

Partitioning and source diagnostics of polycyclic aromatic hydrocarbons in rivers in Tianjin, China

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Distribution of PAHs among water, suspended solids and sediment was under strong influence of naturally occurring organic carbon.

Abstract

Water, suspended particulate matter (SPM), and sediment samples were collected from ten rivers in Tianjin and analyzed for 16 polycyclic aromatic hydrocarbons (PAHs), dissolved organic carbon (DOC), particulate organic carbon (POC) in SPM and total organic carbon (TOC) in sediment. The behavior and fate of PAHs influenced by these parameters were examined. Generally, organic carbon was the primary factor controlling the behavior of the 16 PAH species. Partitioning of PAHs between SPM and water phase was studied, and K_{OC} for some PAH species were found to be significantly higher than the predicted values. The source of PAHs contamination was diagnosed by using PAH isomer ratios. Coal combustion was identified to be a long-term and prevailing contamination source for sediment, while sewage/wastewater source could reasonably explain a short-term PAHs contamination of SPM.

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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a group of persistent organic priority pollutants, ubiquitous in various environmental systems, and have resulted in much concern due to their toxicity, carcinogenicity and mutagenicity (US EPA, 1993). PAHs are formed and emitted primarily during incomplete combustion (pyrogenic source) of organic matter from different sources, such as combustion engines, home heating, power generation from fossil fuels, industrial activities, and biomass burning (Broman et al., 1991; Heemken et al., 2000). The productions of coke, black carbon, coal tar pitch, and asphalt have been identified as important anthropogenic sources of PAHs (Countway et al., 2003). Noncombustion-

derived petrogenic PAHs are also sources for contamination (Naes and Oug, 1997).

The aquatic ecosystem is one of the major sinks of PAH contamination (Tao et al., 2003), which has received most attention because of their lipophilic characteristic and bioconcentration effect (Haitzer et al., 1998). PAHs enter the aquatic environment through atmospheric deposition, industrial and residential wastewater discharge, oil pollution by ships, or urban and surface runoff (Heemken et al., 2000). Aquatic systems are not only important sinks in the global cycling of PAHs, but are also secondary sources of contamination (Sanders et al., 1996). Fresh water systems have received more attention for PAH contamination, although most studies focused on sediment or water phase (Christensen and Bzdusek, 2005). Thus, a comprehensive study of PAH behavior including water, suspended particulate matter, sediment, and sediment pore water phases would be most informative (Mitra and Dickhut, 1999).

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In aquatic systems, PAHs exist in freely dissolved, dissolved organic matter (DOM) associated, suspended particulate matter (SPM) associated, and sediment-associated phases. The distribution of PAHs among these phases is primarily controlled by physical/chemical properties of the individual species, such as solubility, vapor pressure, and sorption coefficient, as well as the characteristics of each phase (Readman et al., 1984; Zhou et al., 1999). Suspended organic and inorganic particles are ubiquitous in surface waters and are important vectors for the transport and distribution of contaminants in aquatic ecosystems.

The characteristics of different sorbents are also a critical factor. Particulate sorption dynamics of PAHs are of great importance for their distribution, revolatilization, sedimentation, and resuspension (Broman et al., 1991; Leppard et al., 1998). Dissolved organic matter has generally linear and reversible partitioning behavior (Xing and Pignatello, 1997; Xia and Pignatello, 2001) and fast equilibrium. In contrast, soot particles have high organic carbon to oxygen ratio and are viewed as being comprised of “glassy” organic matter responsible for strong PAH sorption, nonlinear adsorption behavior, and slow mass transfer rates (Xia and Pignatello, 2001; Rockne et al., 2002). In an organic matter rich system, the physical/chemical interaction of PAHs with organic matter is the dominant mechanism to determine the behavior and fate of PAHs. This interaction affects dispersal patterns, bioavailability and ultimate impact on aquatic organism, and may also reflect sources of PAHs.

Combustion of different fossil fuels produces PAH emissions with different signature. Thus, it is possible to identify the sources based on their PAHs emission “fingerprints” (Yunker et al., 1996). Furthermore, these source signatures can be altered by environmental processes such as photodegradation, volatilization, and solubilization, which act selectively or differentially on individual PAH species (Simpson et al., 1996; Zhang et al., 2005). As a result, by using the differences in reactivity and solubility of two PAH isomers, such as phenanthrene/anthracene, fluoranthene/pyrene, benz[a]anthracene/chrysene, benzo[b]fluoranthene/benzo[k]fluoranthene, indeno[1,2,3-cd]pyrene/benzo(g,h,i)perylene, or benzo[a]pyrene/benzo[g,h,i]perylene, both the source and delivery routes for the PAHs can be examined (Gschwend and Hites, 1981).

