



Concentration and source identification of polycyclic aromatic hydrocarbons and phthalic acid esters in the surface water of the Yangtze River Delta, China

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Received 19 April 2011; revised 04 July 2011; accepted 19 August 2011

Abstract

The pollution from polycyclic aromatic hydrocarbons (PAHs) and phthalic acid esters (PAEs) in the surface water of the rapidly urbanized Yangtze River Delta region was investigated. Fourteen surface water samples were collected in June 2010. Water samples were liquid-liquid extracted using methylene chloride and analyzed by gas chromatography-mass spectrometry. Concentrations of PAHs and PAEs ranged 12.9–638.1 ng/L and 61–28550 ng/L, respectively. Fluoranthene, naphthalene, pyrene, phenanthrene, di-2-ethylhexyl phthalate, and di-*n*-butyl phthalate were the most abundant compounds in the samples. The water samples were moderately polluted with benzo[a]pyrene according to China's environmental quality standard for surface water. The two highest concentrations of PAHs and PAEs occurred in samples from Taihu Lake, Wuxi City and the western section of Yangchenghu Lake. Potential sources of pollution at S7 were petroleum combustion and the plastics industry, and at Yangchenghu Lake were petroleum combustion and domestic waste. Pollution in samples from the Beijing-Hangzhou Grand Canal originated from diesel engines. There were no obvious sources of pollution for the other water samples. These results can be used as reference levels for future monitoring programs of pollution from PAHs and PAEs.

Key words: polycyclic aromatic hydrocarbons; phthalic acid esters; Yangtze River Delta; surface water

DOI: 10.1016/S1001-0742(11)60782-1

Introduction

Polycyclic aromatic hydrocarbons (PAHs) and phthalic acid esters (PAEs) are ubiquitous environmental contaminants, which mainly originate from the incomplete combustion of carbonaceous materials and from the plastics and cosmetics industries, respectively. PAHs are recognized as persistent organic pollutants under the Aarhus Protocol, and are of concern because of their toxicity and mutagenicity (Lohmann et al., 2009). Environmental pollution with PAEs has been shown to adversely affect male reproductive development in humans (Swan et al., 2005). Consequently, PAHs and PAEs are classified as persistent toxic substances, and their control is required in China's environmental quality standard for surface water and by many other countries.

Assessment of the surface water concentrations of PAHs and PAEs has attracted attention in recent decades (Petrovic et al., 2002; Wang et al., 2007; Mei et al., 2009; Murray et al., 2010). One important area for this type of assessment is the Yangtze River Delta (YRD), which is a triangular-shaped territory including Shanghai, southern Jiangsu Province and northern Zhejiang Province in East

China. The YRD is dotted with 250 lakes and a network of rivers totaling 40,000 km. Because of rapid economic development and urbanization in this region, water quality in the YRD is of concern. Previous studies have suggested that PAHs and PAEs are the main organic pollutants in the Yangtze estuary area (Liu et al., 2006; Ou et al., 2009). However, studies on pollution from PAHs and PAEs in the surface water of the YRD are rare.

The present study was conducted to assess the concentrations and potential sources of PAHs and PAEs in the surface water of the YRD in China. The PAHs and PAEs results were used to assess the levels of contamination, pollution sources, and the ecological effects. These data may also be used for the assessment of the changes in concentration of these pollutants with time in this area.

1 Materials and methods

1.1 Chemicals and reagents

A mixed stock standard solution of PAHs containing naphthalene (Nap), acenaphthylene (Acy), acenaphthene (Ace), fluorene (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene (Flt), pyrene (Pyr), benzo[a]anthracene

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(BaA), chrysene (Chr), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), indeno[1,2,3-c,d]pyrene (IP), dibenzo[a,h]anthracene (DahA), and benzo[g,h,i]perylene (BghiP) each at 200 mg/L, a deuterated PAHs internal standard (phenanthrene-d10, pyrene-d10, and chrysene-d12), and a PAHs recovery standard (fluoranthene-d10) were purchased from AccuStandard Inc. (USA). A mixture of six PAEs, including dimethyl phthalate (DMP), diethyl phthalate (DEP), di-*n*-butyl phthalate (DBP), butyl benzyl phthalate (BBP), di-2-ethylhexyl phthalate (DEHP), and di-*n*-octyl phthalate (DOP), and deuterated PAEs internal standards (diethyl phthalate-d4, di-*n*-butyl phthalate-d4, and di-2-ethylhexyl phthalate-d4) were obtained from Dr. Ehrenstorfer GmbH Inc. (Germany). Methylene chloride and *n*-hexane (for organic residue analysis) were obtained from J. T. Baker (Phillipsburg, USA). Deionized water was produced by a Milli-Q system (Simplicity, Millipore Co., Molsheim, France).

1.2 Field sampling and sample treatment

The sampling was conducted on June 2010. Locations of the sampling stations are shown in Fig. 1. Fourteen surface water samples were collected from eight sites in

Suzhou City, three in Wuxi City, and three in Nantong City (Table 1).

