Oxygenated, nitrated, methyl and parent polycyclic aromatic hydrocarbons in rivers of Haihe River System, China: Occurrence, possible formation, and source and fate in a water-shortage area

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HIGHLIGHTS

- Methyl-PAHs, oxy-PAHs, and PAHs were detected in rivers, but no nitro-PAHs.
- 2-MN, 9-FL, and AQ were the three highest-concentration SPAHs.
- OPAHs were possibly transformed from the PAHs especially at higher temperature.
- Wastewater treatment plant effluent was the major source for the SPAHs and PAHs.
- The major amount of SPAHs and PAHs entered the farmland through irrigation.

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ABSTRACT

Substituted polycyclic aromatic hydrocarbons (SPAHs) occur ubiquitously in the whole global environment as a result of their persistence and widely-spread sources. Some SPAHs show higher toxicities and levels than the corresponding PAHs. Three types of most frequently existing SPAHs, oxygenated-PAHs (OPAHs), nitrated-PAHs (NPAHs), and methyl-PAHs (MPAHs), as well as the 16 priority PAHs were investigated in this study. The purpose was to identify the occurrence, possible transformation, and source and fate of these target compounds in a water shortage area of North China. We took a river system in the water-shortage area in China, the Haihe River System (HRS), as a typical case. The rivers are used for irrigating the farmland in the North of China, which probably introduce these pollutants to the farmland of this area. The MPAHs (0.02–0.40 µg/L in dissolved phase; 0.32–16.54 µg/g in particulate phase), OPAHs (0.06–0.19 µg/L; 0.41–17.98 µg/g), and PAHs (0.16–1.20 µg/L; 1.56–79.38 µg/g) were found in the water samples, but no NPAHs were detected. The concentrations of OPAHs were higher than that of the corresponding PAHs. Seasonal comparison results indicated that the OPAHs, such as anthraquinone and 2-methylanthraquinone, were possibly transformed from the PAHs, particularly at higher temperature. Wastewater treatment plant (WWTP) effluent was deemed to be the major source for the MPAHs (contributing 62.3% and 87.6% to the receiving river in the two seasons), PAHs (68.5% and 89.4%), and especially OPAHs (80.3% and 93.2%) in the rivers. Additionally, the majority of MPAHs (12.4 kg, 80.0% of the total input), OPAHs (16.2 kg, 83.5%), and PAHs (65.9 kg, 93.3%) in the studied months entered the farmland through irrigation.

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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a type of ubiquitously present pollutants in the environment. Much attention has been paid to the sixteen PAHs designated as priority pollutants and regulated by the United States Environmental Protection Agency (USEPA) due to their

potential teratogenicity, mutagenicity, and carcinogenicity (Ross and Nesnow, 1999). The three types of most commonly detected substituted polycyclic aromatic hydrocarbons (SPAHs) in the environment, including oxygenated-PAHs (OPAHs), nitrated-PAHs (NPAHs), and methyl-PAHs (MPAHs), could be emitted from the same sources as the PAHs, such as incomplete combustion, vehicle engines, and spilled oil (Nikolaou et al., 1984; Manoli et al., 2000; Bamford and Baker, 2003; Lundstedt et al., 2007; Tsapakakis and Stephanou, 2007). In addition, the NPAHs and OPAHs may also be formed from the oxidation of PAHs by chemical and/or microbiological processes (Bamford and Baker,

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2003; Lundstedt et al., 2007; Wang et al., 2007; Haritash and Kaushik, 2009; Kojima et al., 2010). Generally speaking, NPAHs and OPAHs show higher toxicity than their parent PAHs, such as mutagenicity and carcinogenicity (Durant et al., 1996; Umbuzeiro et al., 2008). Meanwhile, the OPAHs can cause allergic diseases (Kojima et al., 2010). 1-nitropyrene was found in a drinking water source of Japan with a relatively low concentration (1 ng/L), accounting for 1% of the total genotoxicity (Ohe and Nukaya, 1996). Wang et al. (2011a) reported that the direct acting mutagenicity of Beijing particulate matter (PM) caused by the OPAHs and NPAHs was 2 times higher than that of the indirect mutagenicity caused by the PAHs, though the OPAH and NPAH concentrations only contributed 8% to the total PAH concentrations. In polluted river sediment, the fraction of the extracts containing the polar PAHs (including NPAHs) showed higher toxicities than those containing the non-polar PAHs like PAHs (Lübcke-von Varel et al., 2011). The OPAHs were weak inducers of in vitro estrogenic activity, similar to that of benzo[a]pyrene in river sediments (Machala et al., 2001).

