downstream of Sanlitun, where many nightclubs are situated. The drugs METH, KET, and EPH were expected to enter the rivers from the clubs through direct or indirect emissions, thereby contributing to the high level of drug contamination in the surface water. The entertainment centers are important sources of abused drugs and affect their geographical distribution patterns, which were also confirmed by Irvine et al. (2011) and Zhang et al. (2017).

Figure 2 shows the spatial distribution of drugs of abuse in sediments. In contrast to their distribution in water, the total concentrations of abused drugs in sediments did not vary significantly among the sites (between 2.6 and 32.4 ng/g dw). More than four species were detected at sites B2–B5, B9, and B10, and at least one illicit drug was detected for the rest of the sampling sites. In the sample sediments, METH and EPH were detected at high concentrations, and this finding was consistent with that for surface water. In theory, the distribution patterns of abused drugs in the sediments have been formed for a long time and are associated with the emission types of drug, and the consumption habits in the study area, and the environmental behavior of these drugs in surface water and sediments.

3.3 Partition of abused drugs between sediment and water

Pseudo-partitioning coefficients (PPC) were calculated to understand the environmental fate of abused drugs in the aqueous environment. The PPC values (K_D) were calculated by dividing the detected level in the sediment by the aqueous concentration (Kim and Carlson, 2007). Table 3 shows that the PPC values in Beiyunhe River ranged from 407.9 to 2158.6 L/kg for AMP, 89.7 to 242.4 L/kg for METH, 324.3 to 431.8 L/kg for KET, 16.6 to 405.7 L/kg for EPH, 113.8 to 983.8 L/kg for COC, 48.6