Surface water samples were taken from the top layer (0–40 cm) using a 2 L pre-cleaned stainless steel barrel. Samples were collected with pre-cleaned 1.25 L brown glass containers. The water samples were transported to the laboratory after sampling, and processed immediately. About 1.0 L of each water sample was spiked with the PAHs recovery standard (fluoranthene-d10, 200 ng) and then extracted by liquid-liquid extraction in a separatory funnel using 3 × 50 mL of methylene chloride. The combined solvent extracts were dried over anhydrous granular sodium sulfate and concentrated in a rotary evaporator (R-210, Buchi, Swiss). The residue was dissolved in *n*-hexane to give a final volume of 1.0 mL. Twenty microliters of the mixture standard solution of deuterated phenanthrene, deuterated pyrene, and deuterated chrysene (10 mg/L) was added to the solution as an injection internal standard for PAHs determination. Ten microliters of the mixed standard solution of deuterated diethyl phthalate, deuterated di-*n*-butyl phthalate, and deuterated di-2-ethylhexyl phthalate (40 mg/L) was added to the solution as an injection internal standard for PAEs determination. The samples were then transferred to a glass microvial for GC injection.

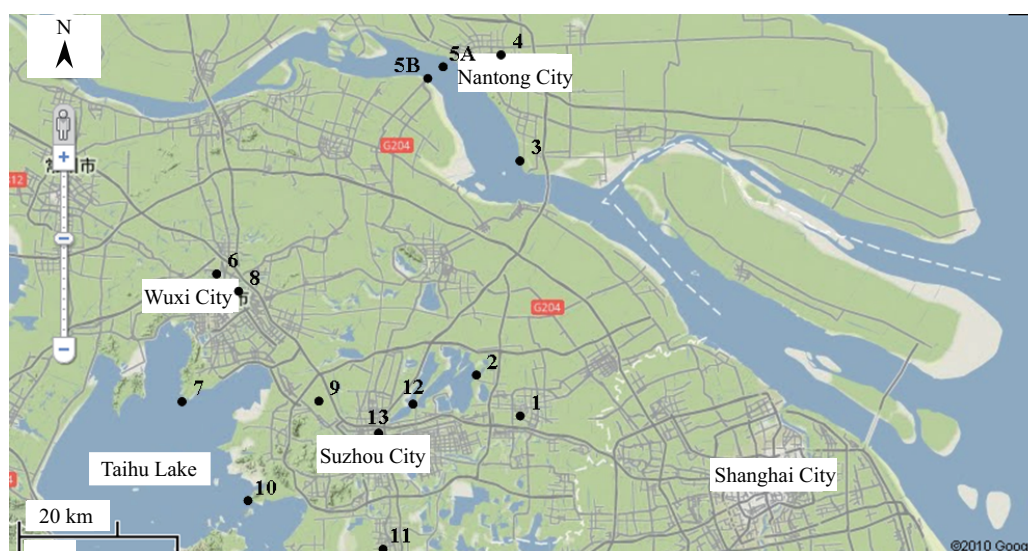


Fig. 1 Surface water sampling locations in the Yangtze River Delta, China

Table 1 Sampling information for water samples from the Yangtze River Delta, China

Sample number	Type of water	Location
S1	Urban River	Industrial park of Kunshan, Suzhou City
S2	Lake	Eastern section of Yangchenghu Lake, Suzhou City
S3	Yangtze River	Development zone, Nantong City
S4	Urban River	Urban area, Nantong City
S5A	Yangtze River	Middle of the Yangtze river, Nantong City
S5B	Yangtze River	Shore of Zhangjiagang, Suzhou City
S6	Canal	Water from the Beijing-Hangzhou Grand Canal, Wuxi City
S7	Lake	Taihu Lake, Wuxi City
S8	Urban River	Urban area, Wuxi City
S9	Canal	Water from the Beijing-Hangzhou Grand Canal, Suzhou City
S10	Lake	Taihu Lake, Suzhou City
S11	Canal	Water from the Beijing-Hangzhou Grand Canal in Wujiang, Suzhou City
S12	Lake	Western section of Yangchenghu Lake, Suzhou City
S13	Urban River	Urban area, Suzhou City

1.3 Instrumental analysis

The determination of PAHs and PAEs was performed on a gas chromatography-mass spectrometer (GC-MS) (QP2010 Plus, Shimadzu, Japan) equipped with a fused silica capillary DB-5ms column (30 m × 0.25 mm i.d., film thickness 0.25 μm, Agilent, USA) using electron ionization with selective ion monitoring mode. High purity (99.999%) helium was used as the carrier gas at 0.98 mL/min. The injector, transfer line, and ion source temperatures were 250, 300, and 230°C, respectively. The oven temperature program for PAHs was as follows: initial temperature 60°C, held for 1 min; increased to 160°C at 10°C/min; increased to 260°C at 8°C/min; and increased to 300°C at 6°C/min, held for 10 min. The oven temperature program for PAEs was as follows: initial temperature 60°C; increased to 180°C at 10°C/min; increased to 250°C at 5°C/min; and increased to 280°C at 5°C/min, held for 6 min. Two microliters of each sample was injected in splitless mode.

Suspended particulate matter (SPM) was determined gravimetrically by filtering bulk water through preweighed quartz fiber filter. Total carbon (TC) and total organic carbon (TOC) were obtained using a total organic carbon analyzer (TOC-V CSH, Shimadzu, Japan).