Tianjin, China's third largest industrial center with an area of 12,000 km² and a population over 9.5 million, is located in the lower reaches of Hai River near Beijing and adjacent to the Bohai Sea. The Tianjin urban/industrial complex is highly impacted with rapid industrialization and urbanization. Industry and automobiles are two major sources of pollution. On average, the industries burn 15 million tons of coal a year and discharge 180 million tons of wastewater. Ten major rivers/canals in the study area collect the majority of natural runoff and industrial and domestic effluents in Tianjin. Most of these rivers carry a significant amount of wastewater from Tianjin and Beijing urban areas (Tianjin Environmental Protection Bureau, 2001). A large portion of the discharged water is used in agricultural irrigation (within an area of 3500 km²) due to the severe shortage of water resources in the Tianjin area. PAHs are among the most ubiquitous hydrophobic organic pollutants in

Tianjin. PAH sources include the coking industry, domestic and industrial coal combustion, automobile emissions, and open-air biomass burning.

To provide an overall picture of PAH contamination in Tianjin's rivers, an extensive survey was conducted with concurrent sampling of water, SPM, and sediment. Our previous paper quantitatively provided the levels and spatial variations of PAH contamination (Shi et al., 2005). This study particularly focused on the partitioning among the three phases and PAH source identification. A better understanding of the geochemical processes, transport, and fate of PAH contamination at a mechanistic level is essential for public safety management.

2. Materials and methods

2.1. Sample preparation and PAH analysis

Fifty-four sediment and 30 water (containing suspended particulate matter) samples were collected from ten rivers in Tianjin. At each location, sediment samples were collected from three to five adjacent points, and well mixed. All samples were frozen immediately and kept at -18 °C before analysis. Sample preparation, PAH analysis, and analytical quality controls were reported in detail in our previous paper (Shi et al., 2005), and will only be described briefly here. After centrifuging or filtering and freeze drying, sediment and SPM samples were extracted by accelerated solvent extraction (ASE300, Dionex), cleaned via silica gel (US EPA Method 3630C, 3600B), and analyzed by GC/MS (Agilent 6890 GC, 5973 MSD) in both total ion scan and selected ion monitoring (SIM) modes. Water samples were first filtered (Sartorius glass fiber filter, ~0.5 μm, ashed at 450 °C) and extracted by solid phase micro-extraction (SPME, 100 μm film thickness coatings of poly(dimethylsiloxane), Supelco), then analyzed by GC/MS with external PAH standards. SPME was performed by filling a 3.4 ml Supelco vial with filtrate, and were agitated with a stir bar for 1 h at 1000 rpm. The 16 PAHs detected in sequence were: naphthalene (NAP), acenaphthylene (ACY), acenaphthene (ACE), fluorene (FLO), phenanthrene (PHE), anthracene (ANT), fluoranthene (FLA), pyrene (PYR), benz[a]anthracene (BaA), chrysene (CHR), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), indeno[1,2,3-cd]pyrene (IcdP), dibenz[a,h]anthracene (DahA), benzo[g,h,i]perylene (BghiP). The 16 PAHs standard mixture was purchased from ChemService (PPH-10JM, ChemService Inc.). Organic carbon and grain size analytical methods are available in the supplementary information.

2.2. Analytical quality controls

For individual PAH analysis, the method detection limits were on average 50–250 ng/g (dry wt.) for 2–10 g of sediment with GC/MS total scan mode, 1 ng/ml for 4 ml water sample, and 1 ng/g (dry wt.) for 0.1 g SPM with GC/MS SIM mode. The recoveries ranged from 76% to 127% at spiking levels of 10 ng/g and 50 ng/g for 16 spiked individual PAH species. PAH concentrations of each sample were corrected by corresponding recoveries. Procedure blanks were run simultaneously with every set of samples (10–16 samples per set) and were subtracted from the analytical results. No less than 20% replicate samples were examined in sediment PAH analysis to further monitor the precision of analytical results. DOC and TOC were determined in triplicates with a relative standard deviation less than 1%. Sediment granularity was measured for 6 times for each sample to obtain better replication.

