

Contamination of rivers in Tianjin, China by polycyclic aromatic hydrocarbons

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Coal combustion is suggested as a recent local source of PAHs in this area.

Abstract

Tianjin urban/industrial complex is highly polluted by some persistent organic pollutants. In this study, the levels of 16 priority polycyclic aromatic hydrocarbons (PAHs) were tested in sediment, water, and suspended particulate matter (SPM) samples in 10 rivers in Tianjin. The total concentration of 16 PAHs varied from 0.787 to 1943 µg/g dry weight in sediment, from 45.81 to 1272 ng/L in water, and from 0.938 to 64.2 µg/g dry weight in SPM. The levels of PAHs in these media are high in comparison with values reported from other river and marine systems. Variability of total concentrations of PAHs in sediment, water, and SPM from nine different rivers is consistent with each other. No obvious trends of total PAHs concentration variations were found between upstream and downstream sediment, water, and SPM samples for most rivers, which indicate local inputs and disturbances along these rivers. The spatial distributions of three-phase PAHs are very similar to each other, and they are also similar to those found in topsoil. However, their chemical profiles are significantly different from that of topsoil. The change of profiles is consistent with the different aqueous transport capability of 16 PAHs. Low molecular weight PAHs predominance suggests a relatively recent local source and coal combustion source of PAHs in the study area.

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1. Introduction

As typical persistent organic pollutants and semi-volatile organic contaminants, polycyclic aromatic hydrocarbons (PAHs) are widely distributed in various environmental media (Blumer, 1976; Hites et al., 1977; Laflamme and Hites, 1978; Neff, 1979; Means et al., 1980; Gschwend and Hites, 1981). PAHs are of environmental concern due to their toxic, mutagenic,

and carcinogenic potentials (IARC, 1987). Four- to seven-ring PAHs are highly mutagenic and carcinogenic, two- or three-ring PAHs are less mutagenic but can be highly toxic (Fernandes et al., 1997). For these reasons, understanding PAH's behavior, transport, fate and environmental risk to ecological systems, especially for aquatic environment, is very important.

The primary environmental sources of PAHs include both anthropogenic inputs and biological conversion of biogenic precursors (Means et al., 1980). Fossil fuel combustion, waste incineration, coal gasification and liquefaction processes, petroleum cracking, and the

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production of coke, carbon black, coal tar pitch, and asphalt have been identified as important anthropogenic sources of PAHs (Countway et al., 2003). Industrial wastewater, sewage, road runoff/street dust and petroleum related activities are other important sources of PAHs. A minor portion of PAHs also originates from discharges of non-combusted fossil fuel products (Bouloubassi et al., 1991; Näf et al., 1992).

Organic contaminants in aquatic systems may exist in several forms, including free dissolved phase, the phase bounded to dissolved organic matter (DOM), adsorbed to suspended particulate matter (SPM), and associated with surface sediments (Readman et al., 1984; Zhou et al., 1998; van Brummelen, et al., 1998). The distribution of PAHs among these phases is mainly controlled by the intrinsic physical–chemical properties of the individual compounds, such as solubility, vapor pressure, and adsorption coefficient (Readman et al., 1984; Zhou et al., 1998). A three-phase partitioning model has been used to describe the behavior of PAHs in particles, DOM, and freely dissolved phase (Mitra and Dickhut, 1999). Due to the particle character, a fraction of the total sediment PAH concentration is sequestered in a physical–chemical form that is unequilibrium partitioning on the time scale of 30–50 years (McGroddy and Farrington, 1995). Besides partitioning, to determine the fate of PAHs in aquatic environment, several transport and transformation processes can also be considered at the sediment–water interface (Mackay, 2001).

In China, intense industrial and commercial activities in the coastal area caused adverse effects on the aquatic system. Tianjin, China's third largest industrial center, is located in northern China near Beijing and adjacent to the Bohai Sea. The Tianjin urban/industrial complex, containing about 11 200 km² of land, and having a population of 10 million, is highly polluted with the development of industry and rapid urbanization. Industry and automobiles are two major sources of pollution. On average, the industrial corporation burned 15 million tons of coal per year and discharged 180 million tons of wastewater. Rivers in the Tianjin area are severely polluted with high loads of persistent organic pollutants (Tao et al., 2003). A majority of the rivers in the area are filled with wastewater from Tianjin and Beijing urban areas (Tianjin Environmental Protection Bureau, 2001).

Confronted with water shortage in agriculture, both wastewater irrigation and sludge application have been common practices in this area for more than 40 years. Tianjin's suburban area, covering approximately 3500 km², is dominated by farmlands irrigated with wastewater (Tianjin Environmental Protection Bureau, 1996, 2001; Wang et al., 2002).

The purpose of the present work is to quantify the distribution, composition, and assess the spatial

variability of the 16 U.S. EPA priority PAHs (Keith and Telliard, 1979) in rivers in Tianjin area, to provide data for comparison with other areas, and to assess the potential harm to public health.

2. Materials and methods

2.1. Sample collection, storage, and preparation

Tianjin (39°N, 117°E) is located downstream of Hai River, China. Hai River, at one time, was one of the important drinking water resources of the Tianjin area. However, it is now polluted by urban and agriculture runoff. Many natural rivers are located in the north-eastern and southwestern area of Tianjin city and these rivers are mainly polluted by agriculture or industry. To protect Hai River, two canals are used to collect 530-million m³ civil wastewater per year. Because of the lack of rainfall, wastewater is stored in the river for a long period of time, which aggravates the pollution, especially the pollution of the sediments. In addition, an influx of polluted water from upstream further exacerbates the problem. Contaminants released from the sediment could also enhance the river pollution.

To try to understand the contamination and behavior of PAHs in the river system in this area, 54 sediment samples and 30 water and SPM samples were collected from 10 major rivers in the study area. The sampling locations are indicated in Fig. 1. Surface sediment samples were collected by using grab sampler, and water and SPM samples were collected by using cylinder samplers. All the samples were frozen immediately and transported to the laboratory and kept in the refrigerators at –18 °C before analysis. To eliminate randomness, sediment samples were collected from three to five adjacent points for each site.

After centrifuging (> 3000 rpm, Centrifuge TDL-5, China) and freeze drying (EYELA-FDU-830, Japan), every sediment sample was rubbed to granular powder to pass through a 70-mesh sieve and homogenized. Water samples were filtrated with water through glass fiber filters (~0.5 µm, Sartorius, Ø = 47 mm, ashed at 450 °C before using) to separate SPM. The SPM samples were also freeze dried and stored in aluminum foil in desiccators until extraction.

2.2. Extraction

The procedures used for the analysis of PAHs in sediment and SPM samples were based on the modified procedure of U.S. EPA Method 3545 (pressurized fluid extraction), 3630C (silica gel cleanup), 3660B (sulfur cleanup), and 8270C (GC/MS quantitation) (U.S. EPA, 1986). To summarize, samples were extracted from

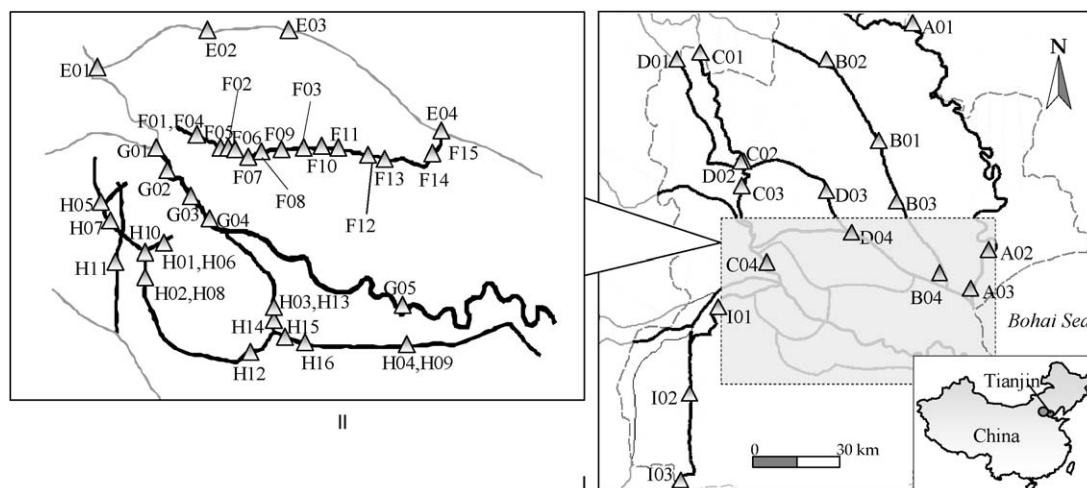


Fig. 1. Sampling area and location (A, Ji Canal; B, Chaobai New River; C, North Canal; D, Beijing Pollution Canal; E, Yongding New River; F, North Pollution Canal; G, Hai River; H, South Pollution Canal; I, South Canal. J, Yinluanrujin River is not illustrated in this figure).

various matrixes, followed by some cleanup procedures, and then analyzed by GC/MS.