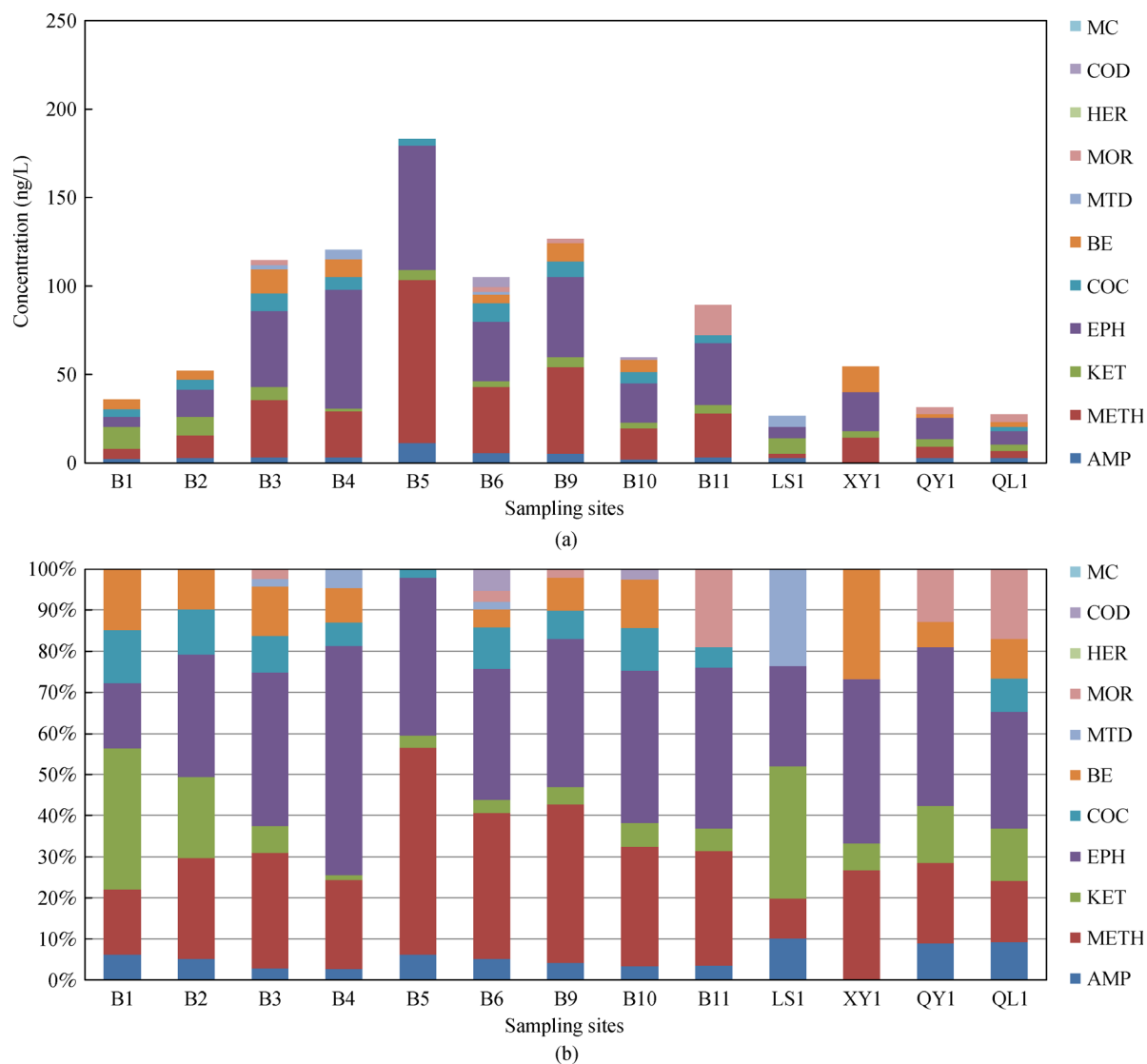


Fig. 1 (a) Concentrations of abused drugs in surface water samples; (b) Average contribution of each compound to the total drugs in water.

Table 3 Pseudo-partitioning coefficient of selected abused drugs

Compounds	K_D (L/kg)			K_{oc} (L/kg)	n	Values in references ^{a)} (L/kg)
	Min	Max	Mean	Mean		
AMP	407.9	2158.2	1214.0	3.03×10^4	5	–
METH	89.7	242.4	149.3	3.88×10^3	6	–
KET	324.3	431.8	378.1	8.12×10^3	2	–
EPH	16.6	405.7	168.0	4.25×10^3	11	–
COC	113.8	983.8	469.5	1.19×10^4	7	3000
BE	48.6	317.0	179.6	4.77×10^3	4	200
MOR	285.2	574.2	450.9	1.22×10^4	3	–

Note: a) From references Plósz et al. (2013).

to 317.0 L/kg for BE, and 285.2 to 574.2 L/kg for MOR. The average PPC values of COC and BE in this study (469.5 and 179.6 L/kg) were lower than those in the literature (3000 and 200 L/kg) (Plósz et al., 2013) probably

due to the different physicochemical properties of the environment matrix in different research areas. Table 3 also shows the PPC values of some other abused drugs that have not been reported before. In this study, the