3. Results and discussion

3.1. Relationship between TOC, DOC, and SPM content

Levels of PAH contamination in Tianjin's rivers were described in our previous paper (Shi et al., 2005). The

concentrations of sediment TOC, SPM POC, and water DOC showed similar spatial variations to PAHs, which indicate fraction of organic carbon is an important factor in determining behavior of PAHs in the study area. Arithmetic and geometric means, minimum, maximum, median, the 25th, the 75th, and the 95th percentiles of organic carbon concentrations in sediment, SPM, and water samples are summarized in Fig. 1. The average SPM content was 0.066 ± 0.041 g/L. It should be pointed out that the geometric mean of sediment TOC (5.8%) was 1.5 to 30 times higher than the other 11 major riverine sediments in eastern China (Wang et al., 1997). Water DOC (28.7 mg/L) was also extremely high for fresh river water, and DOC content in some regions were even higher than that of the Great Dismal Swamp, USA (Johannesson et al., 2004). Both high SPM and high organic carbon contents indicated that the study area was severely polluted, and the behavior and fate of PAHs might be deeply affected by these factors.

Sediment TOC and water DOC was not significantly correlated, so was SPM POC and water DOC. However, sediment TOC was positively correlated to SPM POC (Fig. 2a), and water DOC was correlated to SPM contents (Fig. 2b). The positive correlation between sediment TOC and SPM POC indicated that, in the study area, biogeochemistry processes were important to some degree, while the non-linear relationship suggested slightly different sources of SPM and sediment. The positive correlation between water DOC and SPM content suggested common pollutant source for these rivers, for example, wastewater from domestic or industrial sectors.

3.2. Factors affecting the content of dissolved phase PAHs

DOC is one of the most important factors influencing the behavior, fate, and toxicity of dissolved phase PAHs in water (Haitzer et al., 1998; Tremblay et al., 2005). Most PAHs are

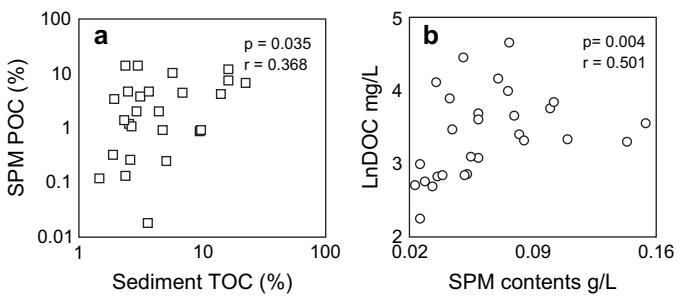


Fig. 2. Relationship between (a) suspended particulate matter particulate organic carbon (SPM POC) and sediment total organic carbon (TOC); (b) water dissolved organic carbon (DOC) and SPM contents (Site A03 and F03 was not plotted in b as outliers because of the markedly high SPM levels).

hydrophobic and considerably insoluble, and prefer to bind to colloids, dissolved organic matter, or SPM in water. Sorption to colloids and DOM could increase the total apparent dissolved concentration of PAHs, which includes freely dissolved PAHs, DOC associated PAHs, and PAHs associated with colloidal or fine-grained particles (Fernandes et al., 1997). Processes including sorption/desorption, partitioning, volatilization, deposition, and photolysis could account for the abiotic transport and transformation of total dissolved phase PAHs.

SPME with external standard would only determine the freely dissolved PAH concentrations (Poerschmann et al., 1997). Usually, the sum of freely dissolved PAHs and DOC associated PAHs can be obtained by either liquid–liquid extraction (LLE), solid phase extraction (SPE) or SPME with deuterated internal standards (Poerschmann et al., 1997; Hawthorne et al., 2005). In this study, only freely dissolved PAHs phase was measured, and the total dissolved PAHs content was calculated by measured DOC concentration and partition coefficient (K_{DOC}) from the literature (Table 1, Poerschmann et al., 1997; Li and Lee, 2000). For the 16 PAHs, $\log K_{DOC}$ ranged from 2.79 (NAP) to 5.87 (IcdP). Considering an average DOC level of 34 mg/L in Tianjin's rivers, the percentages of freely dissolved phase PAHs among the total dissolved PAHs ranged from 98% (NAP) to 3.8% (IcdP).

Positive correlation was found between 2-ring and 3-ring dissolved phase PAHs and DOC at 0.01 or 0.05 levels of significance; however, freely dissolved ≥ 4 -ring PAHs were not significantly correlated with DOC concentration (Figs. 3 and 4). Two-ring and 3-ring PAHs contributed to 86% of freely dissolved $\sum PAH_{16}$, so that the positive correlation between freely dissolved $\sum PAH_{16}$ and DOC contents was also observed. The calculated DOC associated 4-ring or higher PAHs accounted for 56–96% total dissolved PAHs. Thus, it was not surprising that the statistical examination showed a positive correlation between total dissolved PAH concentrations and DOC content for all 16 species (Fig. 4, filled bar). It should be noted that K_{DOC} values were taken from the literature, and could be affected by various factors, such as sorbent characteristics (Tremblay et al., 2005) or ionic strength. Thus, the calculated total dissolved PAHs content was only a rough approximation for the previous experiment. The

