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Distribution and source assessment of polycyclic aromatic hydrocarbons levels from Lake IJssel (the Netherlands) and their responses to hydrology

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• Abstract

Based on field efforts in Lake IJssel (the Netherlands) from 2000 to 2010, dynamics of 15 priority PAHs in suspended particulate matter (SPM) and in seawater were determined. This study examined time-varying changes in PAH concentration and composition, apportioned potential anthropogenic sources, and quantified their linkages to hydrological factors. The sum of individual PAHs (defined as Σ_{15} PAHs) varied widely throughout the study period in Lake IJssel, ranging from 0.76 to 9.66 mg/kg in SPM and from 0.014 to 0.136 $\mu\text{g/L}$ in seawater. High molecular weight PAHs were the most abundant PAH compounds, responsible for 73%–97%. Seasonal variation in Σ_{15} PAHs level was distinguished, peaked in late winter and early spring, and reached a minimum in summer. Over site, the heavy contamination was found at the river mouth (e.g., Genemuiden). The driving factors of SPM and water temperature controlled the fate of PAHs. Principal component analysis and diagnostic ratios suggested that PAHs may have been derived from different input sources through various transport pathways, *for example*, coal combustion source and petroleum source. The findings are useful for filling the knowledge gap of PAH dynamics in Lake IJssel and Wadden Sea, which exerts significant influences on lake's environment. © 2020

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• Practitioner points

- HMW PAHs (4–6 rings) were the most abundant PAH compounds.
- Heavy contamination was found in the mouth of IJssel River.
- Time-varying change in PAHs level was significantly correlated with riverine input.
- PAHs sources were apportioned via principal component analysis and diagnostic ratios.

• Key words

hydrological impact; Lake IJssel; polycyclic aromatic hydrocarbons; source apportionment; suspended particulate matter

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs), one group of persistent organic pollutants (POPs), have raised a worldwide concern on marine environment and human health, due to their environmental properties of carcinogenicity, toxicity, and mutagenicity (Boehm, Murray, & Cook, 2016; Moeckel, Monteith, Llewellyn, Henrys, & Pereira, 2014; Tang et al., 2018). PAH compounds have been found in air, water, suspended particulate matter (SPM), soil, and sediments (Hu et al., 2014; Inam et al., 2018; Kannan, Johnson-Restrepo, Yohn, Giesy, & Long, 2005; Liu et al., 2017; Niu et al., 2020; Ruge, Muir, Helm, & Lohmann, 2015). These compounds enter the environment via several pathways, for example, atmospheric PAHs, terrestrial PAHs, and PAHs in the water column. PAHs in aquatic environment are a key to controlling the ecological risks posed by such chemicals in seawater and sediments. Because of

the low vapor pressures of PAHs, compounds with five or more rings exist mainly adsorbed to particulate matter, while those with four or fewer rings will occur both in the dissolved and particulate phases (Yuan et al., 2015).

Estuarine/coastal waters play an important role in transporting organic pollutants from land to sea and in discharging pollutants from river to open ocean (Niu et al., 2018; Verlaan & Spanhoff, 2000). They are characterized by strong gradients of factors such as salinity, as well as inorganic and organic pollutants as a result of riverine input and sewage outfalls in the complex estuarine environment (Liu et al., 2017; Timoney & Lee, 2011). The ecosystems have been suffering extensively from different anthropogenic pressures due to excess input of PAHs (Laane et al., 2013; Wang, Guan, Ni, Luo, & Zeng, 2007) and atmospheric outflow (Lang, Tao, Liu, Zhang, & Simonich, 2008). During these processes, environmental correlations of PAHs dynamics served as mutual functions, which could be explained by cumulative effects of physical, chemical, and biological properties. Thus, investigation of PAHs in estuary can provide useful information for further understanding of environmental processes and transport of contaminants.