In recent years, the OPAHs, NPAHs, and MPAHs have been taken into serious consideration because of their high toxicities to living organisms and pollution levels in the environment. Studies on the OPAHs and NPAHs in the atmospheric and soil environment have been much more common than those in the aquatic environment (Smith and Harrison, 1996; Dimashki et al., 2000; Lundstedt et al., 2006; Wang et al., 2011a; Wei et al., 2012). The SPAHs might enter the aquatic environment through atmospheric deposition and surface runoff. However, in the aquatic environment, there have been only limited studies on the SPAHs. In coastal waters in Japan, the pollution levels of anthraquinone (3.9–200 ng/L) were much higher than those of anthracene (<0.2–4.7 ng/L) (Kurihara et al., 2005). We proved in our recent study that the MPAHs and OPAHs did exist, but no NPAH was detected in the rivers located in Beijing and Tianjin, China (Qiao et al., 2013). Hung et al. (2012) verified that the NPAHs occurred in the aqueous phase of the river samples, but at relatively low levels (5.2–7.5 ng/L). Transformation from the PAHs might also occur in the surface aquatic environment to the NPAHs and OPAHs (Kochany and Maguire, 1994). Consequently, studies on the occurrence and source of OPAHs, NPAHs, and MPAHs in the natural aquatic environment should be expanded.

The pollution of SPAHs and PAHs has spread in the whole global environment. In this study, we took a river in the water shortage area of the Haihe River System (HRS), as a typical case, due to the fact that the pollution in this type of area is relatively severe. HRS is located at the North China Plain, connecting the megacities of Beijing and Tianjin. The water shortage becomes more and more severe with the increasing population (Varis, 2006) and pollution caused by the industrialization of megacities (Jiang, 2009). In order to reduce the water pollution and reuse the treated water, 60 wastewater treatment plants (WWTPs) have been built in Beijing thus far, the capacity of which account for 95% of the total amount of the wastewater discharge in Beijing. However, the effluent from the WWTPs was also found to be a major source for the dissolved PAHs in the river (Qi et al., 2013). Meanwhile, over 90% of WWTP effluent is discharged to the agricultural land area within 100 km downstream of Beijing (Pernet-Coudrier et al., 2012). Thus, the PAHs probably enter the soil and even the crops and vegetables through irrigation (Tao et al., 2004), which may pose potential risks to human health from food, vegetables (Wang et al., 2011c), and groundwater consumption. Consequently, it is essential to identify the source and pathway of PAHs and their derivatives with higher toxicity in the wastewater-receiving rivers of this typical water shortage area.

The purpose of this study was to investigate the occurrence, source and fate of PAHs, and especially the SPAHs in a water shortage area of North China. Firstly, the occurrence of SPAHs and PAHs was investigated in river water samples. Moreover, seasonal variations of these targets were compared to gain primary understanding of the source of the SPAHs and PAHs in the aquatic environment. Finally, mass flows were calculated to further evaluate the source and fate of the SPAHs and PAHs.

2. Materials and methods

2.1. Sample collection

We investigated 15 sites along the Wenyu River, North Canal, and Yongdingxin River in HRS (Fig. 1). The Wenyu River starts from the Shahe reservoir (RW-1) in Beijing. From RW-5 to RW-13, the river is called the North Canal. Then, it converges with the Yongdingxin River at RW-13 in Tianjin, and flows to the Bohai Bay after RW-15. The WWTP effluent (WWTP-1 to WWTP-4) and untreated wastewater (WW-1 to WW-3) in Beijing were also investigated between RW-1 and RW-7. The capacity of the 4 studied WWTPs accounts for 67% of the total 60 WWTP capacity in Beijing. Both dissolved and suspended particulate samples were collected in the non-heating season (August) and heating season (December), 2011. For each sampling point, one sample was collected in each season. As to the river samples, the sampling point was located in the middle of the river, at 0.5 m under the surface of the river. Each water sample was stored in a 4 L amber glass bottle. The information on the sampling sites and the WWTPs is listed in Table S1 and Table S2, respectively. After transport to the laboratory, the water samples were filtered through glass microfiber filters (Millipore GF/F, 142 mm diameter, 0.7 µm pore size) pre-combusted at

Fig. 1. Sampling sites in the Haihe river system.

