Partitioning and sources of PAHs in wastewater receiving streams of Tianjin, China

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Abstract Polycyclic aromatic hydrocarbons (PAHs) partitioning among dissolved phase, suspended particulate matter, pore water, and sediment was studied in one moderately contaminated river (Yongding New River) and two highly contaminated drainage canals (South Drainage Canal and North Drainage Canal) of Tianjin, China. PAHs concentrations in sediment (ranged from 0.2 to 195 $\mu\text{g/g}$) showed positive relations with both total organic carbon contents (ranged from 0.7% to 31.1%, dw) and black carbon contents (ranged from 0.1% to 2.1%, dw) in the sediments. Moreover, most of the measured organic carbon normalized partition coefficients of PAHs in the three streams were 0.76 to 1.54 log units higher than the predicted values. These indicated that strong and nonlinear sorption

of PAHs by carbonaceous geosorbents such as black carbon (BC) existed in the streams, and BC was an important part of the carbonaceous particles controlling the partitioning of PAHs in the sediments of this study. PAH component ratio analyses suggested that PAHs in the three streams, effluent samples from wastewater treatment plants, and soil samples by the riverbank had similar main sources, which is coal/petroleum combustion. We suggested the transportation and transformation of both carbonaceous particles and PAHs during wastewater treatment process, surface runoff, etc, should be studied further in order to make decisions on PAHs controlling measures.

Keywords PAHs · Partition · Organic matter · Black carbon · Component ratio

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Introduction

Polycyclic aromatic hydrocarbons (PAHs) enter rivers and estuaries by direct wastewater discharges, riverine inflow and atmospheric deposition. They then become subject to distribution and accumulation among the water column, suspended particulate matter, bottom sediments, and biota. It is well-known that dissolved organic matter in water as well as organic material in

suspended particulate matter (SPM) and sediment are important vectors for PAH's partition and behavior among various phases in the rivers.

In the early 1990s, Weber et al. (1992) hypothesized that organic matter consisted of a heterogeneous mix of sorbents, for example, “soft” and “hard” carbon. Researchers observed that heterogeneity in naturally occurring carbonaceous materials (CMs) caused sorption processes of hydrophobic organic compounds (HOCs) in sediments to occur as a combination of absorption into amorphous organic matter and adsorption onto condensed forms of CMs such as black carbon (BC), coal, and kerogen, collectively termed “carbonaceous geosorbents” (CG) (Allen-King et al. 2002; Cornelissen et al. 2005). Many studies reported that adsorption of PAHs onto CG can greatly affect their bioavailability and toxicity as “sequestration” of PAHs in sediments often takes place (Gustafsson et al. 1997; Luthy et al. 1997; Nam et al. 1998; Rockne et al. 2002; Shor et al. 2003; Abu and Steve 2005).

High PAHs levels have been reported in streams of Tianjin previously (Qi et al. 2010a, b) as well as other organic pollutants (Shi et al. 2005; Yang et al. 2005; Shao et al. 2005). Investigation of the partitioning and sources of pollutants would lead to a better understanding of risk. However, previous reports regarding the partitioning of these pollutants in different phases are not widely available because of the extremely complex matrix in this area. We focus on Yongding New River which acts as both a water resource for agriculture irrigation and a waterway for flood control in wet seasons and two drainage canals, South Drainage Canal and North Drainage Canal, which were greatly influenced by the development and urbanization of Tianjin. The object of this study was to further interpret the measurement data of PAHs (Qi et al. 2010a) in order to explain the role of organic matter on partitioning of PAHs in view of our previous studies (Qi et al. 2010b). The in situ partitioning of PAHs between the dissolved phase (DP), suspended particulate matter (SPM), pore water (PW), and sediment in the streams of Tianjin was studied. PAHs compo-

sitions in sediment as well as in soils by riverbank were investigated to speculate the origins of PAHs in the streams.

Materials and methods

Sampling streams

The map of the sampling area and the locations of sampling sites are indicated in Fig. 1. South Drainage Canal, which is 67.5 km, originates from the Xianyanglu wastewater treatment plant (WWTP) and flows into Bohai Bay in the Tangu area of Tianjin. North Drainage Canal is 33 km, originates from Zhaoguli pump station and merges into Yongding New River. Yongding New River is 62 km and originates from the downstream of North Canal which flows through Beijing. Many rivers and canals merge into Yongding New River, such as Airport Drainage Canal, Beijing Drainage Canal, Chaobai New River, Ji Canal, Jinzhong River and North Drainage Canal, etc. Yongding New River is one of the flood-discharging channel of Tianjin and acts as an important input path of Yongding River, North Canal, Chaobai New River, and Ji Canal into the Bohai Sea.