In this study, the dissolved PAHs in Lake IJssel, the north of Netherlands (Figure 1), were at a relatively lower level. Thus, the particulate PAHs were our main concern. Lake IJssel, connecting to the western Wadden Sea, was an ecologically complicated zone. The Wadden Sea was a shallow sea with tidal flats off the Netherlands, Germany, and Denmark. Previous studies (Duinker, Van Eck, & Nolting, 1974; Niu, Gelder, Zhang, Guan, & Vrijling, 2015; van Raaphorst & de Jonge, 2004) have reported that the Wadden seawater, containing levels of organic and inorganic contaminants, exchanged with the North Sea water during every tidal cycle. The contaminants of the Rhine and Meuse rivers entered into the western Wadden Sea via the Dutch coast and Lake IJssel (Verlaan & Spanhoff, 2000). SPM in the Wadden Sea originated from the rivers and sluice systems and from local primary production. Zimmerman and Rommets (1974) reported that in the western Wadden Sea, 7% of the water was from the Rhine River and 15% was from Lake IJssel. Therefore, Lake IJssel played an important role in the Wadden Sea ecosystem, and even in the North Sea ecosystem. The North Sea seemed like a potential receptor of PAHs and contributed notably to global pollution via air-water exchange.

However, studies on PAHs were performed in the Wadden Sea (Laane et al., 2013), and limited discussion has been given in Lake IJssel and the adjacent zone. Studies of their relations to hydrology and anthropogenic contamination still remained poorly documented. Therefore, an understanding of how PAHs are dispersed is of central importance to the Dutch coastal ecosystem. The objectives of this study are (a) to investigate changes in PAH concentration and composition, temporally and spatially; (b) to present their environmental fate; and (c) to apportion their potential anthropogenic sources.

MATERIALS AND METHODS

This section described the materials and methods used in the study. Sampling sites N1–N8 distributed all around Lake

IJssel. Based on a large number of dataset from 2000 to 2010, Pearson's correlation and principal component analysis were performed to present environmental controls and to partition the potential anthropogenic sources.

Study site

The organic contaminants in Lake IJssel were received via the IJssel River, a branch of Rhine River, and were then transported into the North Sea through the Wadden Sea and IJmuiden channel. Sampling sites (N1–N8) in Lake IJssel were investigated to assess the spatiotemporal variations in PAH concentration and composition. N1 (52°22'39.58", 4°56'27.48") locates in the IJmuiden channel, discharged a large amount of pollutants from the big city of Amsterdam; N2 (52°16'45.40", 5°20'47.94") receives the pollutants from the cities of Almere and Amsterdam; N3 (52°21'8.10", 5°34'12.56") transports the contaminants from the cities of Ermelo, Nunspeet, and Dronten, along a branch of IJssel River; N4 (52°37'17.02", 5°57'0.26"), N5 (52°35'50.65", 5°49'11.96"), and N6 (52°35'45.89", 5°43'18.02") locate in an intersection of rivers, and discharge the pollutants into Lake IJssel; N7 (52°33'19.10", 5°11'44.62") is in the center zone of Lake IJssel, presented the main lake property; and N8 (53°2'52.29", 5°18'13.76") shows the characteristics both of Lake IJssel and Wadden Sea. Of these, PAHs levels at sites N1–N7 were detected each month, and PAHs at site N8 were seasonally detected (February, May, August and November). Samples were analyzed for 15 priority PAHs designated by the U.S. Environmental Protection Agency (EPA), named as naphthalene (Nap), acenaphthylene (Acy), acenaphthene (Ace), fluorene (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene (Fluo), pyrene (Pyr), benzo[a]anthracene (Ba), chrysene (Chr), benzo[b]fluoranthene (Bb), benzo[k]fluoranthene (Bk), benzo[a]pyrene (Bap), dibenzo[a,h]anthracene (Dib), benzo[g,h,i]perylene (Bg), and indeno[123-cd]pyrene (Ind).

Sample collection and statistical analysis

Water samples were extracted from the surface water. PAH analysis was performed using gas chromatography-mass spectrometry (GC-MS; Agilent, 6890, Agilent, 5973). The analytical procedures and quality controls used for the extraction and measurement of particulate PAHs have been described in our previous studies (Liu et al., 2017; Niu et al., 2018). Water samples were firstly filtered via a vermicular system with GF/D (3 µm pore) and GF/F (0.7 µm pore) glass fiber filters (Whatman International Ltd. UK) and precombusted at 450°C for 4 hr before use. The extraction of particulate PAHs was performed with an extraction cell using accelerated solvent extractor (ASE) according to the EPA-3545A method. The solid samples (10 g) were freeze-dried. The surrogate standards were added before extraction. The extraction solvent was Me₂CO:CH₂Cl₂ (v:v, 1:1). The solid samples were extracted for 10 min at 100°C and 1,500 psi. Subsequently, the solvent was exchanged with n-hexane and the volume was further reduced to ca. 1 ml using a weak N₂ flow. The final extract was cleaned up and fractionated using a 1:2 Al₂O₃/SiO₂ gel glass.



