

Surface water polycyclic aromatic hydrocarbons (PAH) in urban areas of Nanjing, China

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ABSTRACT

The concentration, sources and environmental risks of polycyclic aromatic hydrocarbons (PAHs) in surface water in urban areas of Nanjing were investigated. The range of \sum_{16} PAHs concentration is between 4,076 and 29,455 ng/L, with a mean of 17,212 ng/L. The composition of PAHs indicated that 2- and 3-ring PAHs have the highest proportion in all PAHs, while the 5- and 6-ring PAHs were the least in proportion. By diagnostic ratio analysis, combustion and petroleum were a mixture input that contributed to the water PAH in urban areas of Nanjing. Positive matrix factorization quantitatively identified four factors, including coke oven, coal combustion, oil source, and vehicle emission, as the main sources. Toxic equivalency factors of BaP (BaP_{eq}) evaluate the environmental risks of PAHs and indicate the PAH concentration in surface water in urban areas of Nanjing had been polluted and might cause potential environmental risks. Therefore, the PAH contamination in surface water in urban areas of Nanjing should draw considerable attention.

Key words | BaP_{eq}, PAH, positive matrix factorization, surface water

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INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are organic compounds, which include two or more fused aromatic rings of carbon and hydrogen atoms (Zhu *et al.* 2004). The USEPA has classified 16 PAHs as priority pollutants because of their carcinogenicity, teratogenicity and mutagenicity (Wang *et al.* 2015). PAHs come mainly from anthropogenic activities like industrial processing, vehicle emissions, waste incineration, oil spills, and chemical manufacturing (Lv *et al.* 2014). Moreover, natural processes like volcanic eruptions, diagenesis, and forest fires can also form a certain amount of PAHs (Wang *et al.* 2017).

In recent years, much research on PAH pollution of surface water has been conducted all over the world, such as China (Zhang *et al.* 2011, 2013, 2015; Nagy *et al.* 2013a; Lv *et al.* 2014), USA (McDaniel & Zielinska 2015), Japan (Hayakawa *et al.* 2016), Ghana (Amoako *et al.* 2011), France (Net *et al.* 2014), India (Dhananjayan *et al.* 2012), Hungary (Nagy *et al.* 2013b), and Egypt (Badawy & Ema-baby 2010). Most researchers concentrate on the PAH concentrations in aquatic environments and environmental health risks but none of the studies focus on surface water in urban areas of Nanjing, China.

Nanjing, the provincial city of Jiangsu, is a main port along the Yangtze River. Many famous lakes like Xuanwu Lake and Mochou Lake are also located in the city. Nanjing is a comprehensive industrial city dominated by chemicals, electronics, and automobiles. Nowadays, the city has many serious environmental problems because of the population, industrial manufacture, and traffic. Moreover, the urbanization level of Nanjing is high because the population has exceeded 8 million and more than 6 million live in the urban areas.

In this study, 20 surface water samples were collected from urban areas of Nanjing. The concentration, sources, and environmental risk of PAHs in this water body were analyzed. The results can be a reference for evaluating the quality of the aquatic environment in urban areas of Nanjing.

MATERIALS AND METHODS

Sampling and preparation

Twenty surface water samples were collected from the water body in July 2015 (Figure 1). All the samples were collected