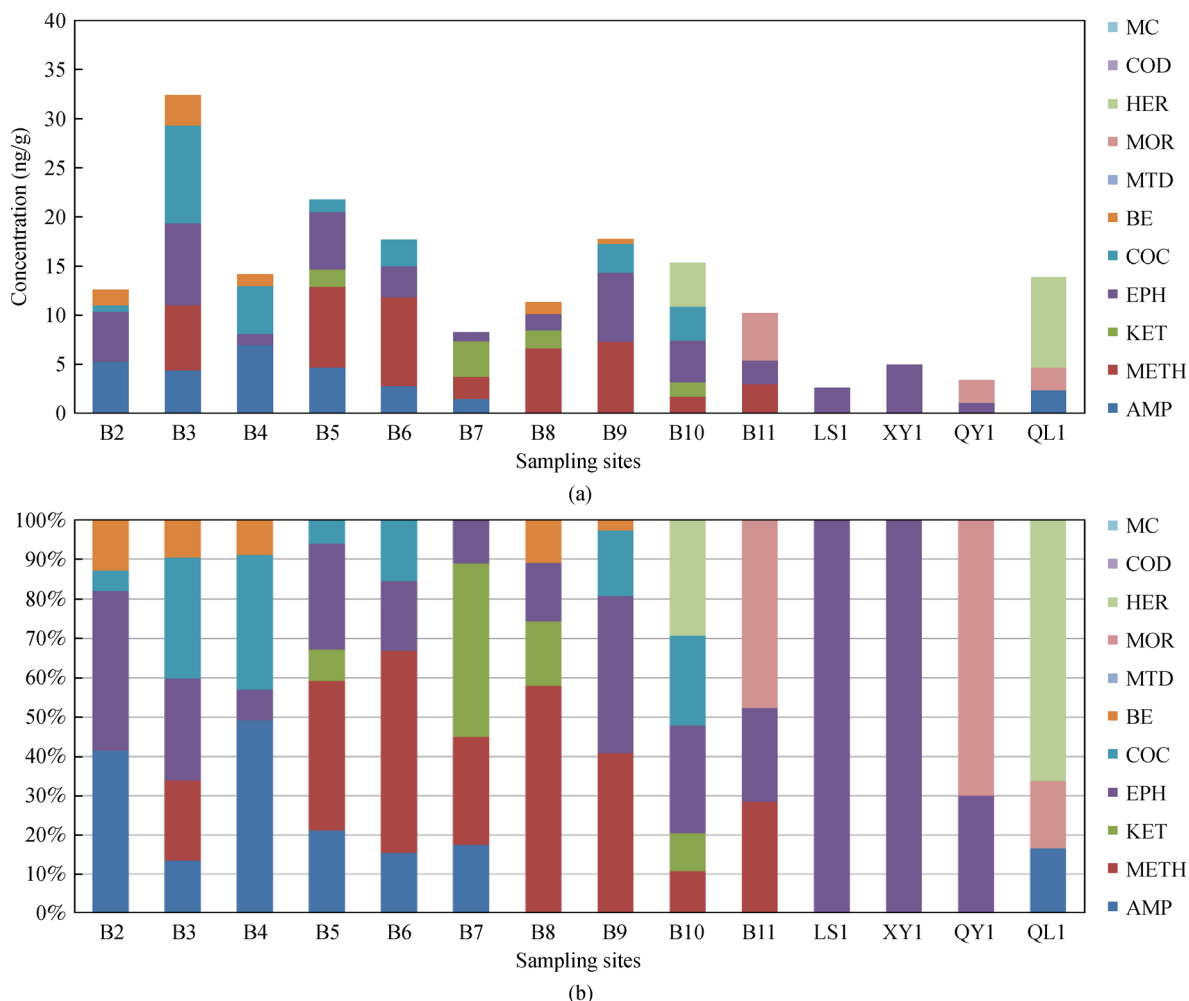


Fig. 2 (a) Concentrations of abused drugs in sediment samples; (b) Average contribution of each compound to the total drugs in sediment.

partitioning behaviors of the selected drugs between the sediment and overlying water were determined by field observations. The partitioning between the sediment and the pore water more accurately reflects the sorption characteristics of contaminants in the aquatic environment than the partitioning between the sediment and the overlying water, because the pore water is closer to the sediment than to the overlying water (Cheng et al., 2014; Xu et al., 2014). The physicochemical properties of sediment play important roles in the partitioning of abused drugs between the sediment and surface water. K_{oc} value (organic carbon normalized partition coefficient) was determined to correct the field-derived sediment-water distribution coefficient and reduce the variability among samples (Ahrens et al., 2010; Kwadijk et al., 2010).

$$K_{oc} = K_D/f_{oc}, \quad (3)$$

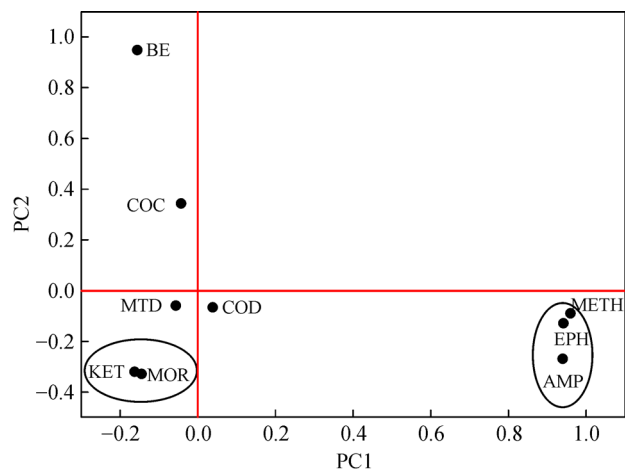
where f_{oc} is the sediment organic carbon fraction, and K_D is PPC values.