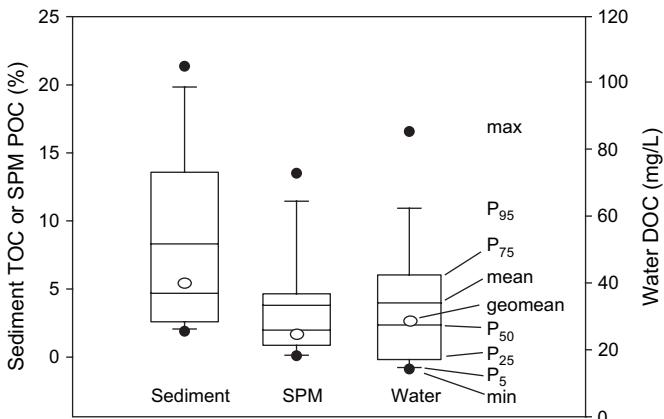


Fig. 1. Total organic carbon (TOC), particulate organic carbon (POC), and dissolved organic carbon (DOC) concentrations in sediment, suspended particulate matter (SPM), and water in Tianjin's rivers. The results are presented as maximum, minimum, arithmetic and geometric means, median (p_{50}), the 5th (p_5), the 25th (p_{25}), the 75th (p_{75}) and the 95th (p_{95}) percentiles.

Table 1
Comparison of $\log K_{OC}$ -observed and $\log K_{OC}$ -predicted in the study area

PAHs	$\log K_{DOC}^a$	$\log K_{ow}^b$	$\log K_p^{\text{obs}}$	$\log K_{OC}^{\text{obs}}$	$\log K_{OC}^{\text{pred}c}$	$\log K_{OC}^{\text{obs}} - \log K_{OC}^{\text{pred}}$
NAP	2.79	3.37	12894	5.41	2.99	2.42
ACY	3.96	4.00	222175	6.65	3.61	3.04
ACE	3.66	3.92	10154	5.31	3.53	1.78
FLO	3.75	4.18	49826	6.00	3.79	2.21
PHE	4.12	4.57	66299	6.12	4.17	1.95
ANT	4.00	4.54	68917	6.14	4.14	2.00
FLA	4.58	5.22	46415	5.97	4.82	1.15
PYR	4.62	5.18	21125	5.63	4.78	0.85
BaA	5.15	5.91	26079	5.72	5.50	0.22
CHR	5.16	5.86	7331	5.17	5.45	-0.28
BbF	5.70	5.80	19652	5.59	5.39	0.20
BkF	5.56	6.00	20437	5.61	5.59	0.02
BaP	5.68	6.04	7824	5.19	5.63	-0.43
IcdP	5.87	6.50	5387	5.03	6.08	-1.05
DahA	5.59	6.75	52072	5.02	6.33	-0.31
BghiP	5.65	6.50	22288	5.65	6.08	-0.43

^a $\log K_{DOC}$ values refer to Poerschmann et al., 1997; Li and Lee, 2000.

^b $\log K_{ow}$ values refer to Mackay et al., 1992.

^c $\log K_{OC}^{\text{pred}} = 0.989 \log K_{ow} - 0.346$; Karickhoff, 1981.

deuterated internal standards should be spiked to a DOM-water system, to acquire experimental K_{DOC} values (Poerschmann et al., 1997).

DOM was not only an important pool for dissolved heavy PAHs, but also a facilitator for the accumulation of freely dissolved light PAHs (2-ring and 3-ring) in Tianjin's rivers, although only 2–31% of them were directly associated with DOC. Two explanations were proposed: first, DOM could significantly reduce the speed of photodegradation of PAHs primarily through competitive light absorption and the quenching of PAH* (active state) (Schwarzenbach et al., 2003). Thus, the high DOC content preserved the high levels of dissolved light PAHs. Second, as discussed previously, DOC was positively correlated to SPM content probably because of the common origin.

As indicated in Fig. 3, the relationships between PAHs and DOC were complicated, and the lower correlation coefficients ($r < 0.5$) indicated deviation from the linear relationship. This suggested that there could be other factors, such as SPM content, affecting the concentration of dissolved phase PAHs (Fernandes, 1997). The correlation between freely dissolved phase $\sum PAH_{16}$ concentration and SPM contents in ten rivers was statistically significant (Spearman's rank correlation,

$r = 0.745$, $p < 0.01$, Fig. S1 in supplementary information), which was consistent with the so-called particle concentration effect (Voice et al., 1983; Zhou et al., 1999). It should be noted that the field measurement was not as ideal as a laboratory experiment, and various inorganic matrices might be encountered in the field samples. For instance, the freely dissolved $\sum PAH_{16}$ concentration in river B and river J were not consistent with their SPM contents.