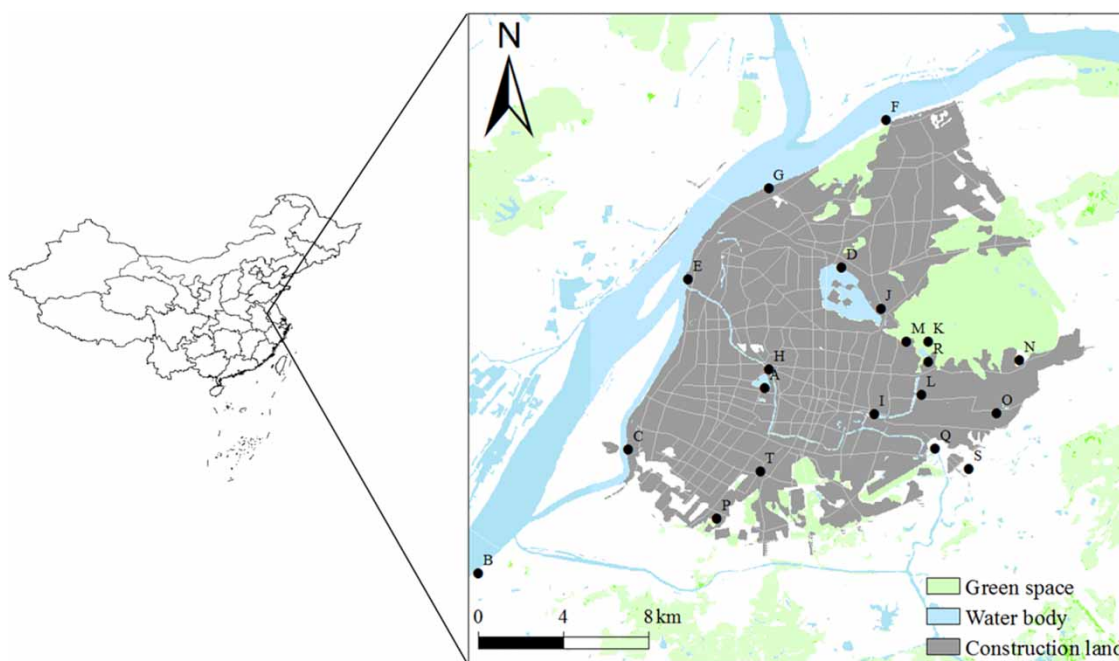


Figure 1 | Sampling sites of surface water in urban areas of Nanjing, China. A. Mochou Lake (ML) a; B. Yangtze River (YR) a; C. Yangtze River (YR) b; D. Xuanwu Lake (XL) a; E. Yangtze River (YR) c; F. Yangtze River (YR) d; G. Yangtze River (YR) e; H. Mochou Lake (ML) b; I. The East Water Park (EWP); J. Xuanwu Lake (XL) b; K. Qianhu Lake (QL); L. Yueya Lake (YL); M. Pipa Lake (PL); N. Wukesong Reservoir (WR); O. Youyi River (YYR); P. Nan River (NR) a; Q. Qiqiaowen Wetland Park (QWP); R. Yanque Lake (YQL); S. Qinhuai River (QR); T. Nan River (NR) b.

with a water bottle and stored in brown bottles. All the water samples were taken back to the laboratory quickly. Finally, all of the samples were kept in a refrigerator at 4 °C until analysis.

Chemicals

Each of the PAH standards (Supelco, Bellefonte, PA, USA) had a concentration of 2,000 µg mL⁻¹. The organic solvents (HPLC grade) include *n*-hexane, dichloromethane, acetone, and methanol, which are used for sample preparation and analysis. Silica gel (through 100–200 mesh sieve) was activated by using acetone, dichloromethane, and *n*-hexane in order. After extraction, silica gel was baked at 130 °C for 16 h in an oven. In addition, Na₂SO₄ was warmed at 450 °C for 5 h in muffle and then placed in a well-closed container.

Extraction of PAHs

Water samples were filtered on pre-combusted glass fiber (GF/F) membranes (Whatman, UK). Filtered samples were passed through a C₁₈ solid phase extraction cartridge (Supelco, Bellefonte, PA, USA), and the flow velocity was controlled at 5 mL min⁻¹. Before sample filtration, the columns were activated with dichloromethane (5 mL), then

methanol solvent (5 mL) and ultra-pure water (5 mL) in turn. The target compounds were extracted from the column with dichloromethane (10 mL). The eluted PAHs were purified by passage through a glass chromatographic column fitted with a stopcock, and then filled in 5 g activated silica gel and 5 g Na₂SO₄. After cleaning, the dichloromethane solvent that contained PAHs was evaporated to nearly dry, then the organic solvent was replaced by *n*-hexane. Finally, the collected PAH fraction was evaporated to 1 mL under a nitrogen blowing instrument.

Analysis of PAHs

The PAH eluates of the water were measured by gas chromatography-mass spectrography using Shimadzu QP2010 Ultra with a 30 m × 0.25 mm Rtx-5MS column (0.25 µm film thickness, fused silica capillary). Helium was used as the carrier gas. The original temperature of 80 °C was maintained for 2 min, then ramped from 80 °C to 180 °C at 20 °C min⁻¹ and next to 290 °C at 10 °C min⁻¹ and maintained for 15 min. In addition, the injector temperature was held at 290 °C. The ion source was kept at 230 °C. The temperature of interface was maintained at 280 °C. A 1 µL aliquot of sample elution was injected into a splitless model. The MSD was operated in the electron

impact model. Besides, the data were acquired using the selective ion monitoring mode. The relative retention time and the selected ions were used to identify 16 PAHs.

Quality assurance and quality control

A strict procedure of quality assurance and quality control was conducted. Blank samples were analyzed every 5 samples. PAHs in the blank samples were not detected in this experiment. Duplicates were conducted every 5 samples, and if the difference of the analyzed value exceeded $\pm 15\%$, the samples were reanalyzed. An external standard method was used for identifying and quantifying the 16 PAHs. Mean recoveries of individual PAHs were 88.9–109.6% for water samples. The present PAH concentration values were not corrected.