1.4 Quality control and quality assurance

All data were subject to strict quality control procedures. Field blanks and spiked blanks were used to determine any background contamination, which showed little Nap, Flu, Phe, DBP, or DEHP. For the 16 PAH standards, the recoveries of spiked blanks ($n = 3$) varied from 76.2% to 109% (relative standard deviations < 10.2%). For the six PAE standards, the recoveries of spiked blanks ($n = 3$)

varied from 67.3% to 124% (relative standard deviations < 20.5%). The average recoveries of the spiked recovery standard (surrogate, fluoranthene-d10) varied from 86.3% to 93.7% in all the real water samples. The method detection limits were around 1.0 ng/L for all the 16 PAHs and 2.0 ng/L for the six PAEs.

1.5 Data analysis

Samples with concentrations below the method detection limit were assigned a value of zero for concentration calculations. The concentrations were corrected by the field blanks data, but not further corrected by the surrogate recovery data. Statistical analyses were performed with SPSS 16.0 (SPSS Inc., Chicago, IL).

2 Results and discussion

2.1 Concentration and distribution

The concentrations of SPM, TC, TOC, PAHs, and PAEs in surface water from the YRD at different sampling sites are shown in Table 2.

2.1.1 PAHs

The total PAH concentrations in the surface water varied from 12.9 ng/L at S10 to 638.1 ng/L at S12 (mean 201.1 ng/L, median 117.5 ng/L). The highest level was found in the sample collected from S12 (western section of Yangchenghu Lake, Suzhou City). This location is a transport hub that many heavy trucks pass through every day. High concentrations (468.7 and 437.4 ng/L) were also found in samples from S7 and S6, which were sampled from Taihu Lake and BHGC in Wuxi City, respectively. Surface water samples from BHGC (S6, S9, and S11) had

Table 2 Concentrations of suspended particulate matter, total carbon and organic carbon, PAHs, and PAEs in surface water from the YRD

Station	S1	S2	S3	S4	S5A	S5B	S6	S7	S8	S9	S10	S11	S12	S13
Suspended particulate matter (SPM) (mg/L)	13.02	23.20	29.22	20.38	0.57	43.30	185.70	12.94	22.33	130.60	3.69	136.30	10.39	22.64
Total carbon (TC) (mg/L)	46.59	27.68	18.67	24.44	18.13	18.91	26.71	23.22	26.79	22.57	21.62	23.27	25.50	20.74
Total organic carbon (TOC) (mg/L)	6.58	5.31	2.45	2.57	1.96	2.47	3.77	4.59	3.92	3.73	3.98	4.61	5.05	2.40
Naphthalene (Nap) (ng/L)	40.6	22.6	1.4	7.6	57.5	12.2	18.4	79.8	16.4	24.9	6.1	24.5	81.9	6.4
Acenaphthylene (Acy) (ng/L)	2.3	1.2	n.d.	n.d.	1.9	n.d.	4.1	5.5	2.5	2.6	n.d.	2.3	7.4	n.d.
Acenaphthene (Ace) (ng/L)	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Fluorene (Flu) (ng/L)	35.6	20.2	n.d.	n.d.	23.8	n.d.	24.1	28.3	16.5	15.3	n.d.	11.8	20.3	n.d.
Phenanthrene (Phe) (ng/L)	20.3	4.8	n.d.	n.d.	143.0	n.d.	20.7	143.7	5.8	34.6	n.d.	30.7	159.1	n.d.
Anthracene (Ant) (ng/L)	8.8	n.d.	n.d.	n.d.	5.3	n.d.	10.1	7.5	n.d.	10.4	n.d.	5.6	8.8	n.d.
Fluoranthene (Flt) (ng/L)	16.3	2.4	2.5	7.8	14.5	3.6	62.8	53.6	7.5	39.6	3.4	40.7	110.0	4.4
Pyrene (Pyr) (ng/L)	16.4	3.4	1.6	5.9	19.6	2.6	74.6	88.0	7.9	32.4	1.0	30.9	226.4	3.3
Benzo(a)anthracene (BaA) (ng/L)	3.1	n.d.	1.7	2.2	n.d.	3.1	29.7	12.7	1.6	18.2	n.d.	17.2	4.6	1.5
Chrysene (Chr) (ng/L)	6.7	1.2	4.6	3.9	n.d.	3.6	43.1	5.8	1.9	23.2	1.0	21.6	4.7	2.3
Benzo(b)fluoranthene (BbF) (ng/L)	7.8	3.5	10.5	5.1	9.9	5.0	55.6	12.9	3.3	32.7	1.4	30.8	5.6	4.4
Benzo(k)fluoranthene (BkF) (ng/L)	2.0	1.3	1.8	1.2	3.5	1.4	14.8	1.6	n.d.	11.6	n.d.	8.3	1.5	1.4
Benzo(a)pyrene (BaP) (ng/L)	3.4	n.d.	1.6	2.6	n.d.	3.0	34.5	6.8	1.1	21.4	n.d.	19.7	3.4	1.4
Indeno(123-c,d)pyrene (IP) (ng/L)	2.2	n.d.	2.2	1.5	n.d.	1.2	17.7	5.4	n.d.	10.8	n.d.	9.8	1.6	1.1
Dibenzo(ah)anthracene (DahA) (ng/L)	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	6.4	n.d.	n.d.	4.1	n.d.	n.d.	n.d.	n.d.
Benzo(g,h,i)perylene (BghiP) (ng/L)	1.9	n.d.	1.5	1.5	n.d.	1.0	20.8	17.1	n.d.	11.4	n.d.	8.5	2.8	n.d.
Total PAHs (ng/L)	167.4	60.6	29.4	39.3	279	36.7	437.4	468.7	64.5	293.2	12.9	262.4	638.1	26.2
Dimethyl phthalate (DMP) (ng/L)	91	38	34	19	41	8	18	97	20	45	31	73	129	15
Diethyl phthalate (DEP) (ng/L)	62	17	22	15	12	n.d.	3	50	4	10	7	67	86	12
Di- <i>n</i> -butyl phthalate (DBP) (ng/L)	534	152	74	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	64	n.d.	7188	n.d.
Butyl benzyl phthalate (BBP) (ng/L)	15	4	4	n.d.	24	n.d.	4	n.d.	n.d.	n.d.	n.d.	58	72	n.d.
Di-2-ethylhexyl phthalate (DEHP) (ng/L)	1852	667	226	289	1172	671	1105	28403	823	278	341	995	16942	n.d.
Di- <i>n</i> -octyl phthalate (DOP) (ng/L)	10	5	16	7	6	6	6	n.d.	25	25	3	32	343	34
Total PAEs (ng/L)	2564	883	376	330	1255	685	1136	28550	872	358	446	1225	24760	61