There were 16 (Y1 to Y16), seven (N1 to N7), and 11 (S1–S11) sampling sites in Yongding New River, North Drainage Canal, and South Drainage Canal, respectively. Surface water, suspended particulate matters, and pore water samples were collected in June and October of 2007 and January of 2008, respectively. Sediment samples were collected in June of 2007. Four effluent samples from WWTPs or pump station (collecting municipal wastewater and rainwater) including Zhaoguli (ZGL) pump station, Dongjiao (DJ) WWTP, Xianyanglu (XY) WWTP, and Jizhuangzi (JZZ) WWTP (presented by stars in Fig. 1) were collected at the outflow in January of 2008. In addition, nine soil samples by riverbank were collected in June of 2007. They were located in the farmlands near Y2, Y3, Y4, Y5, Y7, N1, N2, N5, and N7 (Fig. 1).

Fig. 1 Map of Tianjin and main streams of the city (*left*); map of the sampling area and the location of the sampling sites in Yongding New River (Y1–Y16), North Drainage Canal (Northsewer, N1–N7), and South

Drainage Canal (Southsewer, S1–S11; *right*). ZGL Zhaoguli pump station, DJ Dongjiao wastewater treatment plant, XY Xianyanglu wastewater treatment plant, JZZ Jizhuangzi wastewater treatment plant

PAHs and organic matters analysis

Detailed information about sampling, PAHs analysis, total organic carbons and black carbons contents determination, quality assurance, and quality control has been described in our previous study (Qi et al. 2010a, b). Briefly, 16 priority PAHs, i.e., naphthalene (Nap), acenaphthylene (Acy), acenaphthene (Ace), fluorene (Fl), phenanthrene (Phe), anthracene (Ant), fluoranthene (Fluo), 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 (Ind), dibenz[a, h]anthracene (DBA), benzo[ghi]perylene (BghiP), were determined with GC/MS in all samples. Total organic carbons (TOC) and black carbons contents in sediments were detected with element analyzer (Vario EL III). Briefly, the meshed sediment (<250 μm) was treated with 10% HCl solution to remove inorganic carbon and dried overnight at 60°C before TOC determining. Subsample upon acidification was further oxidized thermally in a muffle furnace

at 375°C for 24 h before being used for BC determination. Three to 10 mg of sediment was used for TOC and BC analysis. The Geochemical Standard Reference Sample GSS-1 Soil supplied by the National Measurement Science Academy was used as external standard.

Calculation of partition coefficients of PAHs among different phases

To provide insight into phase distribution processes in the three streams of Tianjin, the organic carbon normalized partition coefficients K_{oc} between SPM and surface water, sediment and PW were computed, respectively. First, the solid–water distribution coefficient, K_d ($= C_{SPM}/C_{DP}$ or $= C_{sediment}/C_{PW}$), was calculated. Then the K_{oc} values were computed from the K_d values and the TOC data of SPM or sediment. The TOC contents in SPM samples of this study were not measured. In the calculation of K_{oc} between SPM and DP, the TOC data of SPM cited the average concentration in rivers of Tianjin reported by Shi et al. (2007). It was comparable to the median

Fig. 2 Correlation of total PAHs contents with TOC and BC contents in the sediments (p level of significance; r Pearson correlation coefficient)

values of TOC (3.24%) measured in the sediment samples of this study.

Results and discussion

Partitioning of PAHs among surface water, SPM, PW, and sediment phases

It has been clear that natural organic matter was the most important factors governing the behavior and fate of PAHs in different phases of streams of Tianjin (Shi et al. 2007). As shown in Fig. 2, the contents of PAHs in the sediments showed significant positive relation with both total organic carbon and black carbon contents in the sediments. At level of significance (p) of 0.01, the correlation coefficients were 0.77 and 0.73 between PAHs concentrations with TOC and BC contents, respectively.

Furthermore, BC also played an important role in the association of PAHs in the sediments of Yongding New River, North Drainage Canal, and South Drainage Canal (Fig. 2). The weight fractions of BC in the sediments of our study were 0.12–0.82%, 0.19–1.74%, and 0.12–2.07% for Yongding New River, South Drainage Canal, and North Drainage Canal, respectively (Fig. 3).