Data analysis

The positive matrix factorization (PMF) model, which was developed by Paatero & Tapper (1994), was used to quantitatively identify the source of surface water PAHs in the urban area of Nanjing. This method can be briefly summarized as follows. It defines an original matrix X ($n \times m$), where n was expressed as the number of samples and m was expressed as the number of chemical species, which can be decomposed into two new matrices, namely G and F with an unexplained part E . This expression can be formulated as follows:

$$X = GF + E \quad (1)$$

This equation can be converted into:

$$x_{ij} = \sum_{k=1}^p g_{ik}f_{kj} + e_{ij} \quad (2)$$

where x_{ij} represents the concentration that measured in the i th sample of the j th chemical species, g_{ik} represents source k contribution to the i th sample, f_{kj} represents the j th chemical species concentration in source k , and e_{ij} represents the residual for the i th sample and the j th chemical species.

An objective function is introduced in this model:

$$Q(E) = \sum_{i=1}^n \sum_{j=1}^m \left(\frac{e_{ij}}{u_{ij}} \right)^2 \quad (3)$$

where u_{ij} represents the uncertainty for the i th sample in the j th chemical species. Measurement uncertainties and method detection limits (MDLs) were employed to calculate

the uncertainties. If the sample concentration \leq MDL, the u was expressed as:

$$u = \frac{5}{6} \times MDL \quad (4)$$

If the sample concentration $>$ MDL, the u was expressed as:

$$u = \sqrt{(\text{MU} \times \text{concentration})^2 + (\text{MDL})^2} \quad (5)$$

PMF analysis was conducted using the USEPA PMF 5.0 model (USEPA 2014).

RESULTS AND DISCUSSION

Level and composition of PAHs

Table 1 shows the level of PAH in water at different sites in the research areas. The level of the \sum_{16} PAHs ranged from 4,076 (J) to 29,455 ng/L (O), with a mean of 17,212 ng/L in surface water. The most serious pollution site was at O, which was located at the Youyi River because the river received large quantities of waste water from the industrial activities and residential sources. At sites P and T (Nan River), the total PAH concentration was also high because of the discharge of a large amount of domestic waste into the Nan River. A high total PAH concentration was also found at Pipa Lake (M) located near Purple Mountain (a famous scenic spot in Nanjing). In the Yangtze River, the total PAH level was relatively low (less than the average value) perhaps because of its greater water mobility. The situation of the PAH pollution in urban areas of Nanjing was compared with other rivers or areas (Table 2). The PAH concentrations in surface water from the urban areas of Nanjing were lower than those in other regions, such as the Daqing surface water (Xiao *et al.* 2015) and Minjiang River (Zhang *et al.* 2004), but higher than those in Jiulong, Taizi, Raba, Nile, Mississippi, and Yellow Rivers (Maskaoui *et al.* 2002; Zhang *et al.* 2007; Badawy & Emababy 2010; Nagy *et al.* 2013b; Song *et al.* 2013; Zhao *et al.* 2015). Our research suggested that the water PAH from the urban areas of Nanjing were in the high pollution level.

On the basis of composition pattern of water PAH, it can be observed in Figure 2 that the 2- and 3-ring PAHs are the highest proportion in all PAHs, which averaged 42.9 and 48.5%. Nap and Phe are the major compounds in the water body. The 4-ring PAHs averaged 6.9%. The

Table 1 | Concentrations of PAH (ng L⁻¹) in surface water of Nanjing urban area, China (N = 20)

Compounds	ML		YR					XL		NR		EWP	QL	YL	PL	WR	YYR	QWP	YQL	QR
	a	b	a	b	c	d	e	a	b	a	b									
Nap	6,181	6,496	6,334	7,696	4,649	3,261	5,011	8,192	1,428	9,079	10,677	4,230	10,155	9,525	8,995	12,495	10,407	4,144	6,552	9,533
Acy	ND	358	523	ND	362	347	346	450	141	1,001	1,164	ND	733	546	846	649	ND	224	543	825
Ace	549	902	795	1,000	747	313	637	878	99	3,224	3,840	713	2,002	1,413	2,850	1,565	3,181	355	1,632	2,480
Fl	838	1,937	1,116	2,080	1,342	855	1,345	1,951	186	4,181	4,047	1,331	3,375	2,430	4,904	2,656	5,605	776	2,939	3,719
Phe	1,503	3,595	1,928	4,022	2,028	2,630	3,236	3,446	926	7,101	6,542	2,018	5,111	4,244	7,603	3,594	8,668	2,454	5,679	5,260
Ant	389	219	545	273	498	744	453	309	238	429	425	319	355	276	482	239	530	205	368	409
Flu	473	305	842	400	698	894	600	372	355	452	361	399	304	300	409	232	457	192	351	293
Pyr	396	259	793	338	645	833	519	335	344	309	240	351	192	217	270	166	326	138	222	222
BaA	206	16	85	31	94	103	51	29	45	27	93	32	25	60	36	19	70	18	26	46
Chr	138	18	91	32	99	106	52	30	54	56	65	34	55	64	111	65	75	38	58	49
BbF	77	17	78	29	86	87	47	28	49	58	91	31	37	ND	54	39	67	27	30	46
BkF	68	18	81	25	87	92	49	26	54	43	72	29	36	ND	11	16	25	18	12	45
BaP	55	12	73	25	76	88	42	25	46	13	69	27	7	ND	20	19	26	1	11	22
IcdP	53	11	57	19	61	69	32	18	34	7	4	21	9	7	15	ND	ND	10	4	14
DahA	67	10	64	18	66	77	34	8	36	32	16	18	3	5	3	5	10	4	4	2
BghiP	32	11	62	20	63	74	32	19	41	26	27	22	ND	ND	15	1	8	14	ND	16
ΣPAHs	11,025	14,185	13,468	16,007	11,600	10,572	12,485	16,117	4,076	26,038	27,733	9,575	22,399	19,087	26,624	21,760	29,455	8,618	18,431	22,981