3.3. Factors affecting the content of suspended particulate matter associated PAHs

The statistical examination showed a significantly positive correlation between SPM associated heavy (≥ 4 -ring) PAH concentrations and POC (Figs. S2, S3, supplementary information). The correlation coefficients were relatively low, probably due to the wide range of PAH concentrations ($\sum PAH_{16}$: 938.28–64189.40 ng/g) and various SPM matrices (based on sediment granularity analysis, and also Fig. 2). Zhou et al. (1999) suggested that there was a good correlation between the FLA and PYR concentrations and organic carbon content on SPM. Usually, such correlations would be more pronounced if samples were further divided to subgroups

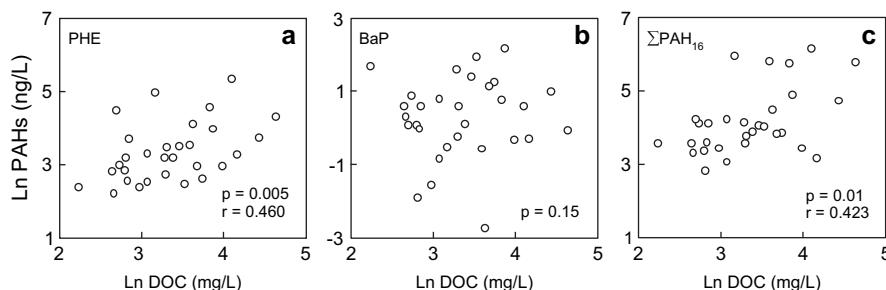


Fig. 3. The relationship between freely dissolved phase PAHs and dissolved organic carbon (DOC). p is the significance of confidence, r represents Spearman's coefficient of rank correlation.

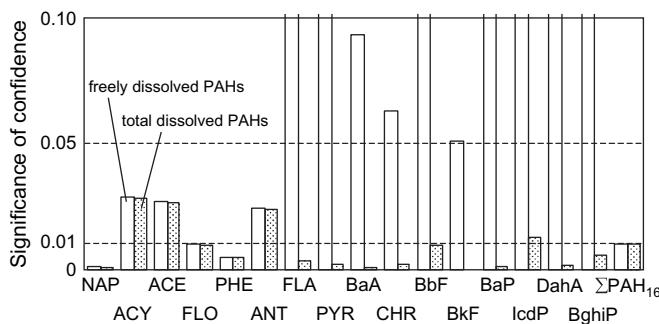


Fig. 4. The significance of bivariate correlation (Spearman's rank correlation) between contents of freely dissolved phase PAHs and DOC or total dissolved phase PAHs and DOC.

according to the degree of contamination (Zhou et al., 1999; Bucheli et al., 2004).

In contrast to freely dissolved PAHs, all six SPM associated light PAHs were not significantly correlated with POC (Figs. S2, S3, supplementary information). It might be explained that low molecular weight PAHs were more volatile (Henry's Law constants $> 4 \times 10^{-5}$ atm·m³/mol) and POC might become a secondary factor in controlling the behavior of light PAHs. The relationship between these light PAHs and POC was not as clear as that of heavy PAHs, probably due to stronger influences of some other processes/factors, such as desorption, volatilization, lipid content of particles, or SPM content. It would be more elucidating if the corresponding processes/factors could be carefully examined in laboratory, and compared to field studies, to address the behavior of different PAH species. Furthermore, Broman et al. (1991) reported that all particle associated PAHs showed no correlation to the concentration of POC. However, SPM associated heavy PAHs are still positively correlated to POC concentration in Tianjin's rivers, probably because POC content of the Broman's study area was relatively low (0.12 ± 0.03 mg/L, Broman et al., 1991), whereas in Tianjin's rivers POC content (3.4 ± 4.5 mg/L) was more than one order of magnitude high.

The relationship between SPM associated PAH concentrations and SPM content was more complex. Non-parameter correlation analysis indicated that 5 of all 6 light PAHs were negatively correlated with content of SPM; however, 4 out of 6 high molecular weight (5–6 rings) PAHs were positively correlated with contents of SPM (Figs. S4, S5, supplementary information). Readman et al. (1984) reported that PAHs with molecular weight >200 Da are highly correlated with the SPM in natural waters. Broman et al. (1991) observed that PAHs with a molecular weight (MW) higher than 230–250 Da showed the same tendency, whereas light PAHs did not. In Tianjin's rivers, except for BbF (MW 252.32 Da) and BghiP (MW 276.34 Da), all the other high molecular weight PAHs (MW >250 Da) were consistent with the above tendency, although the correlation coefficients were relatively low.