After mixing the samples with anhydrous sodium sulfate (1:5 ratio of sediment to sodium sulfate) and activated copper powder (1:1, to desulfurize the extract), each sediment sample is extracted instrumentally by accelerated solvent extraction (ASE300, Donex) with *n*-hexane/dichloromethane (1:1 by volume) for 10 min for two static cycles. Extraction temperature was 125 °C and pressure was 1500 psi. SPM samples were extracted at the same condition, with the exception that sodium sulfate and activated copper powder were not added before extraction.

Dissolved phase PAHs in water samples were extracted from the filtrate by solid phase micro extraction (SPME). SPME syringe and fibers with 100 µm PDMS were obtained from Supelco. Using 3.4 mL Supelco vials, aqueous samples were filled completely and were agitated with a stir bar for 1 h at 1000 rpm, then analyzed by GC/MS without any cleanup procedures. The SPME fiber was aged for 2 h at 250 °C before utilization.

2.3. Cleanup

After accelerated solvent extraction, the extraction effluents produced from sediment and SPM samples were cleaned before quantified analysis. Extracted effluents were reduced to 1–2 mL using a rotary evaporator and purified by the chromatographic column which was filled with 8 g activated silica gel in *n*-pentane environment, with 1 g activated copper powder (to desulfurize), and with 1 g anhydrous sodium sulfate overlaying the silica gel. The column was firstly washed with 25 mL *n*-pentane solvent to remove non-PAHs impurities, such as aliphatic hydrocarbons. Then the

column was washed with another 25 mL mixed solvent of dichloromethane and *n*-pentane (2:3, v/v). The second effluent containing PAHs was collected and concentrated using a rotary evaporator. The effluent is then reduced to 0.1–1.0 mL under a stream of purified N₂ for chromatography analysis.

2.4. Gas chromatograph–mass spectrometry (GC/MS) analysis

All samples were analyzed on a Hewlett–Packard 6890 Gas Chromatograph connected to a Hewlett–Packard 5973 Mass Selective Detector (MSD) (Agilent, U.S.). The chromatographic column was a 30 m × 0.25 mm inner diameter × 0.25 µm film thickness HP-5MS capillary column (Agilent, U.S.) with helium as the carrier gas at a constant flow rate of 1 mL/min. The column was programmed from 60 to 260 °C at 6 °C/min, and then held isothermal for 15 min. The MSD was operated in the electron impact mode at 70 eV. Ion source temperature was 280 °C. The mass spectra were recorded with a scan mode covering the range of 45–400 mass units for sediment analysis, and with a selected ion monitoring (SIM) mode for analyzing the 16 U.S. EPA priority PAHs in water and SPM samples. Quantification was performed by the external standard method by using a 16 PAHs standard mixture (PPH-10JM, Chem Service Inc., U.S.). Identity and retention time of PAHs were also confirmed by this standard. GC/MS data were acquired and processed by using an Enhanced ChemStation (HP G1701CA, Agilent, U.S.). The 16 PAHs detected in sequence were: naphthalene (Nap), acenaphthylene (Acy), acenaphthene (Ace), fluorene (Fle), phenanthrene (Ph), anthracene (An), fluoranthene (Fla), pyrene (Py), benz[*a*]anthracene (BaA), chrysene (Chr), benzo[*b*]

fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), indeno[1,2,3-*cd*]pyrene (InD), dibenz[a,h]anthracene (DahA), benzo[ghi]perylene (BghiP).

2.5. Analytical quality controls

The recoveries ranged from 76% to 127% at spiking levels of 10 ng/g and 50 ng/g for 16 spiked individual PAHs samples. The method detection limits were on average 250–50 ng/g (dry wt) for 2–10 g of sediment, 1 ng/mL for 4 mL water sample, and 1 ng/g (dry wt) for 0.1 g suspended particulate matter. PAHs concentrations were corrected by corresponding recoveries. The procedure blanks were run simultaneously with every set of samples and were subtracted from the analytical results to remove the contribution of contamination in laboratory. No less than 20% replicate samples were examined in sediment PAHs analysis to further monitor the precision of analytical results. The methods developed here are qualified for analyzing 16 priority parent PAHs in sediment, water and SPM in the study area.

2.6. Other analysis and reagents

Sub-samples were used to determine organic carbon contents, granularity and pH values, and SPM contents. TOC of sediment and SPM samples and DOC of water samples were analyzed by using TOC analyzer (TOC-5000A, with SSM-5000A, Shimadzu Corp., Japan). Granularity of sediment samples was analyzed by using laser diffraction particle size analyzer (Mastersizer 2000, Malvern, U.K.), after the normal sample preparation procedure. The pH values of sediment samples were also analyzed by using pH meter (Orion, U.S.). SPM contents were measured by filtering approximately 1 L of water sample through a weighed glass fiber filter, and subsequently freeze drying it. The gain in mass on the glass fiber filter per unit volume of water filtered was defined as SPM contents (Gustafson and Dickhut, 1997).

Before using, anhydrous sodium sulfate and Kuderna-Danish concentrator glassware were heated at 650 °C to remove moisture and organic impurities. Silica gel was heated overnight at 135 °C before use. Sixteen PAHs mixed standards (PAH-Mixture 610/525/550), each at 100 µg/mL were obtained from Chem Service Inc. (West Chester, U.S.). All solvents used for sample processing (*n*-hexane, *n*-pentane, dichloromethane) were analytical grade and were purified by distillation. The solvents used for GC/MS analysis were pesticide residue grade. Active copper powder was prepared by washing with HCl (1 N) and methanol. The silica gel was deactivated at 130 °C for 10 h.

3. Results and discussion

The measured concentrations of 16 PAHs in sediment, water and SPM samples were tested for their distribution pattern using SPSS for windows software (SPSS Inc., U.S.). The results showed the data were right-skewed with leptokurtosis (for 16 individual PAHs and total concentration, skewness coefficient ranged from 3.08 to 6.66, kurtosis coefficient ranged from 9.78 to 46.85). After log transformation, a normal function can be fitted to the data (by skewness-kurtosis test, $p < 0.05$). Other published studies also suggest that natural-log normal distribution is a typical form whenever an area is polluted by PAHs (Kennelcutt II et al., 1994; Iannuzzi et al., 1997; van Belle, 2002). Therefore, geometric, instead of arithmetic, descriptive statistics were used for comparison and statistical tests. The amount corresponding to half the detection limit has been used for the samples that were below detection.

3.1. PAHs contents in sediment

All of the 16 U.S. EPA priority parent PAHs were present in a majority of sediment samples (Table 1). Sediment-associated concentration of $\sum\text{PAH}_{16}$ ranged from 0.787 to 1943 µg/g dry wt in the study area. The geometric mean of $\sum\text{PAH}_{16}$ is 10.98 µg/g dry wt. The greatest concentration of $\sum\text{PAH}_{16}$ was detected at location F05 (1943 µg/g; Fig. 1). PAHs in topsoil were also higher in this area, as indicated in Fig. 8d. The high concentration in this area may be caused by local industrial effluents or atmospheric inputs. PAHs degradation rate was also very slow in the low-dissolved oxygen aquatic environment (Macias-Zamora et al., 2002). It was reported that this river was highly polluted by oxygen demand organic pollutants and the dissolved oxygen content was nearly zero (Tianjin Environmental Protection Bureau, 1996, 2001). In addition, suspended particles in the river absorbed much PAHs, increasing the inputs of sediment PAHs.