Note: naphthalene (Nap), acenaphthylene (Acy), acenaphthene (Ace), fluorene (Fl), phenanthrene (Phe), anthracene (Ant), fluoranthene (Flu), 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 (InP), dibenz[a,h]anthracene (DBA), and benzo[g,h,i]perylene (BP); ND denotes not detected; Mochou Lake (ML), Yangtze River (YR), Xuanwu Lake (XL), The East Water Park (EWP), Qianhu Lake (QL), Yueya Lake (YL), Pipa Lake (PL), Wukesong Reservoir (WR), Youyi River (YYR), Nan River (NR), Qiqiaowen Wetland Park (QWP), Yanque Lake (YQL), Qinhuai River (QR).

Table 2 | Concentrations of PAHs in surface water around the world

Location	Range (ng/L)	Mean	Reference
Jiulong River, China	6,960–26,920	17,050	Maskaoui <i>et al.</i> (2002)
Minjiang River, China	9,900–474,000	72,400	Zhang <i>et al.</i> (2004)
Yellow River, China	548–2,598	1,375	Zhao <i>et al.</i> (2015)
Taizi River, China	455–1,380	907 (dry season)	Song <i>et al.</i> (2013)
Taizi River, China	1,802–5,869	3,235 (wet season)	Song <i>et al.</i> (2013)
Taizi River, China	367–5,795	1,818 (normal season)	Song <i>et al.</i> (2013)
Daqing, China	10,020–5,743,370	1,298,250	Xiao <i>et al.</i> (2015)
Raba River, Hungary	41–437	111	Nagy <i>et al.</i> (2013b)
Nile River, Egypt	1,110–4,364	1,878	Badawy & Emababy (2010)
Mississippi River, USA	62.9–144.7	–	Zhang <i>et al.</i> (2007)
Nanjing	4,076–29,455	17,212	This study

5- and 6-ring PAHs are the least in proportion, which altogether averaged 1.2 and 0.4%, respectively. The reason why LMW PAHs had a very high proportion in total PAHs is that they had relatively high water solubilities and vapor pressures (Wang *et al.* 2014; Zhao *et al.* 2015). Similar research results were also obtained in published data (Nagy *et al.* 2013a, 2013b; Zhao *et al.* 2015). However, Zhang *et al.* (2004) estimated that 5- and 6-ring PAHs occupied the most abundant in 16 PAHs, while 2- and 4-ring PAHs only held 21% of all PAHs.

PAH sources

Diagnostic ratios identify the origin of the pollution by comparing PAH ratios with well-known references and thus

qualitatively distinguish pyrolytic and petrogenic sources. The ratios of Anthracene/(Anthracene + Phenanthrene), and Fluoranthene/(Fluoranthene + Pyrene) were used to distinguish the source of PAHs in this study. The ratio of Fluoranthene/(Fluoranthene + Pyrene) >0.5 corresponds to the biomass burning or coal combustion, the ratio <0.4 corresponds to the petrogenic source, and the ratio between 0.4 and 0.5 corresponds to the petroleum combustion (Wang *et al.* 2017). The ratio of Anthracene/(Anthracene + Phenanthrene) >0.1 corresponds to the pyrogenic source, and the ratio <0.1 corresponds to the petrogenic source (Lv *et al.* 2014). The results of the above ratios are shown in Figure 3. All ratios show that the water PAH sources in the urban areas of Nanjing are from grass/wood/coal combustion. However, the ratios of Anthracene/(Anthracene +