The negative correlation between SPM associated light PAHs and SPM content has not been previously reported, either for laboratory results or field measurements. The negative correlation tendency could be explained by three

hypotheses. First, high SPM content corresponded to high DOC concentration (Fig. 2b), and large amount of DOC competed well with SPM for PAHs, so that the SPM associated PAHs would be lower when SPM content was higher. The above dynamic competition mechanism might be unsubstantial for heavy PAHs due to some irreversible processes such as sequestration of mostly heavy pyrogenic PAHs in the suspended particle (Luthy et al., 1997). Second, it appeared that a considerable amount of the SPM was not from resuspension, but from surface runoff which diluted PAHs in SPM. Third, the high SPM content probably indicated a more intense physically driven geochemical process, which could lead to selective depletion of light PAHs (more volatile, less hydrophobic) due to enhanced desorption and scouring of particle surfaces (Mitra et al., 1999).

3.4. Factors affecting the concentration of sediment PAHs

The characteristics of the sediment, for example, components and species of organic matter and clay minerals, would influence the behavior and fate of sediment associated PAHs (Means et al., 1980). Zhang et al. (2004) reported strong correlation between PAHs and TOC, clay, clay + silt, and claimed that TOC, clay, and clay + silt had a great impact on PAH contamination in the sediment. In Tianjin's rivers, four parameters: TOC, pH, clay, and pelite (silt + clay, <0.0625 mm in diameter of grains) were recorded. All four parameters were strongly correlated with sediment associated PAH concentrations in bivariate correlation ($p < 0.05$), whereas pH, clay, and pelite were all eliminated in a partial correlation analysis when the other parameters were fixed. TOC was the only factor which was strongly correlated with PAHs in sediment in both bivariate (Fig. 5, $p < 10^{-6}$ for all 16 species) and partial correlation analysis. Furthermore, unlike dissolved PAHs or SPM associated PAHs, sediment associated PAHs linearly correlated with organic carbon content ($r > 0.7$ for all 16 species), which indicated that sediment contaminations were primarily controlled by TOC, and less influenced by the other factors such as sediment composition or inorganic matrix in Tianjin's rivers.

Under steady state, distribution of PAHs was expected to follow equilibrium partitioning of the PAHs to sediment organic carbon (Simpson et al., 1996). When organic carbon content is low, the partitioning of PAHs to sediment can be determined by both organic carbon content and the inorganic matrix, such as clay minerals (Maskaoui et al., 2002). For example, for the sediment from Kitimat Harbor, the relationship between PAHs and sediment TOC was significant only for highly contaminated sites where total PAH concentrations were higher than 2 $\mu\text{g/g}$ (Simpson et al., 1996). In Tianjin, the average sediment TOC was $8.3 \pm 6.9\%$, and most sediment samples were highly contaminated ($\sum \text{PAH}_{16} > 2 \mu\text{g/g}$). We observed that TOC was the major factor, and grain size only had a minor contribution.

pH of the studied sediment ranged from 7.3 to 9.2, with an average of 8.1 ± 0.5 . Linearly negative correlation was found

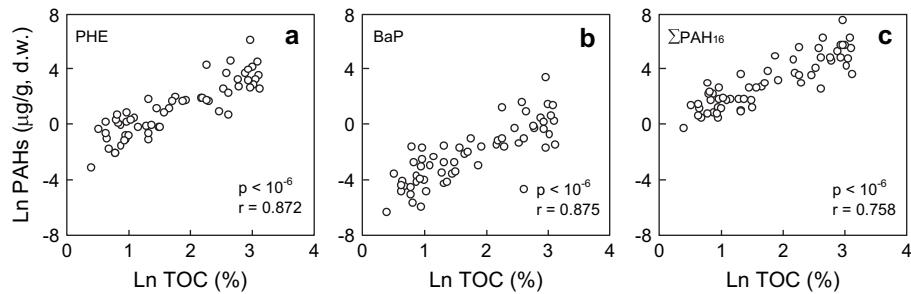


Fig. 5. The relationship between sediment associated PAHs and TOC. p is the significance of confidence, r represents Spearman's coefficient of rank correlation (bivariate).

between sediment pH and TOC (Fig. 6a). It was suggested that lower pH could reduce anoxic degradation rates and contribute to organic matter accumulation (Gale et al., 1992; Enriquez et al., 1993). Moreover, sediment PAH concentrations were apparently negatively correlated with sediment pH (Fig. 6b). However, no significant correlation was obtained if the TOC content was controlled in partial correlation analysis. Marschner et al., observed that partitioning of PYR to soil organic matter was reduced at alkaline pH, and explained that deprotonation of carboxylic and phenolic functional groups would increase polarity of the organic macromolecules leading to less hydrophobic interaction with PYR (Marschner et al., 2005). Bucheli et al. (2004) found that soil pH was negatively correlated with 2 light PAHs, NAP and FLO, and claimed that the sorptive capacity increased at low pH. Unlike their observations, in this study sediment pH was not a significant parameter controlling the behavior of sediment associated PAHs due to the unique sorbent characteristics in Tianjin's rivers.