Total concentration of potentially carcinogenic PAHs ($\sum\text{CPAH}_7$) (BaA, Chr, BbF, BkF, BaP, InD, DahA) ranged from 50 to 219.5 µg/g dry wt. The geometric mean of $\sum\text{CPAH}_7$ is 0.88 µg/g dry wt. The greatest concentration of $\sum\text{CPAH}_7$ was also detected at location F05 (219.5 µg/g).

Compared with the other polluted rivers in the world (Fig. 2), PAHs concentrations in river sediment from Tianjin area are 5- to 1000-fold greater. It is still highly polluted compared with some severely polluted industrial areas, such as Kitimat Harbor and Passaic River. The high value of PAHs occurs concurrently with exceptionally high organic carbon (OC) values. For example, OC ranges from 1.4% to 30% in Kitimat Harbor (Simpson et al., 1996) and from 1.5% to 22.5% in Tianjin Rivers, both of these areas are highly polluted by PAHs (Fig. 2).

Table 1
PAHs contents in sediment ($\mu\text{g/g}$, dry wt.) of nine rivers in Tianjin, mean \pm S.D.

	Ji Canal ($n = 3$)	Chaobai New R. ($n = 4$)	North Canal ($n = 4$)	Beijing Pollu. Ca. ($n = 4$)	Yongding New R. ($n = 4$)
Nap	2.80 ± 1.97	0.80 ± 0.47	1.77 ± 1.42	2.78 ± 5.04	4.46 ± 7.07
Acy	0.28 ± 0.23	0.18 ± 0.08	0.32 ± 0.24	0.35 ± 0.46	0.29 ± 0.39
Ace	0.51 ± 0.61	0.15 ± 0.13	0.49 ± 0.40	0.42 ± 0.35	0.42 ± 0.43
Fle	0.77 ± 0.55	0.30 ± 0.18	0.49 ± 0.20	0.66 ± 0.91	0.88 ± 1.23
Ph	1.55 ± 1.53	0.49 ± 0.49	1.43 ± 0.74	1.93 ± 2.92	2.31 ± 3.67
An	0.54 ± 0.44	0.32 ± 0.23	0.82 ± 0.67	1.69 ± 2.79	0.90 ± 1.32
Fla	1.04 ± 0.93	0.51 ± 0.39	1.23 ± 0.41	2.00 ± 2.75	1.82 ± 2.75
Py	0.51 ± 0.45	0.29 ± 0.22	0.78 ± 0.32	1.14 ± 1.57	3.14 ± 5.78
BaA	0.16 ± 0.19	0.07 ± 0.09	0.21 ± 0.11	0.24 ± 0.28	0.30 ± 0.47
Chr	0.20 ± 0.22	0.09 ± 0.10	0.26 ± 0.10	0.33 ± 0.44	0.31 ± 0.47
BbF	0.15 ± 0.14	0.05 ± 0.03	0.13 ± 0.03	0.25 ± 0.32	0.23 ± 0.36
BkF	0.01 ± 0.01	0.00 ± 0.00	0.02 ± 0.01	0.03 ± 0.04	0.03 ± 0.04
BaP	0.05 ± 0.06	0.03 ± 0.03	0.10 ± 0.06	0.09 ± 0.09	0.11 ± 0.19
InD	0.06 ± 0.04	0.08 ± 0.07	0.13 ± 0.10	0.29 ± 0.46	0.10 ± 0.14
DahA	0.03 ± 0.01	0.05 ± 0.03	0.05 ± 0.03	0.05 ± 0.03	0.03 ± 0.05
BghiP	0.03 ± 0.04	0.04 ± 0.03	0.06 ± 0.04	0.05 ± 0.02	0.07 ± 0.11
$\sum\text{PAH}_{16}$	8.66 ± 7.39	3.41 ± 2.58	8.23 ± 4.85	12.2 ± 18.4	15.4 ± 24.4

	North Pollution Canal ($n = 14$)	Hai River ($n = 5$)	South Pollution Canal ($n = 12$)	South Canal ($n = 3$)
Nap	26.2 ± 23.1	4.81 ± 4.56	38.6 ± 63.4	12.1 ± 8.20
Acy	6.07 ± 5.49	0.59 ± 0.68	0.43 ± 0.37	0.40 ± 0.32
Ace	66.7 ± 66.5	2.00 ± 3.43	0.92 ± 1.15	0.70 ± 0.58
Fle	45.6 ± 73.5	3.47 ± 5.72	1.32 ± 1.36	1.04 ± 0.82
Ph	69.9 ± 112	17.8 ± 31.9	5.34 ± 5.37	3.93 ± 3.31
An	34.0 ± 53.0	4.32 ± 7.59	2.83 ± 2.76	1.13 ± 1.06
Fla	43.0 ± 84.6	14.5 ± 26.3	2.70 ± 2.33	2.33 ± 1.91
Py	25.6 ± 43.8	8.31 ± 14.7	1.91 ± 1.75	1.79 ± 1.54
BaA	6.83 ± 13.2	1.99 ± 3.63	0.72 ± 1.25	0.53 ± 0.57
Chr	7.61 ± 14.0	2.49 ± 4.50	0.63 ± 0.67	0.55 ± 0.51
BbF	5.28 ± 11.0	1.47 ± 2.72	0.42 ± 0.55	0.32 ± 0.28
BkF	0.89 ± 1.62	0.28 ± 0.53	0.07 ± 0.09	0.06 ± 0.06
BaP	3.99 ± 7.90	0.80 ± 1.44	0.19 ± 0.22	0.18 ± 0.19
InD	2.94 ± 6.13	0.81 ± 1.47	0.16 ± 0.19	0.24 ± 0.20
DahA	1.06 ± 2.08	0.43 ± 0.81	0.09 ± 0.14	0.09 ± 0.09
BghiP	2.02 ± 4.92	0.49 ± 0.93	0.07 ± 0.09	0.11 ± 0.13
$\sum\text{PAH}_{16}$	346 ± 518	64.0 ± 110	56.4 ± 81.6	25.4 ± 19.6

Besides having a high PAH concentration, sediment, as compared to other media, such as air and water, has an extremely large total amount of PAHs in the study area (Tao et al., 2003; Wang et al., 2002).

3.2. PAHs contents in water

Most of the 16 EPA priority parent PAHs were also present in a majority of water and SPM samples. Concentration of $\sum\text{PAH}_{16}$ in dissolved phase ranged from 45.81 to 1272 ng/L. The geometric mean of $\sum\text{PAH}_{16}$ is 174 ng/L. The greatest concentration of $\sum\text{PAH}_{16}$ was detected at location F02 (1272 ng/L; Fig. 1). The PAHs concentration in sediment of this area was also higher. On average, PAHs contents in water were 5×10^6 fold lower than those in sediment, which was determined by their low water solubility and great K_{OC} values, and is also in accordance with the result that

PAH contents in surface sediments were higher by a factor of between 10^5 and 10^6 than those in the overlying water column (Witt, 1995). The mean and standard deviation of 16 PAHs experiment data for 10 rivers are presented in Table 2.

Compared with the other polluted areas in China (Fig. 3), PAHs concentrations in river water from Tianjin area were not that high, although the sediments of this area are highly polluted. This is probably due to the different sources of PAHs in these areas. The high PAHs concentrations in water in Jiulong river are possibly caused by relatively recent inputs, the source and patterns of PAHs in that area (Maskaoui et al., 2002). The pattern of PAHs in Tianjin Rivers will be discussed later, and their sources will be further studied. Moreover, PAHs contents in the dissolved phase could be reduced by photolysis and aerobic biodegradation processes, which are not available to

sediment and less available to SPM associated PAHs. The contents of SPM associated PAHs will be discussed later.

3.3. PAHs contents in SPM

Concentration of $\sum\text{PAH}_{16}$ in SPM ranged from 0.938 to 64.2 $\mu\text{g/g}$ dry wt. The greatest concentration of $\sum\text{PAH}_{16}$ associated to SPM was detected at location F03 (64.2 $\mu\text{g/g}$; Fig. 1). The geometric mean of SPM associated phase $\sum\text{PAH}_{16}$ is 8.9 $\mu\text{g/g}$ dry wt, which is on the same level of PAHs contents in sediment. This is the reason why sediment PAHs contamination level is higher, but the dissolved phase PAHs concentration is not that high. The mean and standard deviation of 16 PAHs experiment data for 10 rivers are presented in Table 3.