n.d.: not detected. YRD: Yangtze River Delta.

higher PAH values than the other samples.

The total PAH concentrations in water found in the study area are similar to or lower than those reported for surface waters in other locations in China. Table 3 summarizes the literature data for comparison. The levels of PAHs of the YRD are comparable to those in the Xijiang River, South China (22–138 ng/L) (Deng et al., 2006), Qiantang River, East China (70–1844 ng/L) (Chen et al., 2007), and middle and lower reaches of the Yellow River (179–369 ng/L) (Li et al., 2006). However, the total PAH concentration was much lower than that detected in the Henan reach of the Yellow River (144–2361 ng/L) (Sun et al., 2009) and Daliao River watershed (946–13448 ng/L), Northeast China (Guo et al., 2007). Furthermore, the total PAH concentrations from the YRD in this study were much lower than those reported in nearby water systems, such as the Jiangsu section of the Yangtze River, the Yangtze estuary and coastal areas (Table 3).

Among the 16 PAHs, the most abundant compounds were Flt, Nap, Pyr, and Phe, which represented 13.1%–19.9% of the total concentration. In this study, Nap, Acy, Ace, Flu, Phe, Ant, and Flt were classified as two- and three-ring PAH compounds. Pyr, BaA, and Chr were classified as four-ring PAH compounds. Five- and six-ring PAH compounds include BbF, BkF, BaP, IP, DahA, and BghiP. As clearly shown in Fig. 2, evaluating the PAHs by ring size divided the samples into three groups. The first group included samples from S1, S2, S5A, S7, S8, S10, and S12, which mainly contained two- and three-ring PAHs. The second group contained only the sample from S3, which mainly contained five- and six-ring PAHs. The remainder of the water samples (S4, S5B, S6, S9, S11, and S13) belonged to the third group, and these samples contained similar quantities of two- and three-ring, four-ring, and five- and six-ring PAHs. These results indicate that there are potentially many different sources of PAHs in the YRD.

2.1.2 PAEs

The total PAE concentrations in the surface water varied from 61 ng/L in the sample from S13 to 28,550 ng/L in the sample from S7 (mean 4536 ng/L, median 877.8 ng/L). The two highest PAE concentrations occurred in the samples from S7 (28,550 ng/L) and S12 (24,760 ng/L), which were consistent with the PAH results. The levels of PAEs in the YRD were relatively high in comparison

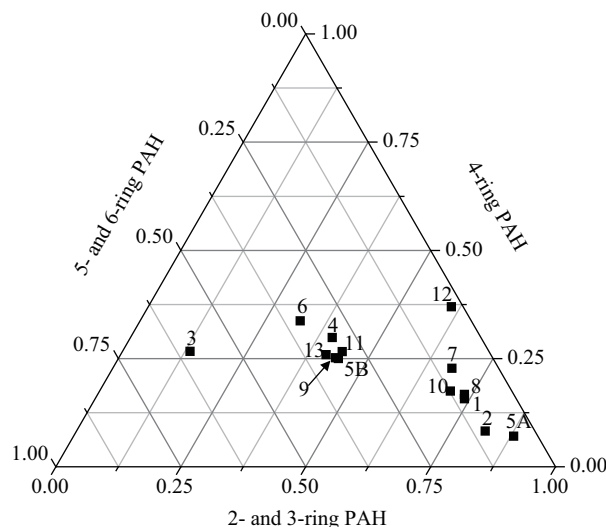


Fig. 2 Grouping of surface water samples from the Yangtze River Delta by PAH type.

with previous studies in China (Table 3). The PAE levels in water were higher than those in urban lakes in Guangzhou, South China (470–6190 ng/L) (Zeng et al., 2009), the Jiangsu section of the Yangtze River (178–1474 ng/L) (He et al., 2011), and the Yangtze estuary area (3380 ng/L) (Liu et al., 2006). They were much lower than the concentrations reported by Wang et al. (2008) for five PAEs in water from the Wuhan section of the Yangtze River (34–91220 ng/L) (Wang et al., 2008).