Based on the above analysis, it was clear that natural organic matter was the most important factor governing the behavior and fate of PAHs in the three phases of rivers in Tianjin. The relationship between PAHs and sediment TOC was the most unambiguous, while the relationships among PAHs and DOC or POC were more complicated. The transport processes between the dissolved phase and particulate phase or between water and sediment, would thus be strongly influenced by organic matter content. PAH transport among water, SPM, and sediment would be linked by particulate organic matter. Since organic carbon content is much easier to measure, the levels of

contamination by PAHs can be approximately estimated for further measurement and assessment. Furthermore, DOM or POM can either retard or accelerate PAH transport and transformation in different aquatic systems (Sabbah et al., 2004), which would significantly influence the bioconcentration (Haitzer et al., 1998), bioavailability, and remediation of PAHs.

3.5. Partitioning of PAHs between SPM and water

As discussed previously, particle–water interaction was one of the dominant processes controlling the distribution and behavior of PAHs in Tianjin's rivers. Qualitatively, PAHs showed an increasing trend in their particle–water phase partitioning from 2-ring up to 6-ring compounds in Tianjin's rivers (Fig. S6, supplementary information). On average, 50% of NAP and the ACY were dissolved in the aqueous phase, while the heavy PAHs showed the strongest enrichment in the particulate phase (up to 99%). Similar results were reported by Heemken and coworkers for PAHs in the River Elbe at Hamburg, where particle associated 6-ring PAHs reached up to 80% (Heemken et al., 2000). In this study, only freely dissolved PAHs were measured by SPME, thus, the ratios were even higher.

Quantitatively, the values of partition coefficient (K_p) and organic carbon normalized partition coefficient (K_{OC}) could help understand the processes that control the behavior and fate of PAHs in river systems in Tianjin (refer to supporting information for details). A number of researchers have pointed out that particulate associated PAHs were not readily exchangeable with the dissolved phase but were present as either being occluded or tightly bound to fine-grained particles (Karickhoff et al., 1979; Fernandes et al., 1997; Luthy et al., 1997). In this field measurement, all six light PAHs were much more enriched in the particle phase than expected; however, this tendency was not significant for middle and high molecular weight PAHs (Table 1). It should be noted that total dissolved phase PAH concentrations were calculated by SPME measurements and literature K_{DOC} values. For middle and high molecular weight PAHs, 56–96% dissolved PAHs were associated with DOC, thus, any uncertainties in sampling and measurements would be significantly magnified by calculation.

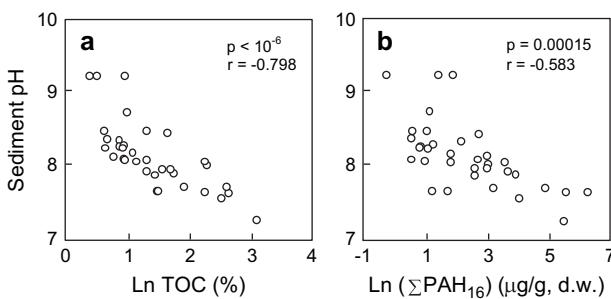


Fig. 6. The relationship between sediment pH and sediment TOC (left), sediment pH and sediment associated $\sum\text{PAH}_{16}$ concentration. r represents Spearman's coefficient of rank correlation (bivariate), p is the significance of confidence.

3.6. Source apportionment

The PHE/ANT and FLA/PYR are the most commonly used ratios to apportion PAHs. The PHE/ANT is usually large, while the FLA/PYR is low for fuel oil (Colombo et al., 1989). However, a ratio of $PHE/ANT < 10$ and $FLA/PYR > 1$ indicates contamination of PAHs from combustion processes (Benlahcen et al., 1997).

PAH isomer ratios of PHE/ANT and FLA/PYR were examined for the 53 sediment sampling sites. Except for E01, all sites satisfied the criteria of $PHE/ANT < 10$ and $FLA/PYR > 1$ (Fig. 7). This indicated that, for the sediment, combustion processes were the dominant source. In detail, sediment samples from urban areas (for example, sites F01, F04, and H07. For map of sampling site, see Fig. 1 in Shi et al., 2005) had relatively lower FLA/PYR values than those from remote sites (such as A02 and A03), which was consistent with the work of Neff (1979) and Gschwend and Hites (1981). $\sum PAH_{16}$ content at site F15 was 15–300 times lower than the other sites on river F, which might be related to the fact that its FLA/PYR ratio (6.1) was much higher than all the others. Site E1 probably had a different contamination source. Furthermore, the PYR-FLA and ANT-PHE plots gave good linear relationship (Fig. S7, supplementary information), indicating a uniform composition of the isomer PAHs throughout the study area (Readman et al., 1987).