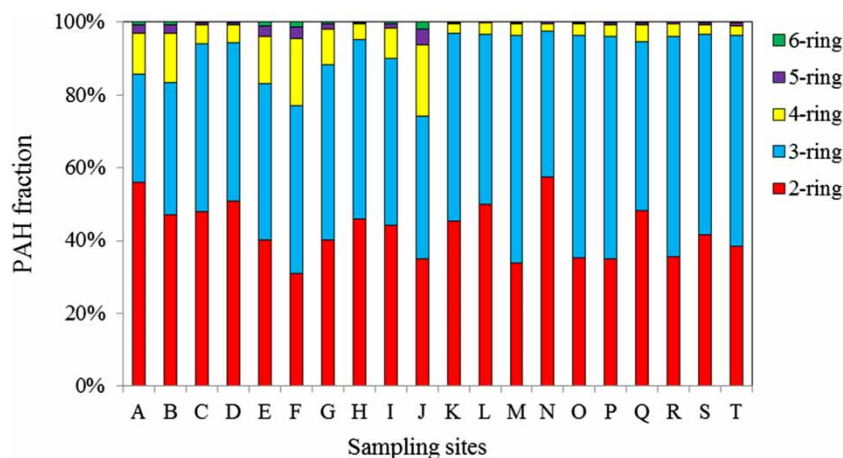


Figure 2 | Composition of parent PAH in surface water of urban areas of Nanjing, China. 2-ring PAHs include naphthalene; 3-ring PAHs include acenaphthylene, acenaphthene, fluorene, phenanthrene and anthracene; 4-ring PAHs include fluoranthene, pyrene, benzo[a]anthracene and chrysene; 5-ring PAHs include benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene and dibenzo[a,h]anthracene; 6-ring PAHs include indeno[1,2,3-cd]pyrene and benzo[g,h,i]perylene.

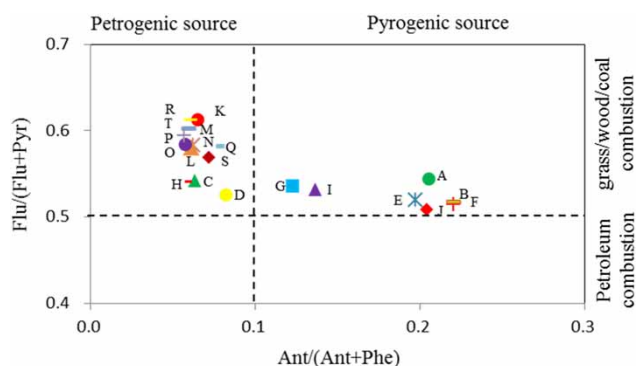


Figure 3 | Diagnostic ratios of PAH in the surface water in urban areas of Nanjing, China.

Phenanthrene) at some sites (A, B, E, F, G, I, J) are higher than 0.1, which indicates that the main source for these sites was pyrogenic. The ratios are lower than 0.1 at other sites indicating a petrogenic source. In conclusion, a mixture of combustion and petroleum sources contributed to PAHs in water at the urban areas of Nanjing.

A PMF model is used to quantitatively identify the sources of PAHs in surface water. In this study, three to

six factors are carefully examined. Finally, four appropriate factors are identified as the sources of surface water PAHs in urban areas of Nanjing. Figure 4 shows the source composition profiles on the basis of the four-factor solution.

Factor 1, explaining 26.00% of the 16 PAHs, was mainly composed of Nap. It was reported that Nap could be derived from sources of incomplete combustion and considered to have evaporated from coal tar (Simcik *et al.* 1999; Larsen & Baker 2003). As a consequence, factor 1 was classified as an oil source. Factor 2, explaining 32.83% of the 16 PAHs, was mainly composed of Phe, Flu, Ace, and Ant. The factor profile of Flu and Phe always originated from coke ovens (Duval & Friedlander 1981). Khalili *et al.* (1995) indicated Flu was the dominating PAH in the coke oven molecular characteristic. Factor 2 was classified as coke oven. Factor 3, explaining 29.12% of the 16 PAHs, was mainly composed of Ace, Acy, and Flu. It could be identified as coal combustion because the significant characteristic in coal burning was Acy and Flu (Masclat *et al.* 1987; Khalili *et al.* 1995). Therefore, this factor is classified as the coal combustion. Factor 4, explaining 12.05% of the 16