Figure 1. Sketch map of Lake IJssel in the north of Netherlands and sampling sites N1–N8, in which N1–N8 distributed at Amsterdam IJtunnel, Eemmeer, Wolderwijd, Genemuiden, Kampen, Ketelmeer west, Markermeer, and Doove Balg coast, respectively.

Lake IJssel received freshwater input from the IJssel River. However, the PAHs were mainly attributed to human contamination sources. The particulate PAH compounds were expressed in mg/kg. In this study, the target analyses contained 15 priority PAH compounds (EPA). The sum of 15 individual PAHs at the sampling sites N1–N7 was defined as Σ_{15} PAHs, while for the 11 individual PAHs at the site N8 was defined as Σ_{11} PAHs. Pearson's correlation (significance level $p < .05$) and principal component analysis (PCA, eigenvalue > 1.0) were performed to present environmental fate and potential anthropogenic sources (Larsen & Baker, 2003; Liu et al., 2017), using the software IBM SPSS 19.0. The similarity and difference of individual PAHs were also explored with PCA. Origin 8.0 was used to plot the measurement data. Linear regression analysis was performed to give insight in the supplement information of environmental controls of particulate PAHs.

RESULTS

This section firstly examined the seasonal variation of hydrology in Lake IJssel, which would largely influence the PAH levels. And then the time-vary changes in PAH concentration and composition were presented.

Seasonal variation in hydrology

Hydrological cycles in Lake IJssel can be reflected in changes in the lake parameters, including water temperature (T), salinity, and SPM in this case. The observed hydrological parameters at three representative sites of N1, N7, and N8 showed significant seasonal patterns (Figure 2). At Amsterdam IJtunnel (N1), water temperature varied from 3.4 to 24.3°C, with an annual mean of 12.7°C, and the monthly mean water temperature in the wet season (May–October, 18.2°C) was higher than that in the dry season (November–April, 7.7°C). The monthly mean SPM concentration ranged from 0.003 to 0.023 mg/L, with an annual mean of 0.011 mg/L. SPM concentration in the wet season (0.017 mg/L) was higher than that in the dry season (0.007 mg/L), similar trend as the water temperature. At the site of Markermeer (N7), the monthly mean water temperature and SPM varied from 0.5 to 21.6°C and 0.009 to 0.368 mg/L, respectively. The significant differences were found both in temperature and SPM, and higher SPM values were detected in the dry season (0.079 mg/L) than that in the wet season (0.035 mg/L). While at the site of Doove Balg coast (N8), the monthly mean salinity ranged from 17.38 to 31.41‰, with an annual mean of 24.3‰ and standard deviation of 3.08‰, and the mean salinity in the wet season was lower than that in the