Based on the availability of previously reported values as indicators of potential sources of PAHs and differences in photoreactivity of PAHs (Countway et al., 2003), five PAH isomer ratios were calculated for sediment associated PAHs and SPM associated PAHs in the study area (Fig. S8, Table S1, supplementary information). Dissolved phase PAHs were not considered for source apportionment. These ratios were compared with literature data (Table S2, supplementary information).

A three-dimensional plot of field measurements of BaA/CHR, BbF/BkF, and IcdP/BghiP isomer ratios along with five possible sources is shown in Fig. 8. It was clear that sediments were more compositionally similar to coal than other sources, which could indicate a long-term and prevailing

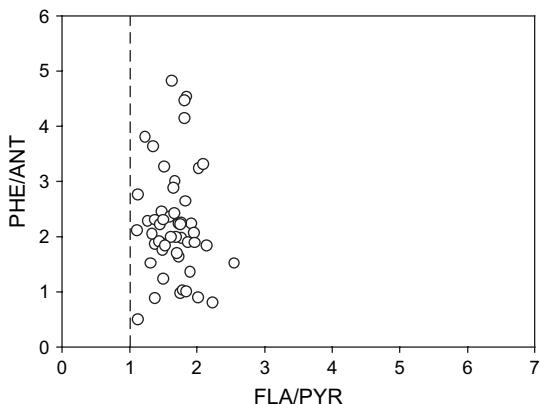


Fig. 7. PHE/ANT-FLA/PYR relationship in sediment samples (Site E1 and F15 were removed as outliers). PHE, phenanthrene; ANT, anthracene; FLA, fluoranthene; PYR: pyrene.

contamination source. It would be reasonable to assume that the source of SPM should be the same as surface sediment because they were thought to be from the same origin. However, in the study area, SPM were more compositionally similar to sewage/wastewater source. Apparently, it suggested that the source of the SPM was not merely from a resuspension process, but with a significant amount of SPM coming from sewage, industrial waste, and urban and surface runoffs. This was understandable because the samples were collected in wet season with frequent precipitations, meaning that the SPM analysis could only explain a short-term contamination source. Nevertheless, the source of SPM associated PAHs could be more carefully examined if the change of ratios during transport was accounted by using the multimedia approach of Tao and coworkers (Zhang et al., 2005). Based on their modeling, rectification factors (RF) for above 3 ratios in the study area were all less than 1, which may suggest these PAH ratios would be smaller than those at the source. As a result, the SPM associated PAHs could move closer to the coal source in Fig. 8. It should be pointed out that, currently, this new approach was only verified using limited surface soil data and sediment phase happened to have the highest uncertainties among all media.

4. Conclusion

1. Extraordinarily high SPM, high organic carbon contents, and high PAH concentrations in the study area suggested the common source of contamination. The behavior and fate of PAHs were strongly influenced by organic carbon content in each phase.
2. Coal combustion was identified to be a long-term and prevailing contamination source for sediment, while sewage/wastewater source could reasonably explain a short-term PAHs contamination of SPM.

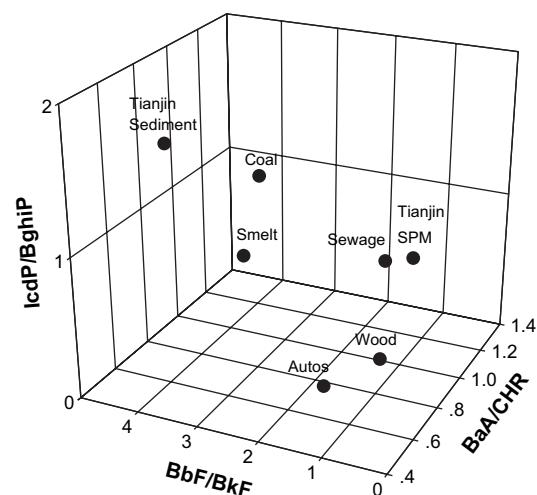


Fig. 8. Comparison of the isomer ratios of the study area and those from various emission sources (shortest distances between Tianjin samples and the sources: 0.42 for SPM and sewage; 1.04 for sediment and coal).

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Appendix. Supplementary information

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.envpol.2006.07.009.

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