Compared with the other polluted areas in the world, PAHs concentrations in river SPM from Tianjing area are relatively high, which is consistent with the high PAHs contents in sediment. However, the SPM phase PAHs in Pearl River is 5-fold greater than those in Tianjin Rivers (Fig. 4).

3.4. Relationship between PAHs in sediment, water and SPM

With the exception of Rivers I and G, variability of $\sum\text{PAH}_{16}$ concentrations in sediment and water from nine different rivers is almost consistent (Fig. 5, upper). The same phenomena could be observed between sediment and SPM samples (Fig. 5, lower). The relationship can be explained by the equilibrium/unequilibrium partitioning behavior of PAHs among particles, dissolved phase, and sediment-associated phase (McGroddy and Farrington, 1995; Zhou et al., 1998). The strong correlation between PAHs concentration from sediment and water was reported in Jiulong River Estuary and Western Xiamen Sea, China (Maskaoui et al., 2002).

The range of SPM from nine different rivers is much smaller than that of sediment, which may indicate a relatively homogeneous fresh PAHs inputs in the study area though the sediment records display relatively diversified results in the whole area. The relatively higher sediment concentration of PAHs, but lower water and SPM concentration of PAHs from River I indicate

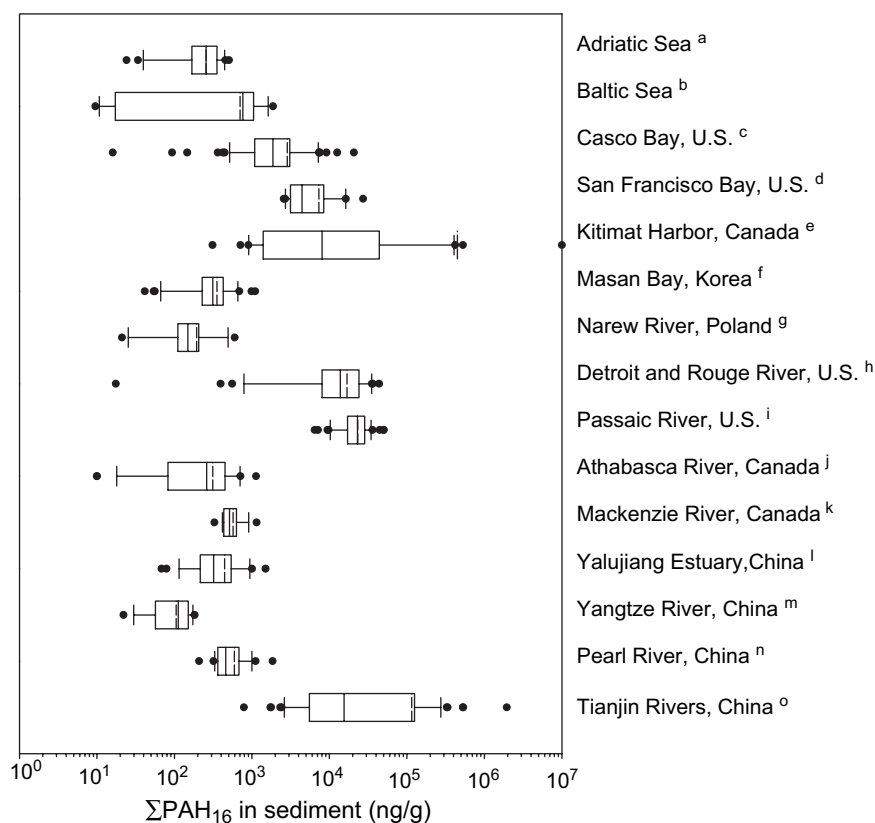


Fig. 2. $\sum\text{PAH}_{16}$ concentration in surface sediment from various riverine or marine sites in the world (ng/g dry wt.) a. Magi, E. et al., 2002; b. Witt, G., 1995; c. Kennelcutt II, M.C., et al., 1994; d. Pereira, W.E., et al., 1996; e. Simpson, C.D., et al., 1996; f. Khim, J.S., et al., 1999; g. Baran, S. et al., 2002; h. Kannan, K., et al., 2001; i. Iannuzzi, T.J., et al., 1997; j. Headley, J.V., et al., 2001. k. Headley, J.V., et al., 2002. l. Wu, Y., et al., 2003. m. Bouloubassi, I., et al., 2001; n. Mai, B.X., et al., 2002. o. This study. The boundaries of the box indicate the 25th and 75th percentiles, the line within the box marks the median. Whiskers on the left and right of the box indicate the 90th and 10th percentiles. The dashed line represents the mean, and the dots represent all the outlying points.

Table 2
PAH content in water (ng/l) of 10 rivers in Tianjin, mean \pm S.D.

PAHs	Ji Canal (<i>n</i> = 2)	Chaobai New R. (<i>n</i> = 3)	North Canal (<i>n</i> = 3)	Beijing Pollu. Ca. (<i>n</i> = 4)	Yongding New R. (<i>n</i> = 3)
Nap	43.5 \pm 2.1	43.4 \pm 12.2	53.7 \pm 13.1	57.6 \pm 58.6	28.0 \pm 20.4
Acy	0.9 \pm 0.03	1.0 \pm 1.1	0.8 \pm 0.4	2.6 \pm 1.4	2.1 \pm 2.7
Ace	2.0 \pm 0.3	2.7 \pm 1.4	3.6 \pm 2.9	10.4 \pm 10.5	7.0 \pm 2.4
Fle	5.1 \pm 1.4	5.8 \pm 2.4	4.9 \pm 2.1	13.9 \pm 8.1	14.5 \pm 2.1
Ph	25.2 \pm 11.6	17.9 \pm 7.3	17.8 \pm 7.7	26.2 \pm 18.7	33.2 \pm 7.0
An	5.0 \pm 2.6	5.5 \pm 4.5	2.6 \pm 1.5	10.2 \pm 3.1	11.4 \pm 13.5
Fla	9.6 \pm 6.9	8.1 \pm 7.3	5.2 \pm 3.2	17.3 \pm 9.4	4.6 \pm 1.8
Py	12.8 \pm 9.6	12.0 \pm 11.7	6.7 \pm 5.1	23.8 \pm 11.8	5.9 \pm 2.3
BaA	4.5 \pm 3.2	2.9 \pm 2.8	2.6 \pm 2.5	9.2 \pm 7.1	2.3 \pm 2.8
Chr	7.4 \pm 4.4	15.2 \pm 20.0	4.8 \pm 3.2	14.4 \pm 10.8	3.8 \pm 4.3
BbF	1.2 \pm 0.8	1.4 \pm 1.4	0.7 \pm 0.6	2.6 \pm 1.9	0.4 \pm 0.5
BkF	1.2 \pm 0.9	1.0 \pm 0.8	0.5 \pm 0.4	2.3 \pm 1.5	0.6 \pm 0.3
BaP	2.9 \pm 1.6	1.7 \pm 1.5	1.9 \pm 1.1	5.4 \pm 3.4	1.5 \pm 0.6
InD	2.6 \pm 0.8	1.1 \pm 0.7	2.9 \pm 1.2	0.8 \pm 0.7	1.0 \pm 0.1
DahA	0.6 \pm 0.03	0.2 \pm 0.1	0.3 \pm 0.2	0.1 \pm 0.06	0.09 \pm 0.06
BghiP	1.8 \pm 0.3	0.7 \pm 0.5	1.4 \pm 1.0	0.6 \pm 0.4	0.4 \pm 0.2
Σ PAH ₁₆	126 \pm 40.2	121 \pm 48.8	111 \pm 31.4	198 \pm 115.4	117 \pm 49.9
PAHs	North Pollu. Ca. (<i>n</i> = 3)	Hai River (<i>n</i> = 5)	South Pollu. Ca. (<i>n</i> = 4)	South Canal (<i>n</i> = 1)	Yinluanrujin River (<i>n</i> = 1)
Nap	224 \pm 332	24.7 \pm 13.5	472 \pm 365	33.1	30.4
Acy	8.8 \pm 4.5	2.1 \pm 2.1	1.0 \pm 0.8	0.2	1.0
Ace	393 \pm 315	4.1 \pm 2.8	10.1 \pm 4.4	1.1	2.0
Fle	212 \pm 146	10.7 \pm 10.2	14.4 \pm 5.2	2.0	3.0
Ph	150 \pm 58.4	32.9 \pm 31.6	53.6 \pm 18.5	12.3	11.0
An	22.2 \pm 11.5	6.7 \pm 6.1	3.9 \pm 0.5	1.0	3.0
Fla	16.2 \pm 5.2	9.9 \pm 10.1	6.5 \pm 1.8	1.8	6.8
Py	17.2 \pm 3.5	14.0 \pm 16.5	7.3 \pm 3.1	1.8	8.4
BaA	2.6 \pm 1.5	1.6 \pm 1.3	2.3 \pm 2.1	0.5	4.2
Chr	5.7 \pm 3.8	3.3 \pm 1.8	3.4 \pm 2.2	1.6	5.9
BbF	0.6 \pm 0.5	0.5 \pm 0.4	0.4 \pm 0.3	0.3	2.1
BkF	0.5 \pm 0.4	0.5 \pm 0.3	0.4 \pm 0.3	0.2	1.6
BaP	1.5 \pm 0.8	1.2 \pm 0.8	1.1 \pm 1.1	0.4	5.3
InD	3.1 \pm 2.6	1.8 \pm 0.4	4.4 \pm 5.3	1.2	8.1
DahA	0.3 \pm 0.2	0.3 \pm 0.1	0.4 \pm 0.3	0.4	0.8
BghiP	1.6 \pm 1.1	1.0 \pm 0.3	2.3 \pm 2.4	0.4	4.8
Σ PAH ₁₆	1060 \pm 211	115 \pm 58.2	583 \pm 358	58.2	98.3