450 °C for 5 h. The dissolved phase samples were extracted within 2 days. The suspended particulate samples were stored in a refrigerator at –20 °C until analysis. All the samples were stored in darkness.

2.2. Chemicals

Thirteen single SPAH standards, including 1-nitropyrene (1-NP, in solid 99.8%), 2-nitrofluorene (2-NF, in solid 99.9%), 3-nitrofluoranthene (3-NF, in solid 100%), 9-nitroanthracene (9-NA, 100 µg/mL), 7-nitrobenz[a]anthracene (7-NBA, 100 µg/mL), 1-methylfluoranthene (1-MF, 10 µg/mL), 2-methylnaphthalene (2-MN, in solid 100%), 2,6-dimethylnaphthalene (2,6-DMN, in solid 100%), 3,6-dimethylphenanthrene (3,6-DMP, in solid 100%), anthraquinone (AQ, 100 µg/mL), 2-methylanthraquinone (2-MAQ, in solid 99.0%), benz[a]anthracene-7,12-dione (BA-7,12-D, 50 µg/mL) and 9-fluorenone (9-FL, in solid 100%), and sixteen USEPA priority PAHs, including naphthalene (Nap), acenaphthylene (Acy), acenaphthene (Ace), fluorene (Fluo), phenanthrene (Phe), anthracene (Ant), fluoranthene (Flua), pyrene (Pyr), benz[a]anthracene (BaA), chrysene (Chry), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), indeno[1,2,3-cd]pyrene (IcdP), dibenz[a,h]anthracene (DBA), and benzo[g,h,i]perylene (BgHiP), in a mixture (200 µg/mL) were purchased from AccuStandard, Inc., New Haven, USA. The physical–chemical information of each target is listed in Table S3. Four surrogate standards, perdeuterated PAHs (acenaphthene-d10, phenanthrene-d10, chrysene-d12, perylene-d12) in a mixture (2000 µg/mL) were also purchased from AccuStandard, Inc. Internal standards for 2-fluorobiphenyl (2-FB, in solid > 96%) and decachlorobiphenyl (PCB209) were obtained from Aldrich Chemical Co., Inc. (Gillingham, Dorset, UK). Additional information on the chemicals is given in the Supporting data.

2.3. Sample pretreatment, instrumental analysis, quality assurance, and quality control

The details of the sample pretreatment and instrumental analysis have been described in a previous study (Qiao et al., 2013). Surrogate standards were added to each of the samples after the filtration and 12 h before the extraction with SPE and ASE. Briefly, the dissolved phase samples underwent reversed solid phase extraction (SPE) with C18 cartridges (500 mg, 6 mL, Supelco), and were eluted with 10 mL dichloromethane and 5 mL hexane. Suspended particulate samples were extracted by an accelerated solvent extraction (ASE300, Donex) with a mixture of 1:1 dichloromethane and acetone. Then, extracts were purified with silica gel/alumina cartridges. Eluted fractions were concentrated to 0.5 mL under a gentle stream of nitrogen. The internal standards (100 ng) were added to each sample before instrumental analysis.

Targets were detected by an Agilent 7890A GC equipped with a 5795C mass detector (GC–MS) with an electron impact (EI) source in the selective ion monitoring (SIM) mode. A DB-17MS fused silica capillary column (30 m length × 0.25 mm diameter × 0.25 µm film thickness) was used for the separation of each compound. Samples (1 µL) were injected in splitless mode. The carrier gas was helium at a flow rate of 1 mL/min. Injector and detector temperatures were kept at 280 °C and 290 °C, respectively. The temperature program was as follows: 60 °C (held for 1 min), to 110 °C at a rate of 20 °C/min, and to 290 °C at 3 °C/min (held for 20 min).

The recoveries were between 50% and 120%. Spike matrix (13 SPAH and 16 PAH standards) samples were measured for both dissolved and particulate samples. Method detection limits (MDLs) and method quantification limits (MQLs) were determined based on the concentrations 3 and 10 times the signal to noise ratio, respectively (Table S4).