The results are shown in Table 3. The values of K_{oc} in Beiyunhe River ranged from 3.88×10^3 to $3.03 \times$

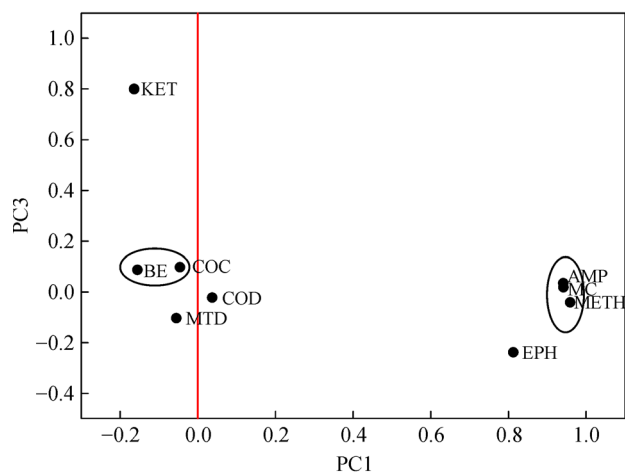
10^4 L/kg. To our knowledge, only few K_{oc} values for abused drugs have been reported.

3.4 Potential sources of abused drugs in Beiyunhe River

Hierarchical cluster analysis (HCA) and principal component analysis (PCA) implemented on SPSS 16.0 for windows were employed to distinguish potential sources of abused drugs in the surface water of Beiyunhe River. These parameters have been adopted from our previous studies (Lv et al., 2014; Lv et al., 2015; Xu et al., 2016). PCA was performed to obtain score plots and factor loadings. The matrix was composed of 24 columns and includes the number of drug species and sampling sites. After varimax rotation, PCA revealed three principal components (eigenvalue higher than 1) accounting for 35.5%, 19.1%, and 13.8% of the total variance. Score plots and factor loading are displayed in Fig. 3. Some drug species including METH, EPH, and AMP exhibited high loadings for PC1. These drugs were associated with high



(a)



(b)

Fig. 3 Principal component plot of abused drugs in surface water.

human consumption and have entered the surface water from STP effluents. Two drugs BE and KET showed high levels for PC2 and PC3, respectively, probably because of their usage as anesthetics in hospitals (McLeod, 2008). Sampling sites such as B3, B4, B5, B6, B9, and B11 located in the main stream of Beiyunhe River exhibited high loadings for PC1 (57.5%) (Fig. 4), indicating that these sampling sites were associated with the emissions from the STPs in the area. Results from PCA indicated that hospital sewage and STP emissions are probably the two main sources of abused drugs in surface water in Beiyunhe River, and this finding agreed with the result by Lin et al. (2010).

The HCA results in Fig. S1 showed that sampling site profiles with similar abused drugs were clustered together. The similar profiles suggested similar source categories in the surface water (Lv et al. 2014). The dendrogram showed that almost all of the anesthetics were clustered into one group, suggesting that the abused drugs can be attributed to a similar source category (i.e., hospitals). Some of the sites

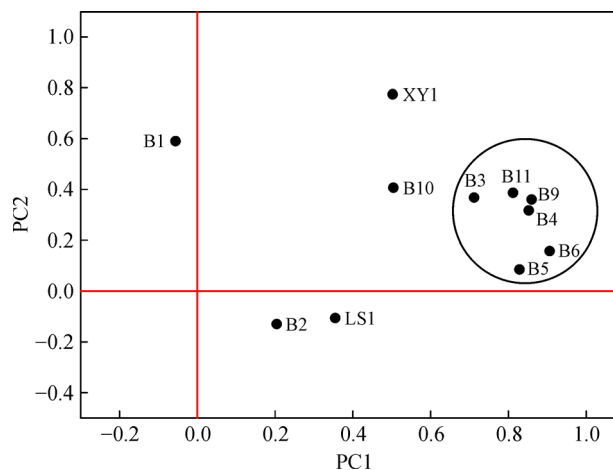


Fig. 4 Principal component plot of sampling sites in surface water.