The ratios of BC contents to TOC contents were 10–24.5%, 9–21.5%, and 6.6–17.9 %, respectively (Fig. 4). These results are comparable to those reported previously, such as 3–13% of TOC for the sediments of New England harbors (Gustafsson and Gschwend 1998), 5–39% of TOC for lake sediments of France (Lim and Cachier 1996), 18.3% of TOC for marine sediment in Zhuhai (Song et al. 2002). However, they were lower than the result of 33.0% of TOC for the river sediment in the Pearl River, 41.0% of TOC for the pond sediment in Guangzhou, China (Song et al. 2002). Cao et al. (2006) reported a detailed organic carbon (OC) and BC aerosols emissions in China. In their study, total emissions were 37.4 Gg OC and 14.4 Gg BC in Tianjin where the three streams of this study are located. That meant BC accounted for 38.5% of OC in the aerosols emission in Tianjin. Comparing with this, the BC to TOC ratios in the sediments of this study were about one to two times lower. This suggested the complex input of organic matters into the canals. If we compare the BC to TOC ratios among the three studied streams, we could find that the ratios in Yongding New River (10–24.5%) were higher than those in the two canals (6.6–21.5%). This proved our hypothesis to some extent as Yongding New River acts as both water resources

Fig. 3 Concentrations of TOC and BC in the sediment from YD R. Yongding New River, SD C. South Drainage Canal, and ND C. North Drainage Canal

Fig. 4 The ratio of BC to TOC concentrations in the sediments from *YD R.* Yongding New River, *SD C.* South Drainage Canal, and *ND C.* North Drainage Canal

for agriculture irrigation and waterway for flood control in wet seasons except receiving wastewater from Tianjin.

BC as well as kerogen carbon and diagenetically aged material are viewed as comprised of “glassy” organic matter responsible for strong HOC sorption, nonlinear adsorption behavior, and slow mass transfer rates (Rockne et al. 2002; Ran et al. 2007). Assuming the overall sediment–water distribution coefficient K_d can be apportioned into the terms representing organic carbon

absorption and BC adsorption, Lohmann et al. found that BC was responsible for over 90% of the total PAH sorption in Boston Harbor sediment and over 80% in New York Harbor sediment (Lohmann et al. 2005). The positive relation between BC contents with PAHs concentrations indicated that BC was an important factor controlling the partitioning of PAHs in the sediments of this study.

The in situ partition of PAHs among different phases was calculated in this study. The calculated partition coefficients between SPM and surface water, sediment and PW, K_{oc} using measured data versus the predicted K_{oc} using Lohmann’s expressions (Lohmann et al. 2005) were listed in Table 1. As is expected, the measured organic carbon normalized partition coefficients $\log K_{oc,obs}$ between SPM and surface water in the three streams were higher than the predicted partition coefficients for all 16 PAHs compounds except DBA. The divergence of $\log K_{oc,obs}$ values from such predictions was highest for lower molecular weight PAHs (with two or three rings) in Yongding New River and South Drainage Canal and exceeded $\log K_{oc,pred}$ by about 0.76–1.32, 0.93–1.38 log units, respectively. While for North Drainage Canal, the

Table 1 Comparison of measured organic carbon normalized SPM-DP, sediment-PW partition coefficients ($\log K_{oc,obs}$) with predicted $\log K_{oc}$ in Yongding New River, South Drainage Canal and North Drainage Canal