The rates of occurrence of the six studied PAEs at the 14 sample locations were in the following order: DMP (100%) > DEP = DEHP = DOP (93%) > BBP (50%) > DBP (36%). DEHP and DBP were the main pollutants among the six PAEs. Processing waste from heavy chemical and plastics industries might contain plasticizers with high DEHP contents. A similar trend was also found in the main stream of the Jiangsu section of the Yangtze River (He et al., 2011). It has been reported that DBP and DEHP are the most commonly used plasticizers worldwide (Staples et al., 1997). However, different pollution sources may lead to different PAE components. In this study, DEHP and DBP accounted for 84.7% and 12.6% of the total PAEs concentration, respectively. Moreover, DEHP was more significantly ($r = 0.981$, $p < 0.01$) correlated with the total PAE amounts than DBP ($r = 0.612$, $p = 0.02$). Domestic waste such as building materials, home furnishings, clothing, and food packaging might contain plasticizers with

Table 3 Comparison of PAH and PAE concentrations in surface water from different water bodies in China

Location	Year	PAHs (ng/L)	BaP (ng/L)	PAEs (ng/L)	DBP (ng/L)	DEHP (ng/L)	Reference
Daliao River watershed	2005	946–13448 (6471)	n.d.–1 872	n.a.	n.a.	n.a.	Guo et al., 2007
Qiantang River	2005	70–1844 (283)	n.d.–11	n.a.	n.a.	n.a.	Chen et al., 2007
Xijiang River, Guangdong	2003–2004	22–138 (n.a.)	n.d.–0.6	n.a.	n.a.	n.a.	Deng et al., 2006
Urban lakes, Guangzhou	2006	n.a.	n.a.	470–6190 (1999)	180–3790	237–1600	Zeng et al., 2009
Yellow River (middle and lower reaches)	2004	179–369 (248)	n.d.–12	n.a.	n.a.	n.a.	Li et al., 2006
Yellow River (Henan Reach)	2005–2006	144–2361 (662)	n.d.–2.5	n.a.	n.a.	n.a.	Sun et al., 2009
Yangtze River (Wuhan section)	2005	n.a.	n.a.	34–91220 (26530)	n.d.–35650	11–54730	Wang et al., 2008
Yangtze Estuary and coastal areas	2006	478–6273 (1858)	10–11	n.a.	n.a.	n.a.	Ou et al., 2009
Yangtze Estuary area	2002–2003	6630	5	3380	1100	1300	Liu et al., 2006
Yangtze River (Jiangsu section)	2004–2005	12–3576 (925)	n.d.–209	178–1474 (902)	105–286	n.d.–836	He et al., 2011
Yangtze River Delta	2010	13–638 (201)	n.d.–34	61–28,550 (4536)	n.d.–7188	n.d.–28403	This study

Data shown in parenthesis are means. n.d.: not detected. n.a.: not available.

high DBP contents. Wang et al. (2008) reported that DBP had the highest content among PAEs studied in water from the Wuhan section of the Yangtze River, and accounted for 59.5% of the total PAEs concentration. DBP was also abundant (53.0%–81.2%) in water from urban lakes in Guangzhou (Zeng et al., 2008).

2.2 Potential toxicological risk assessment

Only BaP, DBP, and DEHP are regulated in China's national environmental quality standard for surface water (GB3838-2002). This standard specifies limits for BaP, DBP, and DEHP of 2.8, 3000, and 8000 ng/L, respectively. In this study, the mean BaP concentration was 7.1 ng/L, which was 2.5 times higher than the standard (2.8 ng/L). However, the mean concentrations of DBP and DEHP in water from the YRD were 5.2 and 2.1 times lower than their limits, respectively. These results show the surface waters from the YRD are moderately polluted by BaP.

Toxic equivalence factors (TEFs) were applied to quantify the carcinogenicity of other PAHs relative to BaP and estimate BaP equivalent doses (Nadal et al., 2004). The total concentrations of the seven carcinogenic PAHs (BaA, Chr, BbF, BkF, BaP, DahA, and IP) ranged from 3.0 ng/L in the sample from S10 to 201.8 ng/L in the sample from S6 (mean 44.6 ng/L; median 19.4 ng/L). According to the United States Environmental Protection Agency, the calculated TEF of BaA, Chr, BbF, BkF, BaP, IP, and DahA are 0.1, 0.001, 0.1, 0.01, 1, 0.1, and 1, respectively. The TEFs were converted to one toxic concentration, and the benzo[a]pyrene toxic equivalent (TEQ) of the seven carcinogenic PAHs was calculated with the following equation:

$$\text{TEQ} = \sum_i C_i \times \text{TEF}_i$$

where, C_i and TEF_i are the concentration and TEF of the carcinogenic PAH i , respectively.