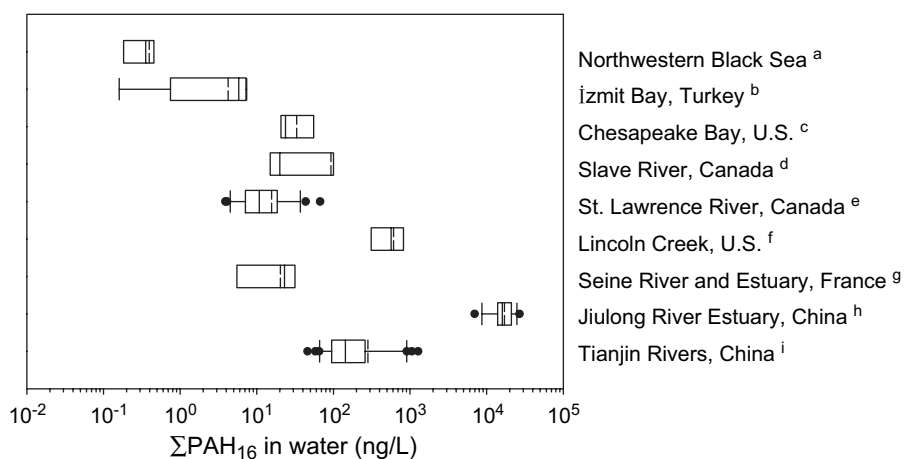


Fig. 3. Σ PAH concentration in dissolved phase from various riverine or marine sites in the world (ng/L) a. Maldonado, C., et al., 1999; b. Telli-Karakoç, F., et al., 2002; c. Gustafson and Dickhut, 1997; d. McCarthy, L.H., et al., 1997; e. Pham, T.T., et al., 1999; f. Crtmkilton and DeVita, 1997. g. Fernandes, M.B., et al., 1997; h. Maskaoui, K., et al., 2002; i. This study. Box-whisker symbols identical to those shown in Fig. 2.

Table 3
PAH content in SPM ($\mu\text{g/g}$, dry wt.) of 10 rivers in Tianjin, mean \pm S.D.

PAHs	Ji Canal (<i>n</i> = 2)	Chaobai New R. (<i>n</i> = 3)	North Canal (<i>n</i> = 3)	Beijing Pollu. Ca. (<i>n</i> = 4)	Yongding New R. (<i>n</i> = 3)
Nap	1.08 \pm 1.29	0.96 \pm 0.30	1.30 \pm 0.32	1.33 \pm 1.65	2.11 \pm 0.93
Acy	0.37 \pm 0.49	0.37 \pm 0.24	0.43 \pm 0.09	0.78 \pm 1.07	0.67 \pm 0.35
Ace	0.21 \pm 0.22	0.21 \pm 0.11	0.26 \pm 0.06	0.43 \pm 0.51	0.36 \pm 0.17
Fle	1.00 \pm 1.27	0.99 \pm 0.49	1.28 \pm 0.31	2.03 \pm 2.86	1.88 \pm 0.89
Ph	2.16 \pm 2.48	2.10 \pm 1.04	2.79 \pm 0.63	4.34 \pm 5.81	4.01 \pm 1.92
An	0.34 \pm 0.41	0.34 \pm 0.20	0.47 \pm 0.12	0.78 \pm 1.09	0.69 \pm 0.37
Fla	0.38 \pm 0.39	0.34 \pm 0.28	0.53 \pm 0.17	0.93 \pm 1.12	0.98 \pm 0.77
Py	0.20 \pm 0.18	0.17 \pm 0.15	0.27 \pm 0.09	0.50 \pm 0.54	0.56 \pm 0.52
BaA	0.07 \pm 0.07	0.05 \pm 0.04	0.08 \pm 0.05	0.25 \pm 0.29	0.50 \pm 0.36
Chr	0.05 \pm 0.04	0.03 \pm 0.03	0.07 \pm 0.05	0.17 \pm 0.20	0.23 \pm 0.23
BbF	0.06 \pm 0.06	0.04 \pm 0.02	0.06 \pm 0.04	0.23 \pm 0.28	0.21 \pm 0.19
BkF	0.04 \pm 0.02	0.05 \pm 0.09	0.06 \pm 0.05	0.10 \pm 0.19	0.15 \pm 0.17
BaP	0.03 \pm 0.03	0.03 \pm 0.03	0.03 \pm 0.02	0.11 \pm 0.20	0.12 \pm 0.14
InD	0.05 \pm 0.03	0.03 \pm 0.03	0.09 \pm 0.08	0.11 \pm 0.21	0.22 \pm 0.31
DahA	0.01 \pm 0.004	0.01 \pm 0.01	0.02 \pm 0.02	0.06 \pm 0.11	0.06 \pm 0.09
BghiP	0.07 \pm 0.08	0.06 \pm 0.02	0.09 \pm 0.05	0.20 \pm 0.34	0.20 \pm 0.25
ΣPAH_{16}	6.11 \pm 7.07	5.78 \pm 2.76	7.83 \pm 2.03	12.3 \pm 14.9	13.0 \pm 6.08
PAHs	North Pollu. Ca. (<i>n</i> = 3)	Hai River (<i>n</i> = 5)	South Pollu. Ca. (<i>n</i> = 4)	South Canal (<i>n</i> = 1)	Yinluanrujin River (<i>n</i> = 1)
Nap	3.42 \pm 2.08	1.67 \pm 0.75	0.88 \pm 0.55	0.001	2.15
Acy	1.43 \pm 0.67	0.80 \pm 0.48	0.42 \pm 0.27	0.054	0.86
Ace	2.25 \pm 1.41	0.44 \pm 0.21	0.30 \pm 0.10	0.045	0.56
Fle	4.16 \pm 2.25	2.08 \pm 1.23	1.15 \pm 0.66	0.240	2.19
Ph	9.47 \pm 3.82	4.33 \pm 2.32	3.00 \pm 1.40	0.453	5.31
An	2.26 \pm 1.23	0.69 \pm 0.38	0.50 \pm 0.18	0.060	0.77
Fla	3.96 \pm 2.41	0.80 \pm 0.46	0.78 \pm 0.35	0.001	0.76
Py	2.82 \pm 1.51	0.39 \pm 0.21	0.61 \pm 0.29	0.001	0.38
BaA	1.95 \pm 0.97	0.12 \pm 0.07	1.47 \pm 1.28	0.001	0.07
Chr	1.80 \pm 0.97	0.09 \pm 0.04	0.38 \pm 0.26	0.001	0.06
BbF	2.03 \pm 1.37	0.12 \pm 0.03	0.37 \pm 0.23	0.030	0.20
BkF	1.58 \pm 1.19	0.07 \pm 0.10	0.22 \pm 0.15	0.001	0.00
BaP	2.33 \pm 2.45	0.02 \pm 0.02	0.13 \pm 0.11	0.003	0.03
InD	1.83 \pm 1.31	0.08 \pm 0.11	0.22 \pm 0.17	0.034	0.01
DahA	1.74 \pm 1.86	0.01 \pm 0.02	0.11 \pm 0.08	0.002	0.01
BghiP	3.28 \pm 2.26	0.09 \pm 0.04	0.35 \pm 0.25	0.012	0.12
ΣPAH_{16}	46.3 \pm 21.3	11.8 \pm 5.65	10.9 \pm 5.07	0.938	13.5