2.4. Partition coefficient calculation

The suspended particulate to dissolved phase partition coefficient (K_d , L/g) of all the targets was calculated as follows.

$$K_d = C_p / C_d \quad (1)$$

where C_p (ng/g) stands for the target concentrations in the particulate phase samples and C_d (ng/L) stands for those in the dissolved phase samples.

2.5. Mass flow calculation

To assess the fate of SPAHs and PAHs in the HRS, mass flows (F , kg/month) were calculated based on the average concentrations of the targets (i) and the available annual discharge data at different sites (j), including RW-1, RW-5, RW-9, RW-13, the 4 WWTPs, and WW source, as follows.

$$F_{\text{river}, i, j} = C_{\text{river}, i, j} \times Q_{\text{monthly}, j} \times 10^{-9} \quad (2)$$

where $C_{\text{river}, i, j}$ stands for the concentration of targets i at site j in August and December, 2011, and $Q_{\text{monthly}, j}$ represents the average annual discharge at site j .

3. Results and discussion

3.1. Occurrence of SPAHs and PAHs and spatial variation

The 4 MPAHs (2-MN, 2,6-DMN, 3,6-DMP and 1-MF), the 4 OPAHs (9-FL, AQ, 2-MAQ and BA-7,12-D), and the 16 PAHs occurred in all the dissolved and particulate phase samples both in the non-heating and heating season. None of the investigated NPAHs were detected in any of the samples, possibly caused by their photo-chemical transformations in the aquatic environment (Chapman et al., 1966), and/or lower concentrations than the MDL (Table S4). We have proved in our method development study that some NPAHs, including 9-NA and 7-NBA, transform to their corresponding OPAHs during the pretreatment process, but no transformation from MPAHs, OPAHs or PAHs occur. This phenomenon indicated that the NPAHs were more susceptible to photo-oxidation than the other target compounds.

On the whole, the concentrations (sum of the dissolved and particulate phase) of Σ MPAHs, Σ OPAHs, and Σ PAHs in the rivers were higher than those in the WWTP effluent, and lower than those in the untreated wastewater (Fig. 2a, b, Table S5). The mass fluxes of WWTP effluent were much higher than those of WW (Table S6), diluting the concentrations of the target compounds in the rivers. It could also be noticed from Fig. 2 that the 4 WWTP effluent points, located between RW-3 and RW-7, slightly diluted the concentrations in the river. By contrast, in the non-heating season, the concentrations from RW-4 to RW-6 were higher than those at the sites upstream and downstream, indicating that there might be other sources besides the WWTP effluent. The lower concentrations in the WWTP effluent than those in the rivers indicated severe pollution in the receiving rivers, possibly impacted by other untreated sewage discharges, atmospheric depositions, and/or surface runoffs, etc. WW discharge (between RW-1 and RW-4) did not seriously influence the pollution levels of the target compounds in the river, due to a small amount of the sewage flux. The total concentrations of SPAHs and PAHs decreased along the Wenyu River and North Canal (RW-1 to RW-12). In the Yongdingxin River (RW-13 to RW-15), the concentrations were higher than before probably as a result of the sewage discharges from Tianjin (Pernet-Coudrier et al., 2012).

In the dissolved phase samples, the concentrations of Σ MPAHs, Σ OPAHs, and Σ PAHs were 0.02–0.40 µg/L, 0.06–0.19 µg/L, and 0.16–1.20 µg/L. The average concentrations of Σ MPAHs, Σ OPAHs, and Σ PAHs in the 15 RW samples were 0.08 µg/L, 0.09 µg/L, and 0.39 µg/L.

Fig. 2. Spatial distribution of the MPAHs, OPAHs, and PAHs in the RW, WW, and WWTP along the investigated rivers during the non-heating and heating season.

respectively, a little lower than those in the 3 WW samples ($0.19 \mu\text{g/L}$, $0.11 \mu\text{g/L}$ and $0.57 \mu\text{g/L}$), and slightly higher than those in the 4 WWTP effluent samples ($0.04 \mu\text{g/L}$, $0.08 \mu\text{g/L}$ and $0.22 \mu\text{g/L}$) (Table S5).

The same results were obtained in the sum concentrations of the dissolved and particulate phase samples, indicating that the concentration contribution of the dissolved phase to the sum concentrations was

Fig. 3. Seasonal comparison of SPAH and PAH concentrations in the RW, WW, and WWTP effluent samples.

more significant than the particulate phase. Similarly, the spatial distributions of all the targets in the dissolved phase samples were relatively the same as the total dissolved and particulate samples.