PAHs	Measured						Predicted logK ^a _{oc,pred}
	logK _{oc,obs} (SPM-surface water)			logK _{oc,obs} (sediment-PW)			
	Yongding New River	South Drainage Canal	North Drainage Canal	Yongding New River	South Drainage Canal	North Drainage Canal	
Nap	4.47 ± 0.72	4.07 ± 0.88	4.41 ± 0.46	3.56 ± 0.67	3.78 ± 0.42	3.85 ± 0.19	3.15
Acy	4.84 ± 0.53	5.07 ± 0.54	4.72 ± 0.44	4.32 ± 0.52	4.20 ± 0.69	4.86 ± 0.26	3.76
Ace	4.44 ± 0.60	4.89 ± 0.55	4.20 ± 0.50	3.76 ± 0.62	3.54 ± 0.55	3.96 ± 0.23	3.68
Fl	4.88 ± 0.53	5.12 ± 0.50	4.60 ± 0.35	4.16 ± 0.52	4.04 ± 0.44	4.42 ± 0.13	3.93
Phe	5.28 ± 0.46	5.51 ± 0.42	5.27 ± 0.28	4.45 ± 0.49	4.31 ± 0.55	5.01 ± 0.34	4.31
Ant	5.30 ± 0.54	5.67 ± 0.44	5.48 ± 0.27	4.89 ± 0.60	5.10 ± 0.74	5.17 ± 0.09	4.28
Fluo	5.58 ± 0.53	5.79 ± 0.46	6.05 ± 0.44	5.26 ± 0.56	4.82 ± 0.57	5.59 ± 0.12	4.94
Pyr	5.65 ± 0.55	5.86 ± 0.45	6.21 ± 0.26	5.43 ± 0.58	5.17 ± 0.49	5.70 ± 0.11	4.90
BaA	5.99 ± 0.62	6.52 ± 0.68	6.80 ± 0.28	5.83 ± 0.48	5.46 ± 0.65	5.55 ± 0.63	5.61
Chry	5.90 ± 0.57	6.10 ± 0.51	6.56 ± 0.26	5.68 ± 0.55	5.54 ± 0.92	5.97 ± 0.09	5.56
BbF	6.22 ± 0.68	5.91 ± 0.56	7.05 ± 0.41	6.87 ± 0.48	6.17 ± 0.65	6.45 ± 0.47	5.51
BkF	6.03 ± 0.67	6.26 ± 0.77	6.77 ± 0.38	6.07 ± 0.53	5.96 ± 0.58	6.28 ± 0.48	5.70
BaP	6.11 ± 0.67	6.30 ± 0.58	7.02 ± 0.39	6.55 ± 0.62	6.16 ± 0.34	6.84 ± 0.29	5.74
Ind	6.55 ± 0.77	6.35 ± 0.82	7.48 ± 0.38	6.72 ± 0.47	6.28 ± 0.67	6.53 ± 0.86	6.19
DBA	5.86 ± 0.75	5.99 ± 0.79	6.87 ± 0.48	4.76 ± 0.65	5.96 ± 0.17	6.69 ± 0.60	6.43
BghiP	6.35 ± 0.65	6.28 ± 0.66	7.08 ± 0.27	6.72 ± 0.48	6.43 ± 0.39	6.48 ± 0.37	6.19

^a $\log K_{oc,pred} = 0.97 \log K_{ow} - 0.12$; Lohmann et al. (2005); the $\log K_{ow}$ values refer to Mackay et al. (1992)

largest discrepancy of $\log K_{oc,obs}$ values from predictions was for PAHs compounds of three to six rings except DBA, which was about 0.89–1.54 log units. Also, most of $\log K_{oc,obs}$ between sediment and PW in the three streams were also higher than the predicted partition coefficients. This could be explained by the strong and nonlinear sorption of PAHs by carbonaceous geosorbents including BC in the sediment (Mcgroddy and Farrington 1995; Bucheli and Gustafsson 2000; Lohmann et al. 2005; Cornelissen et al. 2005, 2006). In addition, the rather slow release of PAHs after an initial rapid release from sediments collected from Yongding New River, South Drainage Canal, and North Drainage Canal PAHs which we reported previously in the desorption experiment (Qi et al. 2010b) also proved this strong sorption of PAHs by carbonaceous particles in the sediment. So we could conclude that both in situ PAHs measurement data and simulated PAHs desorption process in the lab indicated that strong and nonlinear sorption of PAHs by sorbent such as BC existed in the studied streams.

Sources of PAHs in the streams

Coal combustion has been identified to be a long-term and prevailing contamination source for sediment in the rivers of Tianjin (Shi et al. 2007). Our previous study reported that coke oven sources and wood combustion also contributed to the PAHs contamination of Yongding New River, South Drainage Canal, and North Drainage Canal (Qi et al. 2010a). As we can expect, wastewater discharges, surface runoff, and air deposition (both dry and wet) were the possible pathways of carbonaceous particles and PAHs entering the streams. Here, we compare the PAHs isomer ratios in effluent samples from WWTPs that discharge into the studied streams, SPM and sediment samples from the streams, and the soil samples by the riverbank that were collected in this study in June of 2007.