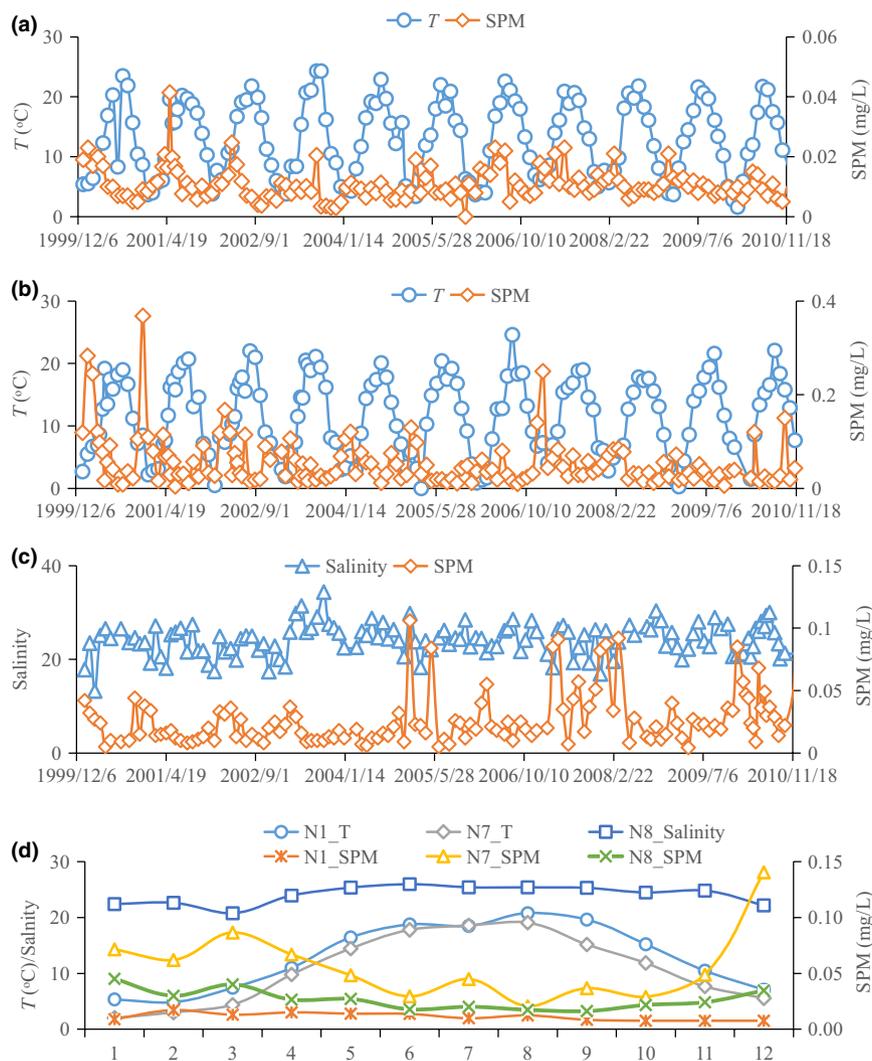


Figure 2. Long-term changes in water temperature (T), salinity, and suspended particulate matter (SPM) from 2000 to 2010 at three representative sampling sites (a, N1; b, N7; c, N8) in Lake IJssel, and seasonal variation in hydrological condition (d).

dry season. The monthly mean SPM concentration ranged from 0.005 to 0.084 mg/L, and the annually mean (0.024 mg/L) was higher than that at Amsterdam IJtunnel (0.011 mg/L), but was lower than that at Markermeer (0.055 mg/L). The water in Lake IJssel was less saline than the Wadden Sea and North Sea, because its seawater was diluted by freshwater originating from the rivers (Laane et al., 2013).

Time-varying change in PAH concentration

PAHs in water. The seasonal variation in total 16 individual PAHs in seawater is displayed in Figure 3. The PAH concentrations in water column were higher in the dry season than that in the wet season. It appeared that heavy contamination occurred in February and December in this case, while the minimum level of contamination occurred in June and July. The sum of dissolved PAHs varied from 0.014 to 0.136 $\mu\text{g/L}$, with a mean value of 0.034 $\mu\text{g/L}$. The higher levels were found at the river mouth (e.g., Kampen), a similar trend as the particulate PAHs. The sequence of the mean concentrations of 16 priority PAHs

in seawater was Fluo (14.33%) > Pyr (14.15%) > Phe (12.81%) > Bb (9.45%) > Bap (5.72%) > Ind (5.30%) > Bg (4.68%) > Dib (4.57%) > Ant (4.15%) > Ba (4.14%) > Bk (3.71%) > Nap (2.91%), Acy (2.91%), Ace (2.91%), and Flu (2.91%).

PAHs in SPM. For evaluation of PAH concentrations in SPM, the distribution of particulate PAHs was not similar to that of the dissolved PAHs (Schwarzenbach, Gschwend, & Imboden, 2005). The PAHs were significantly associated with particles than dissolved in seawater due to their hydrophobicity (Niu et al., 2018). Table 1 shows the mean concentration of 15 individual PAHs in SPM in Lake IJssel. The Nap was heavily contaminated at Kampen and Ketelmeer west. The 3-ring PAHs were mainly distributed at Amsterdam IJtunnel, Genemuiden, Kampen, and Ketelmeer west.