In the particulate phase samples, the average concentrations of Σ MPAHs, Σ OPAHs, and Σ PAHs in the RW samples (2.05 $\mu\text{g/g}$, 1.80 $\mu\text{g/g}$ and 10.70 $\mu\text{g/g}$) were lower than those both in WW (6.11 $\mu\text{g/g}$, 5.75 $\mu\text{g/g}$ and 27.77 $\mu\text{g/g}$) and WWTP effluent samples (4.33 $\mu\text{g/g}$, 4.43 $\mu\text{g/g}$ and 20.80 $\mu\text{g/g}$) (Table S5). The result might be attributed to the partition coefficients, which in RW (10 L/g, 10 L/g, and 11 L/g) was lower than WW (28 L/g, 30 L/g and 24 L/g) and WWTP effluent (MPAH 15 L/g, OPAH 16 L/g and PAH 14 L/g) (Table S7). Similar to the dissolved phase samples, the pollution of MPAHs, OPAHs, and PAHs in WW was more severe than those in the WWTP effluent and the rivers. Along the rivers, the particles in WWTP effluent increased the PAH and SPAH concentrations between RW-4 and RW-7 in the non-heating season, especially WWTP-3; WWTP effluent diluted the concentrations in the heating season (Fig. 2). Particles in the WW did not seriously affect the pollution in the river, resulting from a low flux as in the dissolved phase. The total concentrations of the targets decreased from RW-8 to RW-15, indicating a less severe pollution of the targets on the particles in Tianjin.

For individual target compounds, the average concentrations of Nap, 2-MN, and Phe were the three highest, both in the dissolved (0.15 $\mu\text{g/L}$, 0.08 $\mu\text{g/L}$ and 0.07 $\mu\text{g/L}$) and particulate phase samples (2.82 $\mu\text{g/g}$, 1.87 $\mu\text{g/g}$ and 3.04 $\mu\text{g/g}$) (Fig. 3). In the dissolved phase samples, the concentrations of other MPAHs (2,6-DMN, 3,6-DMP and 1-MF) were relatively low. Two higher-concentration OPAHs were 9-FL and AQ. They were also higher than Fluo and Ant respectively. These higher concentrations are possibly caused by the higher water solubility of the compounds compared to the others in the same group and the corresponding PAHs (Table S3). Additionally, the existence of OPAHs with high concentrations in the dissolved phase might be induced by the possible transformation from the PAHs (Lundstedt et al., 2007; Wang et al., 2007) or other SPAHs such as NPAHs (Chapman et al., 1966), wet deposition, surface runoff or particulate desorption. Chapman et al. (1966) reported that 9-NA could transform to AQ in acetone solution on irradiation in the presence of nitrogen (II) oxide. This could also explain the nonexistence of NPAHs in the aquatic environment, though the NPAHs were prevalent in the atmospheric and soil environment. In the particulate samples, the average concentrations of OPAHs were higher than those of the MPAHs, except 2-MN as in the dissolve phase samples. The relatively high levels of OPAHs in the particulate phase samples might also result from the possible transformation from PAHs and/or NPAHs, dry deposition, surface runoff, and particulate adsorption.

3.2. Seasonal variation of the SPAHs and PAHs for indicating the target behaviors

3.2.1. Seasonal variation of partition coefficient

The behaviors of SPAHs and PAHs could be evaluated by the particulate-aqueous and gas-aqueous partition. The K_d values for individual target were calculated for a better understanding of the SPAHs and PAHs behaviors both in the dissolved and particulate phases of the aquatic environment under natural conditions. The correlations of K_d and $\log K_{ow}$ were investigated (Fig. S1). The correlation coefficient in the heating season ($r^2 = 0.72$) was higher than that in the non-heating season ($r^2 = 0.25$), suggesting that adsorption to particulates was the major behavior of the targets in the heating season. However, the K_d values in the heating season were not always higher than those in the non-heating season (Fig. 4). Only the K_d values of OPAHs and high molecular weight PAHs (HMW PAHs; Flua, Pyr, BaA, Chry, BbF, BkF, Bap, IcdP, DBA and BghiP) in the heating season were higher than those in the non-heating season in the RW samples. Accordingly, particulate-aqueous partition was probably the major process for the OPAHs and HMW PAHs. The K_d values of MPAHs and low molecular weight PAHs (LMW PAHs; Nap, Acy, Ace, Fluo, Phe and Ant) in RW