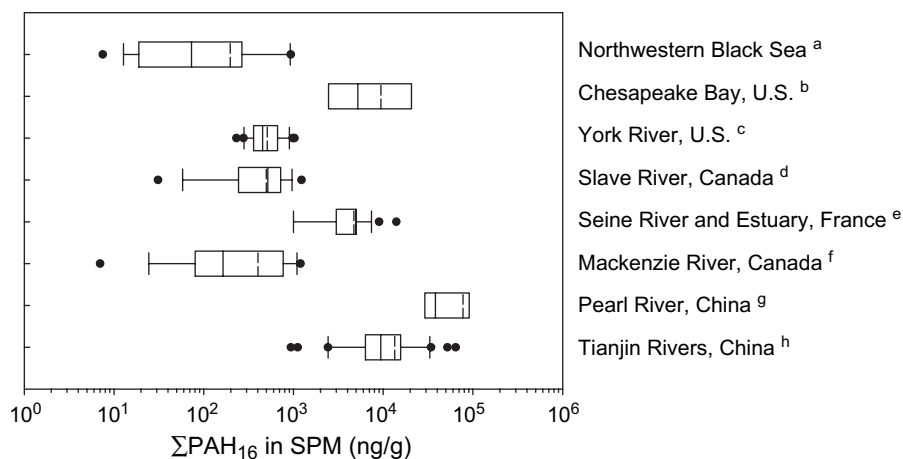


Fig. 4. ΣPAH concentration in SPM from various riverine or marine sites in the world (ng/g dry wt.) a. Maldonado, C., et al., 1999; b. Gustafson and Dickhut, 1997; c. Countway, R.E., et al., 2003; d. McCarthy, L.H., et al., 1997; e. Fernandes, M.B., et al., 1997; f. Headley, J.V., et al., 2002; g. Mai, B.X., et al., 2002. h. This study. Box-whisker symbols identical to those shown in Fig. 2.

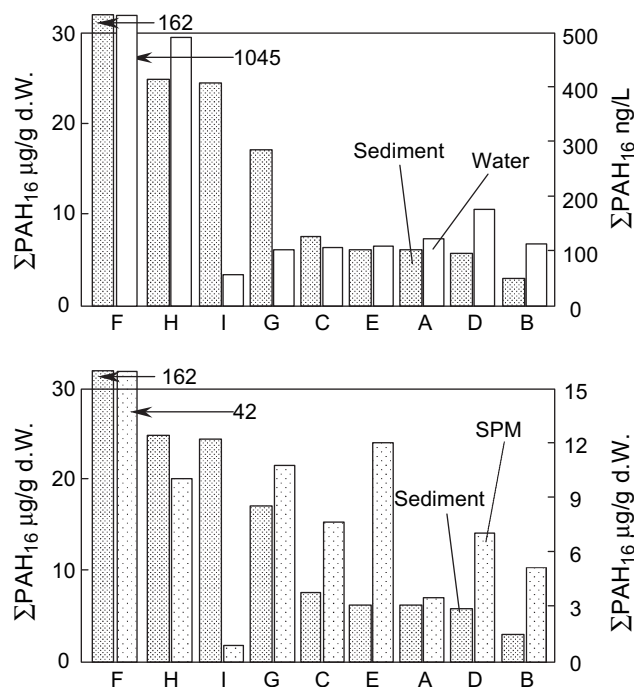


Fig. 5. Comparison of ΣPAH_{16} contents between sediment and water (upper), sediment and SPM (lower) from nine rivers (A to I represent nine rivers as indicated in Fig. 1).

the sedimentation processes with enriched SPM associated PAHs.

3.5. Spatial distribution of PAHs

There are significant differences among ΣPAH_{16} concentrations in sediment from nine rivers. The ΣPAH_{16} concentrations in sediment from River F is 5- to 100-fold greater than in other rivers, and those from Rivers F, G, H, and I are much greater than those from Rivers A, B, C, and D (Fig. 6). Due to high PAHs load, low degradation, and low attenuation, River F has the highest amount of ΣPAH_{16} concentration. The relatively higher values in Rivers G, H, I are also produced by high PAHs load in those areas, which will be discussed later.

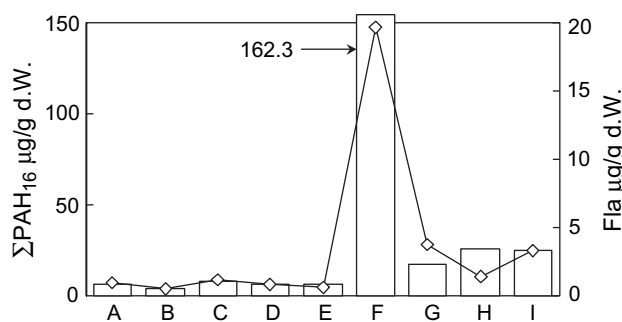


Fig. 6. Contents of ΣPAH_{16} (histogram) and Fla (line) in sediments from nine rivers. A to I represent nine rivers as indicated in Fig. 1.

Fluoranthene is an excellent PAH to represent parental PAHs since it is usually abundant in sediment and the distribution of other parental PAHs in sediment usually follows this compound. Therefore, fluoranthene levels may provide a less ambiguous measure for comparing data from different areas (Heit, 1985; McCready et al., 2000; Qu et al., 2002). The concentrations of fluoranthene in the study area are consistent with ΣPAH_{16} concentrations, as displayed in Fig. 6.

The PAHs concentrations relations between upstream and downstream were relatively complex. Except in rainy seasons, the river is stagnant, which weakens the transport of the pollutants from upstream to downstream. Furthermore, the spatial variability is enhanced by many local inputs. The higher value may be the result of some highly local inputs. For example, for River B, no spatial gradient was found in sediment (Fig. 7a), which suggests localized inputs along the river (Koh et al., 2002; Tianjin Environmental Protection Bureau, 1996, 2001). However, River G is exceptional as a result of great water influx and few local inputs in this river. For instance, the G01 (sediment) suggests a highly polluted source, with a well defined gradient from upstream to downstream along this river (Fig. 7d).

For both Rivers B and G, the gradient in water and SPM samples is not found (Fig. 7b,c,e,f). This is probably because of the other local inputs or disturbance and resuspension. More detailed data and analysis are needed for further interpretation of the pollution characteristics between upstream and downstream.

In conclusion, the different PAHs concentrations between upstream and downstream sediments can better represent the contamination variance in the river than those of water and SPM samples. There is a lack of simple trend for PAHs concentrations from water and SPM, which are much affected by local inputs and disturbances.