The PAHs were divided into two groups based on the number of aromatic rings, low molecular weight (LMW-PAHs; containing 2–3 rings), and high molecular weight PAHs (HMW-PAHs; containing 4–6 rings). High molecular weight PAHs

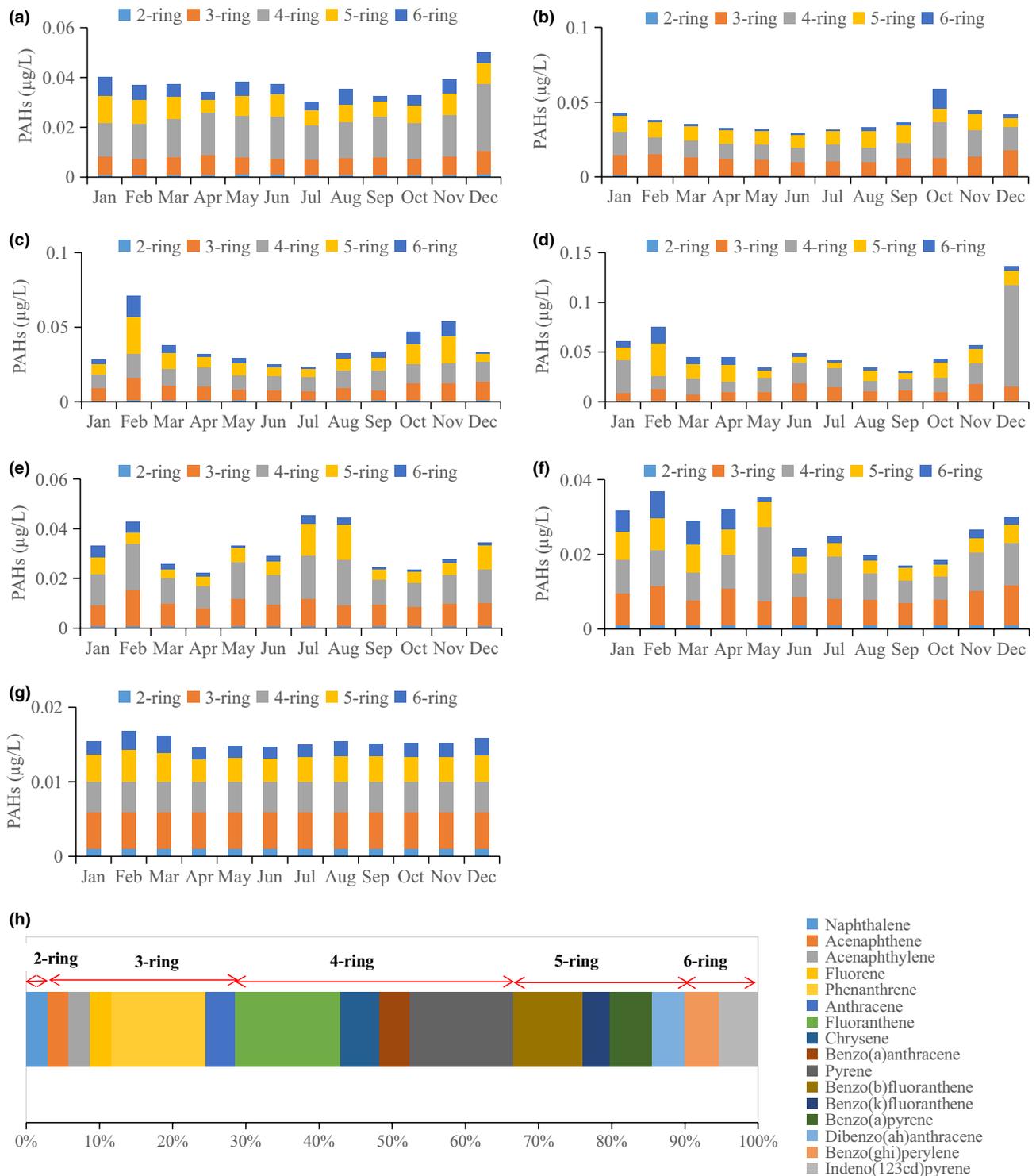


Figure 3. Seasonal dynamics of dissolved PAHs concentration in Lake IJssel from 2000 to 2010 (a, N1; b, N2; c, N4; d, N5; e, N6; f, N7; g, N8); and mean concentrations of individual PAHs in water (h).