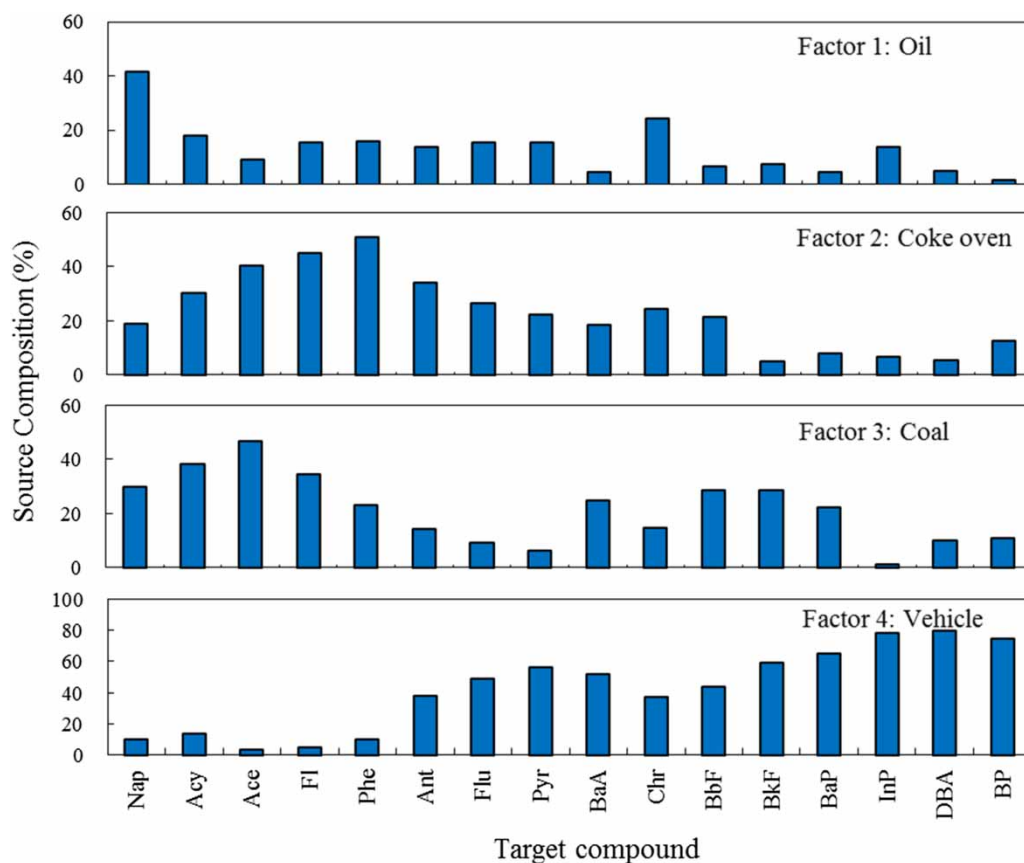


Figure 4 | Source profiles obtained from the PMF model.

PAHs, is mainly composed of DBA, InP, BP, and BaP. In addition, the high weight molecular PAHs are heavily loaded on this factor. This source profile could be identified as automobile exhaust (Miguel & Pereira 1989; Harrison et al. 1996). As a consequence, factor 4 is identified as the vehicle source.

According to the analyses above, the surface water PAH from urban areas in Nanjing are influenced by coke oven, coal combustion, oil source, and vehicle emissions, in that order.

Potential risk assessment

Toxic equivalency factors of BaP (BaP_{eq}) (Nisbet & Lagoy 1992) were used to assess the environmental risks of water PAH in urban areas of Nanjing (Table 3). Figure 5 shows the BaP_{eq} values ranged from 23.15 to 218.01 ng/L. The result indicated that 100% of BaP_{eq} values were higher than the Chinese National Standard (State General Administration of the People's Republic of China for Quality Supervision and Inspection and Quarantine, State Environmental Protection Administration of China 2002) which specifies that a safe value for BaP in surface water is 2.8 ng/L. The results show that the surface water in urban areas of Nanjing was heavily polluted and may cause potential health risks. Therefore, efforts should be taken to control the PAH emissions and to effectively treat the fossil fuel use

Table 3 | Toxicity equivalency factors for individual PAHs in urban area surface water, Nanjing, China

Nap	Acy	Ace	Fl	Phe	Ant	Flu	Pyr
0.001	0.001	0.001	0.001	0.001	0.01	0.001	0.001
BaA	Chr	BbF	BkF	BaP	InP	DBA	BP
0.1	0.01	0.1	0.1	1	0.1	1	0.01

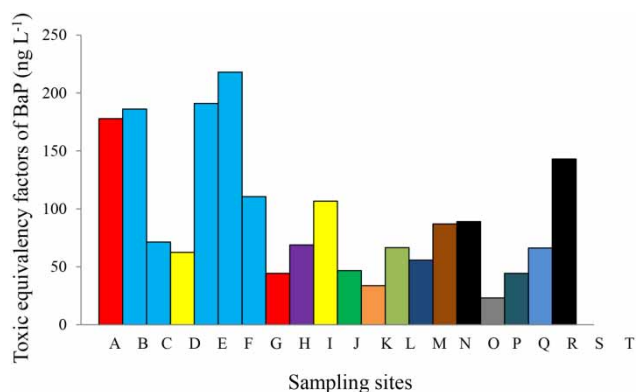


Figure 5 | BaP_{eq} values in the surface water samples in urban areas of Nanjing, China.

in traffic and industrial processes to reduce the PAH environmental concentrations.