resembled one group, indicating that the drugs detected in these sites originated from similar sources. The other site profiles were clustered in another group, revealing that different source categories may have contributed to the surface water in these sites. The Pearson correlations of abused drugs in surface water did not show strong relationships among target drugs, except for AMP and METH (Table S8). In addition to hospital sewage and STP effluents, some other sources of these drugs in surface water were found, such as drugs deliberately dumped and buried directly by drug addicts to destroy the evidence (Li et al., 2016).

3.5 Environmental risk assessment

No chronic data were found for the target compounds in this study. Risks for BE and MC were not evaluated because neither acute toxicity nor chronic value is available from literature. The acute toxicity data and concentrations in surface water of selected drugs of abuse were used to assess risks, and three LC50 or EC50 values for each abused drug were used for the RQ calculations. The data and their sources are shown in Table 4. The values of RQ for selected drugs ranged from 0 to 0.047, indicating low risk and minimal adverse effects. The environmental risks assessed by RQ method in other rivers were also low. For instance, in the Mediterranean River in Llobregat, Spain, the RQ values of the studied drugs were less than 1 (López-Serna et al., 2012). In the rivers of Netherlands, the RQ values of the drugs were in the range of 0.0002–0.38 (Van der Aa et al., 2013). However, the data used in the risk assessment were based on an active sampling method, which represents the status at the sampling moment in the aquatic environment (Mendoza et al., 2014). In the present study, risk assessment showed that the abuse drugs at their present concentrations do not have biologically adverse effects on the aqueous environment in Beiyunhe River.

Table 4 Predicted no effect concentrations (PNECs) (mg/L) for green algae, cladocerans and fish

Analytes	EC ₅₀ (mg/L)			Selected	AF	PNEC (mg/L)	RQ	Reference
	Fish	Cladocerans	Algae					
AMP	28.80	2.22	3.80	2.22	1000	2.22×10^{-3}	0–0.005	Lilius et al. (1994)
METH	20.51	2.51	1.97	1.97	1000	1.97×10^{-3}	0.001–0.047	ECOSAR
KET	8.34	1.13	0.72	0.72	1000	7.20×10^{-4}	0–0.017	ECOSAR
EPH	56.00	3.62	3.91	3.62	1000	3.62×10^{-3}	0–0.019	Sanderson et al. (2004)
COC	45.09	5.48	4.35	4.35	1000	4.35×10^{-3}	0–0.012	ECOSAR
MTD	2.24	0.34	0.17	0.17	1000	1.70×10^{-4}	0–0.037	ECOSAR
MOR	382.64	39.28	43.56	39.28	1000	3.93×10^{-2}	0	ECOSAR
COD	171.79	18.83	18.36	18.36	1000	1.84×10^{-2}	0	ECOSAR

However, investigating their potentially harmful influences on the function of the aquatic ecosystem and human health is necessary.

4 Conclusions

This study reported the distribution of 11 abused drugs in the surface water and sediments in Beiyunhe River, a typical urban river in Northern China. The results showed that the abused drugs in Beiyunhe River were ubiquitous in surface water and sediments. METH and EPH were the two predominant pollutants in both compartments with high levels of contamination and detection frequency. The pseudo-partitioning coefficients of abused drugs were also calculated to further understand their presence in the aqueous environment. The composition of abused drugs was related to effluent discharges and hospital sewage emissions. Risk assessment result revealed that the studied abused drugs in Beiyunhe River will not exert biologically harmful effect to the aquatic ecosystems, but their potential adverse influence on the function of the ecosystem and human health must be addressed.

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