The total TEQ of PAHs in the surface water of the YRD varied from 0.2 ng/L in the sample from S10 to 51.4 ng/L in the sample from S6 (mean 10.4 ng/L; median 3.7 ng/L) (Fig. 3), and the results were consistent with the total concentrations of the seven carcinogenic PAHs. Surface water samples from BHGC (S6, S9, and S11) had higher TEQs than the other water samples. The mean contribution of the seven carcinogenic PAHs to the total TEQ decreased in the following order: BaP (68.9%) >> BbF (13.0%) > DahA (7.3%) > BaA (6.7%) > IP (3.8%) > BkF (0.4%) > Chr (0.1%).

Van Wezel et al. (2000) derived environmental risk levels (ERLs) based on the ecotoxicology and environmental chemistry of DBP and DEHP. The resulting ERLs in water were 10,000 and 190 ng/L for DBP and DEHP, respectively. In the present study, the mean concentrations of DBP and DEHP in the surface water samples from the YRD were 572 and 3840 ng/L. DBP concentrations in water samples from all the locations were below the ERL. By contrast, DEHP concentrations in the water samples exceeded the ERL at all locations except for S13 (not detected). These results show that the surface waters in the

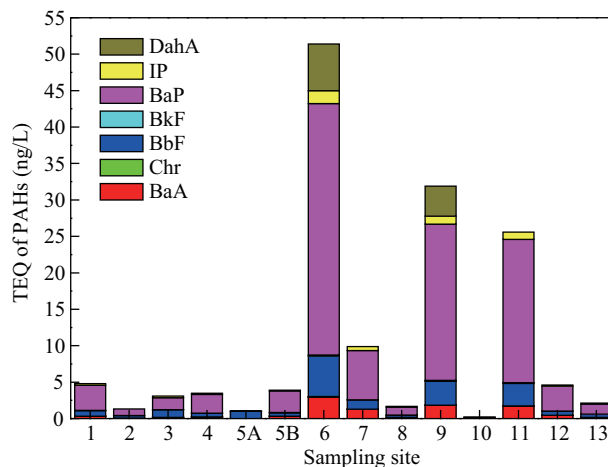


Fig. 3 Toxic benzo[a]pyrene equivalent (TEQ) of the seven carcinogenic PAHs in surface water samples from the Yangtze River Delta, China

YRD are severely polluted by DEHP.

2.3 Source identification

PAHs are introduced into the environment mainly via natural and anthropogenic combustion processes. The anthropogenic PAHs are mainly formed by incomplete combustion of fossil fuels and discharge of petroleum-related materials (Zhang et al., 2004). PAEs are used as plasticizers in numerous consumer products and building materials, with several million tons of phthalates produced worldwide every year for the production of soft polyvinyl chloride (PVC) and other plastics (Guo and Kannan, 2011). PAEs are not chemically bound to plastic materials, and are easily leached into the environment with time and use (Bauer and Herrmann, 1997). In this study, ratios and principal component analysis were used to identify the specific sources of the PAHs and PAEs.

2.3.1 Ratios

The input sources of PAHs in water include atmospheric deposition, urban and municipal waste discharge, industrial effluent, and oil leakage (Wang et al., 2007). The possible sources of PAHs may be identified by diagnostic ratios of individual PAH compounds, because the distributions of homologues are strongly associated with the formation mechanisms of carbonaceous materials for organic species with similar characteristics. Characteristic ratios ($\text{Flt}/(\text{Flt}+\text{Pyr})$, $\text{Ant}/(\text{Ant}+\text{Phe})$, $\text{BaA}/(\text{BaA}+\text{Chr})$, and $\text{IP}/(\text{IP}+\text{BghiP})$) were calculated to identify emission sources in the present study (Fig. 4).

The $\text{Flt}/(\text{Flt}+\text{Pyr})$ ratios in the water were all between 0.33 and 0.61, except for in the sample from S10 (0.78), which indicates petrogenic origin of the PAHs. Our results suggest that the PAHs in the sample from S10 originated from biomass or coal combustion, whereas in the samples from S5A, S7, and S12 PAHs originated from petroleum combustion.

2.3.2 Principal component analysis

Ratios of selected PAH compounds and sample characteristics can be taken as an indirect indicator of the PAH sources. However, interrelation among the factors and the