Fig. 4. Seasonal comparison of partition coefficients: N, the non-heating season; H, the heating season.

samples were higher in the non-heating season, indicating that the gas-aqueous partition might be the significant process for the MPAHs and LMW PAHs. The partition in gas to dissolved phase is controlled by vapor pressures and Henry's law constants values (Manoli et al., 2000). Targets with the two higher values (MPAHs and LMW PAHs, Table S3) prefer to exist in the gas phase, while those with lower ones (OPAHs and HMW PAHs) are susceptible to predominate in the dissolved phase. As a result, the MPAHs and LMW PAHs were more volatilizable at higher temperature, causing the lower concentration in the dissolved phase samples. Consequently, the K_d values were higher in the RW in the non-heating season. As to the WW and WWTP effluent, the K_d values of all the targets were higher in the non-heating season than those in the heating season, demonstrating that the gas-aqueous partition might be the dominant process.

3.2.2. Seasonal variation in the dissolved phase samples

Generally speaking, in all the RW, WW, and WWTP effluent samples, the concentrations of MPAHs and PAHs were higher during the heating season, and the OPAHs were higher during the non-heating season (Fig. 3). The higher concentrations of MPAHs and PAHs in the heating season might be attributed to the increase in domestic combustion sources. By contrast, the higher OPAH concentrations in the non-heating season indicated that other sources must exist besides coal and wood combustion. It has been reported that the OPAHs can be also produced by the oxidation of PAHs (Tsapakis and Stephanou, 2007). A previous study demonstrated that the AQ was an important transformation product of Ant in the aquatic environment (Gómez et al., 2012). Solar radiation might be a factor influencing the transformation (Fan et al., 1996), which could explain the higher concentrations

of OPAHs in the non-heating season. Wu et al. (2010) proved that Ant and BaA could be transformed to AQ and BA-7,12-D and other metabolites by fungi in PAH-contaminated sediment. In the WWTPs, secondary treatment technologies are all activated sludge processes; fungi are prevalent species in the activated sludge, though they are not the dominant ones. Thus, biological transformation processes might be another possible pathway for the transformation from the PAHs to the OPAHs. Additionally, Haritash and Kaushik (2009) have demonstrated that the OPAHs could be formed and accumulated during the biological degradation process.

The possible formation of OPAHs could be analyzed based on the ratios of OPAHs to the corresponding PAHs (Fig. 5) (Walgraeve et al., 2010). Generally speaking, the ratios of the OPAH to PAH were higher than those of the MPAH to PAH. For an individual set of targets, the values of AQ/Ant were much higher than those of 2-MAQ/Ant, and also higher than those of 9-FL/Fluo and BA-7,12-D/BaA. The ratios of the OPAHs to PAHs were higher in the non-heating season in the rivers, possibly due to the fact that the photo-chemical transformations from the PAHs to the OPAHs were easier in this season as discussed above. The higher temperature and stronger solar irradiation might increase the photo-chemical transformation. In the WWTP effluent, the OPAH to PAH ratios also exhibited higher values in the non-heating season (Table S8). Temperature was probably a factor influencing the biological transformation in the WWTPs. The activities of microorganisms were stronger at higher temperature. As to the WW, the bio-transformation and photo-chemical transformation might both become easier during the non-heating season. From another aspect, the OPAHs tended to be in the aqueous phase in the non-heating season and most of the corresponding PAHs were susceptible to present in the aqueous phase in the heating season, as discussed above. This might also result in higher OPAHs to the PAHs values in the non-heating season. With regard to the MPAHs, the ratios of one-methyl PAHs to PAHs (2-MN/Nap and 1-MF/Fluo) were higher than those of two-methyl PAHs to PAHs (3,6-DMP/Phe and 2,6-DMN/Nap). This might be induced by their sources, such as petrogenic or pyrogenic PAHs, biomass combustion, and combustion temperature. The results suggested that the ratios of MPAHs to PAHs in the two sampling seasons did not vary much in the

RW and WWTP effluent samples, implying a similar behavior of both MPAHs and PAHs.