From a regional point of view, the spatial variability of PAHs from sediment, water and SPM is very similar. In general, the PAHs contents near urban and industrial areas are higher than those in suburb areas. The north area is less polluted than the south area, although the upstream inputs from River D (D1, PAHs from SPM, water and sediment are all higher) should not be overlooked (Fig. 8a–c). This distribution pattern suggests that industrial wastes enriched with combustion-derived PAHs may have been directly discharged into the adjacent rivers. They are mainly deposited in the surrounding areas, which form new point sources of PAHs contamination. Furthermore, these characteristics are consistent with the spatial distribution of PAHs in topsoils (Fig. 8d), which may suggest the same sources of PAHs among topsoils and river systems. Another explanation may be that soil particles absorbed PAHs through atmospheric deposition sources

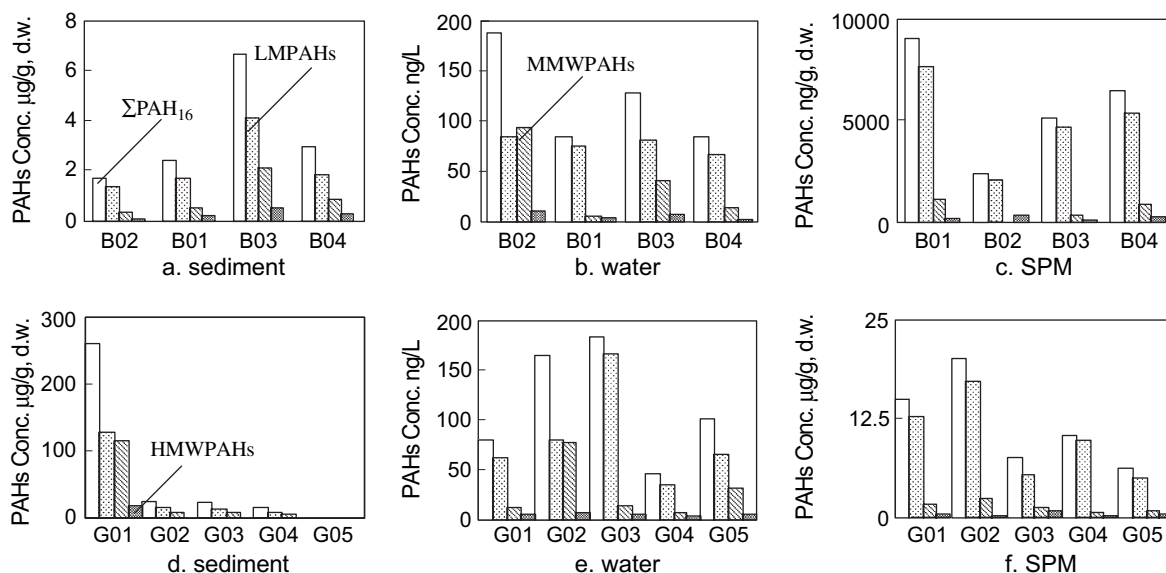


Fig. 7. PAHs contents among upstream and downstream from sediment, water and SPM samples from Chaobai New River (B) and Hai River (G).

processes, which were then carried by watershed runoff processes into rivers. These atmospheric depositions may be the most important sources of PAHs in river systems. The mass transport processes will be discussed later and further studies are needed in this area.

There are still some detailed variances among the spatial distribution of PAHs from sediment, water and SPM. For example, although PAHs contents in sediment and SPM from River G are much higher than in other rivers, the PAHs contents in water from River G are relatively lower than in other rivers. This may be explained by the attenuation process by the large amount of currents in River G (4- to 20-fold greater than the other rivers) as well as relatively better PAHs photolysis and biodegradation condition and rainfall processes in summer.

The spatial distribution of PAHs in SPM is more homogeneous than that in sediment and water, which confirms relatively homogeneous fresh PAHs inputs in the study area mentioned above (Fig. 5, lower). It is not clear as to why the PAHs contents in SPM from B2 and H4 are higher.

3.6. PAHs composition

Analysis of the individual PAHs composition is helpful to track the contaminant source, and illustrate the fate and transport of PAHs in multimedia environment (Gigliotti et al., 2002). Different sources of PAHs have different PAHs patterns. Coke emissions were enriched in the higher molecular weight (HMW PAHs, containing five- to six-ring PAHs) compounds, whereas low temperature pyrolytic processes, such as coal combustion, are dominated by low molecular weight

(LMW, containing two- to three-rings) PAHs (Schneider et al., 2001; Mai et al., 2002). Usually, high molecular weight PAHs with four to six rings predominated in sediment samples (Wakeham et al., 1980; Readman et al., 1987; Khim et al., 1999; Kannan et al., 2001). Contrary to typical individual PAHs composition in sediment in other polluted areas, two- to three-ring PAHs predominated in sediment samples of the study areas (Fig. 9a). More than 95% of the total concentration was represented by PAHs with two to four rings. Nap was the most dominant component, accounting for about 23% of ΣPAH_{16} concentration. Ph was the next dominant PAH comprising approximately 19% of ΣPAH_{16} concentration. LMW PAHs predomination suggests either a local source of PAHs or a relatively recent introduction of these chemicals as it has been shown that small-size PAHs are more labile, and are expected to degrade faster than larger ones (Fernandes et al., 1997; Macias-Zamora et al., 2002; Simo et al., 1997).

The ratio of Nap in water was extremely greater than that in sediment and SPM (Fig. 9), which was consistent with its higher solubility and typically local industrial inputs of the study areas (Tianjin Environmental Protection Bureau, 2001). LMW PAHs are also predominant in water, middle molecular weights (MMW, containing four rings) PAHs and HMW PAHs only accounted for 14% of total PAHs. These observations parallel with the fact that LMW PAHs have higher vapor pressures and water solubilities than HMW PAHs (Mackay et al., 1992).

Ph was the most dominant component in SPM, accounting for 29% of ΣPAH_{16} concentration on average. Although low molecular PAHs are still predominant in SPM, the ratio of both MMW PAHs and

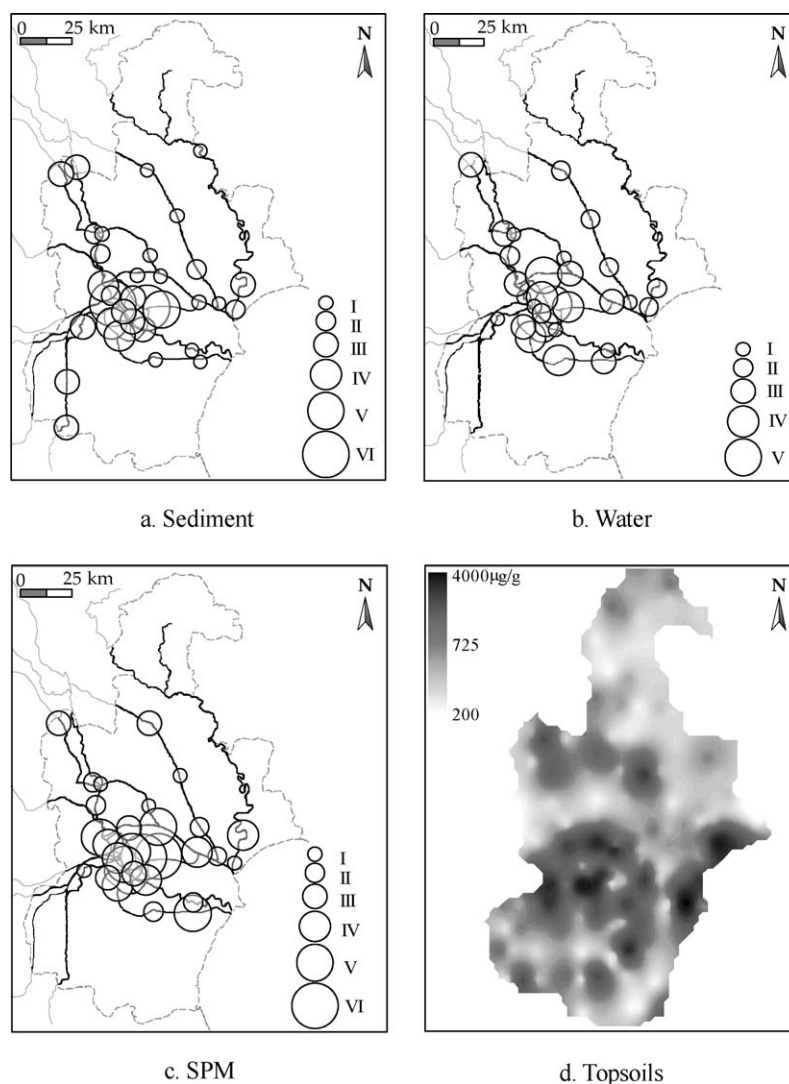


Fig. 8. Spatial distributions of ΣPAH_{16} in sediment, water, SPM and topsoil (sediment—I: 0–5, II: 5–10, III: 10–50, IV: 50–200, V: 200–500, VI: > 500 $\mu\text{g/g}$; water—I: 0–70, II: 70–100, III: 100–500, IV: 500–5000, V: > 5000 ng/L ; SPM—I: 0–5, II: 5–7, III: 7–10, IV: 10–15, V: 15–50, VI: > 50 $\mu\text{g/g}$).