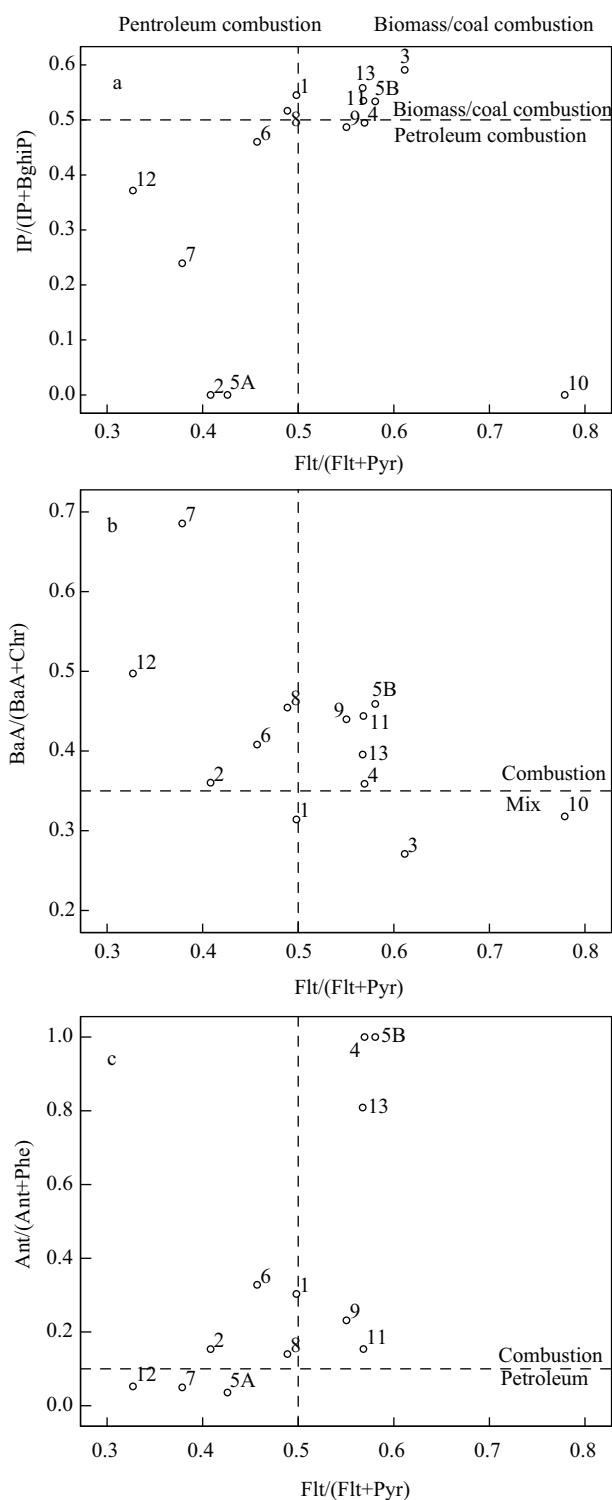


Fig. 4 Ratio plots for Flt/(Flt+Pyr) vs. IP/(IP+BghiP) (a), BaA/(BaA+Chr) (b), and Ant/(Ant+Phe) (c) in the surface water from the Yangtze River Delta, China.

degree of contribution of the pollutant sources is not clear from this analysis.

In this study, principal component analysis (PCA) was used to further evaluate the PAH and PAE sources in the surface water from the YRD (Table 4).

Two principal components (PCs) were extracted and the cumulative variance accounted for 88.4% and 87.7% of the total variance for PAHs and PAEs, respectively.

PC1 for PAHs was responsible for 59.6% of the total

variance. This factor included high molecular weight (MW > 210) PAHs (BaA, Chr, BbF, BkF, BaP, IP, DahA, and BghiP), with lower water solubility (≤ 0.01 mg/L) or high log values of the octanol-water partition coefficient (K_{ow}) (> 5). By contrast, PC2 for the PAHs included low molecular weight (MW < 210) PAHs (Nap, Acy, Flu, Phe, Ant, Flt, and Pyr). Low molecular weight PAHs have both petrogenic and combustion (low temperature pyrolysis) sources, whereas the high molecular weight PAHs are predominantly pyrolytic (Zhang et al., 2004). BghiP has been identified as a tracer of auto emissions. Elevated levels of BkF relative to other PAHs have been suggested to indicate diesel vehicles as a source. IP was also found in both diesel and gas engine emissions (Larsen and Baker, 2003). These results indicate that PC1 for the PAHs suggested vehicular (gas and diesel) sources. As clearly shown in Fig. 5a, surface water samples from BHGC (S6, S9, and S11) had high scores in PC1. It has been reported that Pyr, Flt, Phe, and Ant are predominant in coal combustion profiles (Larsen and Baker, 2003), and NaP is a characteristic marker of creosote or coal tar volatilization. Oil-fired power generation is characterized by two- and three-ring PAHs (Masclat et al., 1986). According to these references, PC2 for the PAHs indicates a mixture of coal and oil combustion sources. Surface water samples (S5A, S7, and S12) had high PC2 scores, and with the ratio results