3.2.3. Seasonal variation in the particulate samples

In the particulate samples, the seasonal variations in the WW and WWTP effluent were not the same as in the RW samples (Fig. 3). Most of the MPAH and PAH concentrations in the RW samples were higher during the heating season, and most of the OPAHs were higher during the non-heating season; whereas in the WW and WWTP effluent samples, the concentrations of all the target compounds were higher during the non-heating season. The result suggested that sources for target compounds in the rivers besides WW and WWTP effluent might exist. Wang et al. (2011b) have demonstrated that the atmospheric deposition is an important pathway for the PAHs to enter the aquatic environment in the Beijing-Tianjin region. Not only the concentrations of PAHs in the deposition particles, but also the deposition fluxes in the heating season were higher than those in the non-heating season, as a result of more coal and biomass burning sources during the heating season in this region. Consequently, the PAHs and SPAHs in the particles of the RW samples might originate from the atmospheric deposition, particularly during the heating season.

In the RW samples, the ratios of OPAHs to the corresponding PAHs did not vary much between the two seasons (Fig. 5), which might due to the easier transformation and weaker adsorption of OPAHs on particles at higher temperature. In the WW and WWTP effluent samples, the ratios of 2-MAQ to Ant were higher than those of AQ to Ant, and the other two sets of target compounds, indicating that the transformation from Ant to 2-MAQ might be enhanced by biological processes. Additionally, the ratios of most OPAHs to PAHs were higher during the heating season, different from in the dissolved phase samples. The adsorption ability can be influenced by the temperature. Lower temperature might improve the adsorption of OPAH to the particulate samples, resulting in a higher 2-MAQ concentration. The same as in the dissolved phase samples, the ratios of MPAHs and PAHs did not vary much during different seasons, also suggesting a similar behavior of both MPAHs and PAHs.

Fig. 5. Ratios of the SPAHs and the corresponding PAHs in the RW, WW, and WWTP samples during the non-heating and heating season.

To further investigate the transformation from PAHs to OPAHs under natural conditions, a simulation experiment should be performed in the presence of solar irradiation to validate the result deduced in this study.

3.3. Mass flow analysis for indicating the source and pathway of SPAHs and PAHs in the receiving rivers

The source and pathway of SPAHs and PAHs could be determined by the mass flows of the target compounds in the river, WWTP effluent, and untreated wastewater. The mass flows of MPAHs, OPAHs, and PAHs at certain sampling sites were calculated based on the water discharge in 2011 (Table S6), which in 2009 was established in the study of Pernet-Coudrier et al. (2012). December in Beijing and Tianjin is a season when domestic combustion is required, increasing the emission of PAHs. Meanwhile, the water flows in this season are the lowest of the whole year, and will not dilute the PAH concentrations. Thus, December, described as the heating season in this study, is a representative season. The conditions in August (the non-heating season) is the opposite, in that there is no emission from domestic combustion, and the water flows are almost the highest of the year.

The total mass loadings of the MPAHs, OPAHs, and PAHs were 15.5 kg, 19.4 kg, and 70.6 kg in the two sampling months (Fig. 6). This is the first time that the mass loadings of MPAHs and OPAHs have been reported. In this study, only 4 MPAHs and 4 OPAHs were investigated. Some other compounds were qualitatively analyzed by a GC-MS but not quantified in the RW and WWTP effluent samples, including 1-methylnaphthalene, 1,6-dimethylnaphthalene, 2,7-dimethylnaphthalene, 2,3,6-trimethylnaphthalene, 1-methylphenanthrene, 4-methylphenanthrene, 2-methylanthracene, and 1,2,4-trimethylanthraquinone. Therefore, the total mass loadings of the actual existing MPAHs and OPAHs in the aquatic environment would be higher than indicated.

The contributions of WWTP effluent to MPAHs (Fig. 6a, b), OPAHs (Fig. 6c, d), and PAHs (Fig. 6e, f) in the receiving rivers were much more significant compared with the untreated wastewater discharge, the upstream and other unknown sources, especially for OPAHs, in the both seasons. The effluent of the 4 WWTPs contributed higher percentages of MPAHs, OPAHs, and PAHs to the river in the heating season

(87.6%, 93.2% and 89.4%) than that of the non-heating season (62.3%, 80.3% and 68.5%) (Fig. S2). WWTP-3, with the largest treatment capacity in Beijing, was the major contributor among the 4 WWTPs. The unknown sources of MPAHs might include the untreated wastewater discharge, atmospheric deposition, and surface runoff. Regarding PAHs, the result in this study was the same as reported by Qi et al. (2013), that PAHs in the receiving rivers mainly came from the WWTP effluent. The unknown source was the second largest contributor for the MPAHs (14.5%) and PAHs (15.6%) in the non-heating season. As discussed above, atmospheric deposition was a definite source included in the unknown sources.