HMW PAHs ascended to 32% as shown in Fig. 9c. This may be explained by the fact that the higher molecular weight aromatics seem to be preferentially absorbed by particular matter and incorporated in sediment (Witt, 1995). Another character is that the chemical profile of the sum of dissolved phase and SPM associated phase PAHs is very similar to the profile of sediment PAHs. It is consistent with reports that there is no selective loss of PAHs via sedimentation (Broman et al., 1991; Näf et al., 1992).

The unique PAHs patterns in sediment suggest a local, relatively recent, coal combustion source of PAHs in the study area, which is consistent with the pollution status in Tianjin. The source of PAHs will be further studied with other evidence.

Although the spatial distributions of PAHs in river systems are similar to those in topsoil, their chemical

profiles are significantly different by chi-square test for goodness of fit (significant level = 0.05). This suggests that soil runoff influx processes are one of the important PAHs loads for river systems in the study area. This inference was further confirmed by both good correlation between the ratio of PAHs pattern in river system/PAHs pattern in soil and molecular weight (Fig. 10, upper; statistically significant, $p < 0.01$), and the correlation between the ratio of PAHs pattern in river system/PAHs pattern in soil and aqueous solubility (Fig. 10, lower; statistically significant, $p < 0.01$). The higher the molecular weight and lower the solubility, the lower the aqueous transport capability. Naphthalene is not used for correlation because of its relatively higher vapor pressure and Henry's law constant (0.085 mmHg at 25 °C, Ambrose et al., 1975; 0.00044 $\text{atm}\cdot\text{m}^3/\text{mole}$, Shiu and Mackay, 1997), which

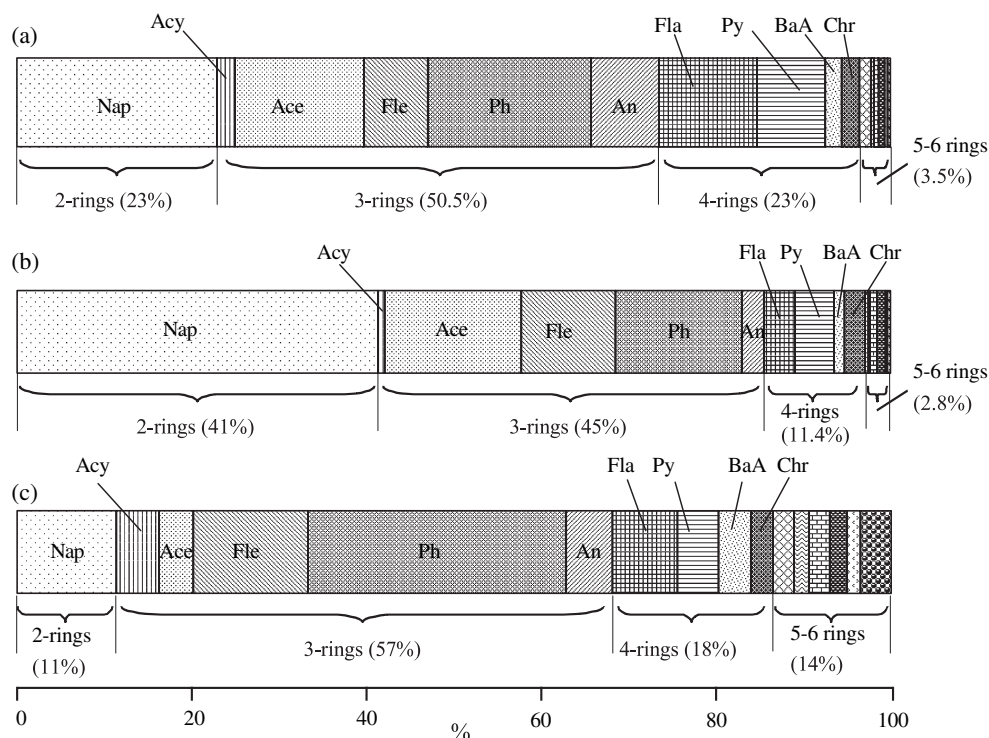


Fig. 9. Mean composition of individual PAHs in (a) sediment (b) water and (c) SPM. The legends after Chr represent: BbF, BkF, BaP, InD, DahA, BghiP, respectively.

determine naphthalene is preferred to transport by atmosphere–water interaction.

As a conclusion, PAHs in river systems came from soil pollutants, however, because of the different aqueous transport capability, the chemical profiles changed during the transportation and transformation processes.

4. Conclusion

1. PAHs contents in sediment, water and SPM of Tianjin Rivers were extraordinarily high, especially from sediment and SPM. On the contrary, PAHs contents in water were relatively low. This may be related to the sources of PAHs in the study area.

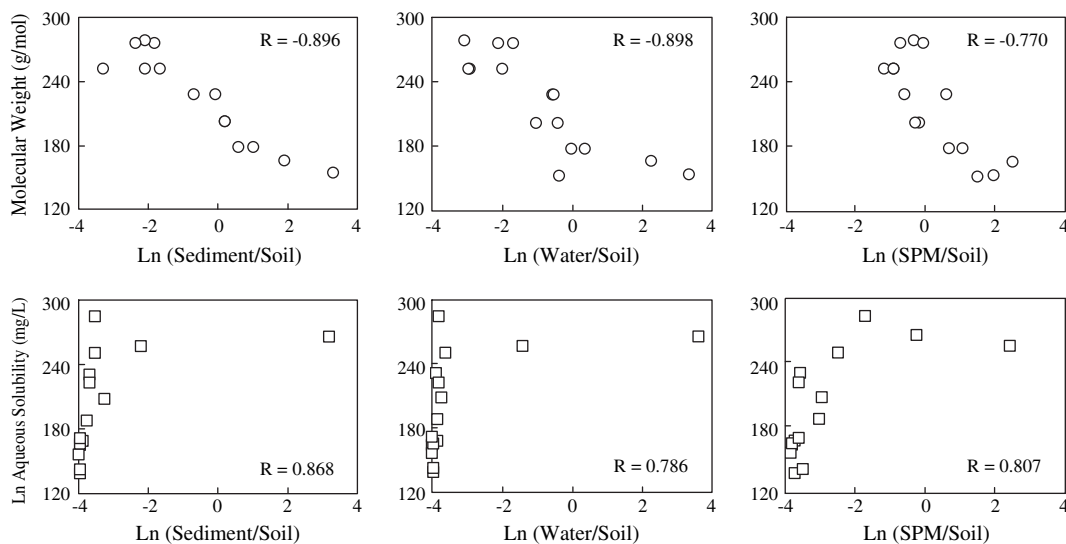


Fig. 10. Aqueous transport capabilities of 16 PAHs. (Aqueous solubilities of 15 PAHs were cited from Mackay, D., et al., 1992. Naphthalene is not used for correlation. R represents correlation coefficient by Spearman's rank correlation analysis.)

2. PAHs contents in sediment of the northern rivers were less polluted than those of the southern rivers and the urban/industrial areas were more polluted than the rural areas. PAHs content patterns in SPM, sediment, and water were related to those in topsoil. The sources of PAHs in the river systems should be further studied.
3. LMW PAHs predominated in sediment, and the percent of LMW PAHs in water was even higher than in sediment, especially for naphthalene, whereas the percent of MMW PAHs and HMW PAHs in SPM were higher than those in both sediment and water.
4. PAHs in river systems came from soil pollutants. The chemical profiles of different media changed during the transportation and transformation processes because of the different aqueous transport capability.

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