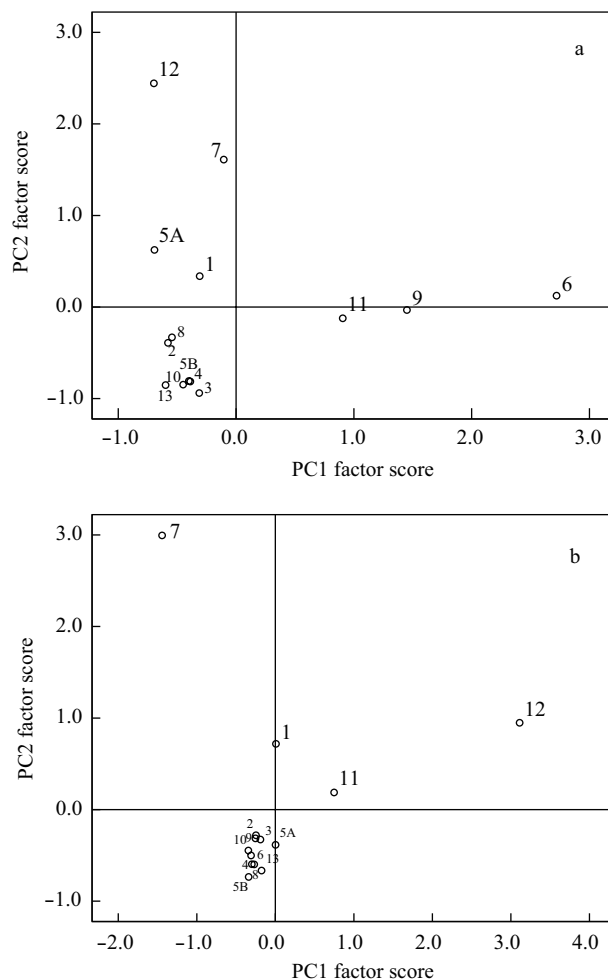


Fig. 5 Score plot of principal component analysis for (a) PAHs and (b) PAEs in surface water from the Yangtze River Delta, China.

Table 4 Principle component analysis for PAHs and PAEs in surface water from the Yangtze River Delta, China

PAHs	PC1 (59.6%)	PC2 (28.8%)	PAEs	PC1 (72.3%)	PC2 (15.4%)
Naphthalene (Nap)	-0.134	0.966	Dimethyl phthalate (DMP)	0.543	0.797
Acenaphthylene (Acy)	0.234	0.942			
Fluorene (Flu)	0.210	0.691	Diethyl phthalate (DEP)	0.616	0.681
Phenanthrene (Phe)	-0.132	0.910			
Anthracene (Ant)	0.601	0.702	Di- <i>n</i> -butyle phthalate (DBP)	0.898	0.286
Fluoranthene (Flt)	0.371	0.848			
Pyrene (Pyr)	0.101	0.883	Butyle benzyl phthalate (BBP)	0.875	0.250
Benzo(a)anthracene (BaA)	0.960	0.217			
Chrysene (Chr)	0.989	0.067	Di-2-ethylhexyl phthalate (DEHP)	0.104	0.926
Benzo(b)fluoranthene (BbF)	0.982	0.098			
Benzo(k)fluoranthene (BkF)	0.968	0.062	Di- <i>n</i> -octyl phthalate (DOP)	0.919	0.235
Benzo(a)pyrene (BaP)	0.989	0.100			
Indeno(123- <i>c,d</i>)pyrene (IP)	0.986	0.125			
Dibenzo(ah)anthracene (DahA)	0.917	0.026			
Benzo(g,h,i)perylene (BghiP)	0.831	0.354			

(Section 2.3.1), this validates that these samples originated from petroleum combustion.

For PAEs, the first two principal components explained 87.7% of the total variability in the surface water. DEHP is the major PAE that leaches from household wastes (Bauer and Herrmann, 1997) and is found in smoke from plastics and refuse burned in open fires (Simoneit et al., 2005). DEP and DBP are the predominant PAEs used in cosmetic and personal care products (Koniecki et al., 2011; Romero-Franco et al., 2011). DOP, DBP, BBP, DEP, and DMP, which are found in high concentrations in domestic waste (e.g. cosmetics, toys, plastic container, and commodities) were the main contributors to PC1 for the PAEs. DEHP, DMP, and DEP, which are produced from the plastic and heavy chemical industries, were included in PC2 for the PAEs. In this study, S12, and S7 had high PC1 and PC2 scores, respectively.

In summary, the pollutants at the two most polluted sites (S7 and S12) originated from petroleum combustion, and were influenced by the plastics industry (S7) and domestic waste (S12). Pollution at S6, S9, and S11 from BHGC originated from diesel-powered ships. At locations S5A and S10, pollution originated from petroleum combustion and from biomass or coal combustion, respectively. There were no obvious sources of pollution for the other water samples, such as S4, S8, and S13 from the urban area, S1 and S3 from the development area, S5B from the shore of the Yangtze River (ferry station), and S2 from the rural area.

3 Conclusions

Concentrations and potential sources of PAHs and PAEs in the surface water of the YRD in China were investigated. Concentrations of PAHs and PAEs ranged from 12.9–638.1 ng/L and 61–28550 ng/L, respectively. In comparison with previous studies in China, the concentrations of PAHs were low and the concentrations of PAEs were high. The two highest PAH and PAE concentrations occurred at locations S7 and S12. Flt, Nap, Pyr, Phe, DEHP, and DBP were the most abundant compounds. Samples from BHGC (S6, S9, and S11) had higher PAH concentrations and TEQ values than the other samples. According to China's relevant

regulatory standard (GB3838-2002), surface waters from the YRD are moderately polluted by BaP. In all of the water samples, DEHP exceeded the ERL, except for site S13. Potential sources of pollution at S7 (Taihu Lake, Wuxi city) were petroleum combustion and the plastics industry. Pollution at S12 (western section of Yangchenghu Lake) originated from petroleum combustion and domestic waste. Samples from BHGC (S6, S9, and S11) were polluted by diesel engines. There were no obvious sources of pollution for the other water samples.

Acknowledgments

This work was supported by the National Basic Research Program of China (No. 2009CB421602), the Water Pollution Control and Treatment Special Project (No. 2009ZX07527-001), the State Key Laboratory of Environmental Chemistry and Ecotoxicology (No. KF2010-20), and the Special Fund for Public Welfare Industry on Environmental Protection (No. 2009467109).

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