Fig. 6 (a, c, e) also illustrated that the mass flows of MPAHs, OPAHs, and PAHs from RW-9 and RW-13 were less than the total contributions of the upstream flow and WWTP, in the non-heating season. A large amount of water was channeled between RW-5 and RW-9 to the Chaobaixin and Qinglongwan rivers for irrigation. Similarly, another large amount of water vanished between RW-9 and RW-13 due to irrigation (Pernet-Coudrier et al., 2012). In the heating season, however, the water fluxes at both RW-9 and RW-13 were 0, demonstrating that all the water from the WWTPs and upstream were discharged to the Chaobaixin and Qinglongwan rivers. In August and December in 2011, a total amount of 12.4 kg MPAHs (80.0% of the total input), 16.2 kg OPAHs (83.5%), and 65.9 kg PAHs (93.3%) were diverted to the farmland in Tianjin. The amounts of the target compounds in the irrigation water in the both seasons were relatively similar. Meanwhile, only a small amount of the pollutants (2.3 kg/month for MPAHs, 1.2 kg/month for OPAHs and 2.8 kg/month for PAHs) entered Bohai Bay in the non-heating season.

Though a majority of wastewater has been treated by the 4 studied WWTPs, the organic micro-pollutants in the effluent still seriously threatened the receiving rivers and the relevant agriculture area. The removal efficiencies of each type of target compounds ranged from 69.8% to 76.0% (Fig. S3), indicating that during a conventional treatment process the removal efficiencies of organic micro-pollutants were not that satisfactory. It has been reported that advanced treatment technologies could be effectively enhanced to remove organic micro-pollutants (Hollender et al., 2009; Hernández-Leal et al., 2011). Thus, if advanced

Fig. 6. Mass flows of the MPAHs, OPAHs, and PAHs from the WWTP effluent WW sources and in the wastewater receiving rivers in the two seasons.

treatment plants become prevalent in Beijing, the contribution of the effluent from the WWTPs to the river environment would be effectively reduced.

4. Conclusions

The 4 MPAHs (0.02–0.40 µg/L in dissolved phase; 0.32–16.54 µg/g in particulate phase), 4 OPAHs (0.06–0.19 µg/L; 0.41–17.98 µg/g), and 16 PAHs (0.16–1.20 µg/L; 1.56–79.38 µg/g) were detected in all the samples. No NPAHs were detected. The concentrations of ΣMPAHs, ΣOPAHs, and ΣPAHs in the dissolved phase followed the trend WW > RW > WWTPs effluent. In the particulate samples, ΣMPAHs, ΣOPAHs, and ΣPAHs concentrations were in the following trend WW > WWTP effluent > RW. For individual target compounds, the concentrations of 2-MN, 9-FL, and AQ were higher than those of the other SPAHs. Meanwhile, the 9-FL and AQ concentrations were higher than that of Fluo and Ant. Seasonal comparison indicated that the MPAH and PAH concentrations were higher during the heating season than those in the non-heating season, while the OPAHs occurred at higher concentrations in the non-heating season. The differences in seasonal variation of the target compounds and SPAH to PAH ratios implied that the OPAHs, such as anthraquinone and 2-methylanthraquinone, were possibly transformed from the PAHs, particularly at higher temperature. Though a majority of the target compounds (69.8%–76.0%) were removed in the WWTPs, the effluents were still a significant contributor to the MPAHs (62.3% in the non-heating season and 87.5% in the heating season), OPAHs (80.3% and 93.2%), and PAHs (68.5% and 89.4%) in the rivers. Additionally, the majority amount of MPAHs (12.4 kg, 80.0% of the total input), OPAHs (16.2 kg, 83.5%), and PAHs (65.9 kg, 93.3%) entered the farmland via irrigation in the two sampling months.

Conflict of interest

The authors claim that none of the materials in this manuscript has been previously published or is under consideration for publication elsewhere. All the authors are aware of and accept responsibility for the manuscript.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.scitotenv.2014.02.050>.

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