Parent PAHs of molecular mass 178 (Ant and Phe), 202 (Fluo and Pyr), 228 (BaA and Chry), and 276 (Ind and BghiP) are commonly used to distinguish between petrogenic sources (leakage of oil or petroleum products) and pyrogenic sources (incomplete combustion of fossil fuel or

wood). Yunker et al. (2002) integrated the four isomer ratios, Ant/178, Fluo/202, BaA/228, and Ind/276, from a large number of environmental samples or single sources. For Ant/178, ratios below 0.1 indicate petrogenic origins, while ratios at 0.1 and above have been attributed to pyrogenic origins. For Fluo/202 and Ind/276, ratios below 0.4 and 0.2, respectively, suggest petrogenic origins while ratios at 0.5 and above indicate fuel combustion. In the case of BaA/228, ratios below 0.2 have been attributed to petrogenic origins and above 0.35 suggest pyrogenic origins.

Ant/178 against Fluo/202 ratios in samples of this study were plotted in Fig. 5. Ratios of Ant/178 and Fluo/202 in most of the sediment samples and all effluent samples of WWTPs were higher than 0.1 and 0.5, respectively, suggesting the predominant pyrogenic source for the PAHs. Although

Fig. 5 PAH cross-plots for the ratios of Ant/178 vs. Fluo/202 in SPM, sediment samples from the streams, soil samples from the riverbank, and WWTPs (represented in stars)

the major PAHs sources to all the sediment samples were similar, detailed characteristics could be identified among the different streams. To be specific, remarkably consistent isomer ratios for PAHs were found in sediments of Yongding New River, indicating the similar sources of the isomer pairs to the different sampling sites (Dickhut et al. 2000). While the cross-plots of isomer ratios in sediments of South Drainage Canal and North Drainage Canal were distributed dispersedly. This might reflect the more complex PAHs input sources to these two drainage canals (Mai et al. 2003).

PAHs sources in surface soil and dustfall have been identified and apportioned (Zuo et al. 2007; Wu et al. 2005). For soil samples in the urban-suburban zone, 37% PAHs was from a combined source of coal and petroleum, 26% was from a combined source of coking and biomass, and 23% was from incineration (Zuo et al. 2007). For dust-fall samples in Tianjin, coal combustion was identified as the main PAHs source (Wu et al. 2005). From Fig. 5 we can see that PAHs source to the soil samples by the riverbank could be identified as the combined source of combustion and petrogenic sources. Comparing with the soil samples by riverbank, PAHs in sediment samples from Yongding New River and Northsewer seemed to be more associated with coal/grass/wood combustion.

Further comparison between PAHs compositions in sediments and soils were carried out by

comparing the PAHs profiles which were generated using the same procedure described in the previous literatures (Li et al. 2003; Bzdusek and Christensen 2004). In brief, the concentrations of PAHs were normalized to that of BaP. Then, the fractions were calculated. The fractional compositions of individual PAHs in sediments and soils are presented in Fig. 6. Comparing with the sediments, PAHs in soils was low in Fluo, Pyr, and BaP, but enriched with BbF, BghiP, and Ind, which indicated more contribution of coking and vehicular sources to PAHs in soils than to those in sediments (Bzdusek and Christensen 2004; Zuo et al. 2007).

Compared with sediment, SPM analysis could only explain a short-term contamination source especially in wet season (Shi et al. 2007). As we can see from Fig. 5, although a combined source from grass/wood/coal combustion and petrogenic source could be identified in SPM, the cross-plots of isomer ratios in SPM samples of Yongding New River were distributed more dispersedly than in sediments.

Generally, PAHs in the sediment of Yongding New River, South Drainage Canal, and North Drainage Canal, effluent samples of WWTPs, and soil samples by the riverbank had similar main sources although the two drainage canals had more complex PAHs input. Comparing with the soil samples by the riverbank, PAHs in sediment samples from Yongding New River and Northsewer seemed to be more associated with coal/grass/wood combustion.

Fig. 6 Fractional composition of PAHs in sediments from Yongding New River and in soils by the riverbank collected in June, 2007

Conclusions

Combining the above analysis about partitioning and sources of PAHs in the studied streams, we could see carbonaceous particles (including black carbon) is an important factor influencing the partitioning of PAHs among different phases in the streams. Coal and petroleum combustion was the main PAHs source in the streams, WWTPs, and soil by the riverbank. The transportation and transformation of both carbonaceous particles and PAHs during wastewater treatment process, surface runoff, etc, should be studied further in

order to make decisions on PAHs controlling measures.

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