CONCLUSIONS

The results show that surface water in the Nanjing area was heavily polluted with PAHs, predominantly 2- and 3-ring PAHs. The diagnostic ratio analysis indicated that a mixture input of combustion and petroleum origin contributed largely to the pollution. A PMF model used to quantitatively identify the sources of pollution indicated that coke oven (32.83%), coal combustion (29.12%), oil (26.00%) and automobile exhaust (12.05%) were the primary sources of pollution. These levels of PAH pollution of surface water in urban areas of Nanjing demand effective efforts to eliminate sources of PAHs and control of water pollution.

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REFERENCES

- Amoako, J., Ansa-Asare, O. D., Karikari, A. Y. & Dartey, G. 2011 Levels of polycyclic aromatic hydrocarbons (PAHs) in the Densu River Basin of Ghana. *Environ. Monit. Assess.* **174**, 471–480.
- Badawy, M. I. & Emababy, M. A. 2010 Distribution of polycyclic aromatic hydrocarbons in drinking water in Egypt. *Desalination* **251**, 34–40.
- Dhananjayan, V., Muralidharan, S. & Peter, V. R. 2012 Occurrence and distribution of polycyclic aromatic hydrocarbons in water and sediment collected along the harbour line, Mumbai, India. *International Journal of Oceanography* **2012**, Article ID 403615.
- Duval, M. M. & Friedlander, S. K. 1981 Source Resolution of Polycyclic Aromatic Hydrocarbons in the Los Angeles Atmosphere: Application of a Chemical Species Balance Method with First Order Chemical Decay. Final report Jan–Dec 80.
- Harrison, R. M., Smith, D. J. T. & Luhana, L. 1996 96/05612 source apportionment of atmospheric polycyclic aromatic hydrocarbons collected from an urban location in Birmingham, UK. *Environ. Sci. Technol.* **30**, 825–832.
- Hayakawa, K., Makino, F., Yasuma, M., Yoshida, S., Chondo, Y., Toriba, A., Kameda, T., Tang, N., Kunugi, M. & Nakase, H. 2016 Polycyclic aromatic hydrocarbons in surface water of the Southeastern Japan Sea. *Chem. Pharm. Bull.* **64**, 625–631.

- Khalili, N. R., Scheff, P. A. & Holsen, T. M. 1995 PAH source fingerprints for coke ovens, diesel and, gasoline engines, highway tunnels, and wood combustion emissions. *Atmos. Environ.* **29**, 533–542.
- Larsen, R. K. & Baker, J. E. 2003 Source apportionment of polycyclic aromatic hydrocarbons in the urban atmosphere: a comparison of three methods. *Environ. Sci. Technol.* **37**, 1873–1881.
- Lv, J., Xu, J., Guo, C., Zhang, Y., Bai, Y. & Meng, W. 2014 Spatial and temporal distribution of polycyclic aromatic hydrocarbons (PAHs) in surface water from Liaohe River Basin, northeast China. *Environ. Sci. Pollut. Res.* **21**, 7088–7096.
- Masclat, P., Bresson, M. A. & Mouvier, G. 1987 Polycyclic aromatic hydrocarbons emitted by power stations, and influence of combustion conditions. *Fuel* **66**, 556–562.
- Maskaoui, K., Zhou, J. L., Hong, H. S. & Zhang, Z. L. 2002 Contamination by polycyclic aromatic hydrocarbons in the Jiulong River Estuary and Western Xiamen Sea, China. *Environ. Pollut.* **118**, 109–122.
- McDaniel, M. & Zielinska, B. 2015 Polycyclic aromatic hydrocarbons in the snowpack and surface water in Blackwood Canyon, Lake Tahoe, CA, as related to snowmobile activity. *Polycycl. Aromat. Comp.* **35**, 102–119.
- Miguel, A. H. & Pereira, P. A. P. 1989 Benzo(k)fluoranthene, Benzo(ghi)perylene, and Indeno(1,2,3-cd)pyrene: new tracers of automotive emissions in receptor modeling. *Aerosol Sci. Tech.* **10**, 292–295.
- Nagy, A. S., Simon, G., Szabó, J. & Vass, I. 2013a Polycyclic aromatic hydrocarbons in surface water and bed sediments of the Hungarian upper section of the Danube River. *Environ. Monit. Assess.* **185**, 4619–4631.
- Nagy, A. S., Szabó, J. & Vass, I. 2013b Occurrence and distribution of polycyclic aromatic hydrocarbons in surface water of the Raba River, Hungary. *J. Environ. Sci. Health A Tox. Hazard. Subst. Environ. Eng.* **48**, 1190–1200.
- Net, S., Dumoulin, D., El-Osmani, R., Rabodonirina, S. & Ouddane, B. 2014 Case study of PAHs, Me-PAHs, PCBs, Phthalates and pesticides contamination in the Somme River water, France. *Int. J. Environ. Res.* **8**, 1159–1170.
- Nisbet, I. C. T. & Lagoy, P. K. 1992 Toxic equivalency factors (TEFs) for polycyclic aromatic hydrocarbons (PAHs). *Regul. Toxicol. Pharm.* **16**, 290–300.
- Paatero, P. & Tapper, U. 1994 Positive matrix factorization: a non-negative factor model with optimal utilization of error estimates of data values. *Environmetrics* **5**, 111–126.
- Simcik, M. F., Eisenreich, S. J. & Lioy, P. J. 1999 Source apportionment and source/sink relationships of PAHs in the coastal atmosphere of Chicago and Lake Michigan. *Atmos. Environ.* **33**, 5071–5079.
- Song, X., Hu, X., He, M., Liang, R., Li, Y. & Li, F. 2013 Distribution and sources of polycyclic aromatic hydrocarbons in the surface water of Taizi River, Northeast of China. *Environ. Monit. Assess.* **185**, 8375–8382.
- State General Administration of the People's Republic of China for Quality Supervision and Inspection and Quarantine, State Environmental Protection Administration of China 2002 *State Standard of People's Republic of China: Environmental Quality Standard for Surface Water (GB3838-2002)*. Standards Press of China, Beijing, China (in Chinese).
- USEPA 2014 *EPA Positive Matrix Factorization (PMF) 5.0 Fundamentals & User Guide*. Online available at: <http://www.epa.gov/heasd/research/pmf.html>.
- Wang, Y., Wang, J., Mu, J., Wang, Z., Yao, Z. & Lin, Z. 2014 Aquatic predicted no-effect concentration for three polycyclic aromatic hydrocarbons and probabilistic ecological risk assessment in Liaodong Bay of the Bohai Sea, China. *Environ. Sci. Pollut. Res.* **21**, 148–158.
- Wang, C., Wu, S., Zhou, S., Wang, H., Li, B., Chen, H., Yu, Y. & Shi, Y. 2015 Polycyclic aromatic hydrocarbons in soils from urban to rural areas in Nanjing: concentration, source, spatial distribution, and potential human health risk. *Sci. Total Environ.* **527–528**, 375–383.
- Wang, C., Wu, S., Zhou, S., Shi, Y. & Song, J. 2017 Characteristics and source identification of polycyclic aromatic hydrocarbons (PAHs) in urban soils: a review. *Pedosphere* **27**, 17–26.
- Xiao, N., Zhao, C., Wang, X. & Gao, X. 2015 Distribution and ecological risk assessment of polycyclic aromatic hydrocarbons in surface water from Daqing City. *Environ. Sci. Technol.* **38**, 78–83 (in Chinese).
- Zhang, Z. L., Hong, H. S., Zhou, J. L. & Yu, G. 2004 Phase association of polycyclic aromatic hydrocarbons in the Minjiang River Estuary, China. *Sci. Total Environ.* **323**, 71–86.
- Zhang, S., Zhang, Q., Darisaw, S., Ehie, O. & Wang, G. 2007 Simultaneous quantification of polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), and pharmaceuticals and personal care products (PPCPs) in Mississippi river water, in New Orleans, Louisiana, USA. *Chemosphere* **66**, 1057–1069.
- Zhang, L., Shi, S., Dong, L., Zhang, T., Zhou, L. & Huang, Y. 2011 Concentrations and possible sources of polychlorinated biphenyls in the surface water of the Yangtze River Delta, China. *Chemosphere* **85**, 399–405.
- Zhang, H., Sun, L., Sun, T., Li, H. & Luo, Q. 2013 Spatial distribution and seasonal variation of polycyclic aromatic hydrocarbons (PAHs) contaminations in surface water from the Hun River, Northeast China. *Environ. Monit. Assess.* **185**, 1451–1462.
- Zhao, X., Qiu, H., Zhao, Y., Shen, J., Chen, Z. & Chen, J. 2015 Distribution of polycyclic aromatic hydrocarbons in surface water from the upper reach of the Yellow River, Northwestern China. *Environ. Sci. Pollut. Res.* **22**, 6950–6956.
- Zhu, L., Chen, B., Wang, J. & Shen, H. 2004 Pollution survey of polycyclic aromatic hydrocarbons in surface water of Hangzhou, China. *Chemosphere* **56**, 1085–1095.

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