(containing 4–6 rings) were the most abundant PAH compounds, with higher concentrations (5.092 mg/kg, 1.438 mg/kg, 1.060 mg/kg, 5.954 mg/kg, 4.354 mg/kg, 4.580 mg/kg, 0.850 mg/kg, and 1.824 mg/kg) than that of low molecular weight PAHs (0.674 mg/kg, 0.266 mg/kg, 0.271 mg/kg, 0.449 mg/kg, 1.586 mg/kg,

kg, 0.750 mg/kg, 0.330 mg/kg, and 0.493 mg/kg). The most abundance of HMW PAHs was at Genemuiden, and the most abundance of LMW PAHs was at Kampen. The sites of Amsterdam IJtunnel, Genemuiden, Kampen, and Ketelmeer were heavily contaminated, with higher levels of Σ_{15} PAHs.

Table 1. Statistics of 15 individual PAH detected in suspended particulate matter (SPM) in Lake IJssel (unit: mg/kg; M, mean; S, scope)

PAH		N1	N2	N3	N4	N5	N6	N7	N8
Nap	M	0.169	0.081	0.086	0.085	0.215	0.25	0.103	–
	S	0.05–0.46	0.05–0.3	0.05–0.29	0.05–0.27	0.04–0.86	0.05–0.59	0.05–0.58	–
Ace	M	0.115	0.056	0.059	0.077	0.112	0.099	0.056	–
	S	0.05–0.56	0.05–0.12	0.05–0.23	0.05–0.20	0.03–0.49	0.05–0.58	0.05–0.11	–
Acy	M	0.096	0.132	0.152	0.112	0.076	0.199	0.172	–
	S	0.05–0.22	0.05–0.8	0.05–0.84	0.05–0.88	0.001–0.49	0.05–3.2	0.05–2.4	–
Flu	M	0.108	0.035	0.034	0.054	0.106	0.114	0.04	–
	S	0.05–0.23	0.01–0.14	0.005–0.09	0.021–0.13	0.04–0.41	0.05–0.20	0.01–0.102	–
Ant	M	0.146	0.025	0.015	0.077	0.185	0.225	0.019	0.03
	S	0.05–0.29	0.01–0.1	0.005–0.06	0.01–0.21	0.02–0.8	0.04–0.44	0.007–0.18	0.016–0.05
Fluo	M	0.877	0.282	0.153	0.986	0.89	0.803	0.135	0.176
	S	0.4–1.9	0.07–0.78	0.07–0.42	0.23–2.39	0.2–2.4	0.32–1.14	0.01–0.71	0.088–0.31
Chr	M	0.482	0.139	0.057	0.574	0.493	0.455	0.057	0.083
	S	0.15–0.94	0.03–0.45	0.007–0.1	0.01–1.5	0.07–1.2	0.21–0.66	0.01–0.31	0.043–0.14
Ba	M	0.43	0.102	0.041	0.519	0.448	0.385	0.042	0.074
	S	0.16–0.86	0.03–0.3	0.01–0.08	0.19–1.1	0.08–1.2	0.11–0.57	0.01–0.29	0.038–0.13
Pyr	M	0.818	0.224	0.103	0.9	0.726	0.638	0.096	0.131
	S	0.31–1.6	0.04–0.75	0.02–0.26	0.24–2.0	0.14–1.5	0.33–0.96	0.01–0.53	0.064–0.24
Bb	M	0.659	0.191	0.091	0.721	0.571	0.563	0.079	0.134
	S	0.09–1.4	0.04–0.474	0.03–0.19	0.21–1.56	0.07–1.4	0.13–0.77	0.02–0.35	0.075–0.22
Bk	M	0.302	0.085	0.037	0.338	0.269	0.26	0.047	0.059
	S	0.1–0.65	0.02–0.21	0.01–0.06	0.06–0.73	0.01–0.77	0.11–0.36	0.01–0.72	0.032–0.10
Bap	M	0.509	0.089	0.425	0.862	0.876	0.601	0.283	0.256
	S	0.12–1.2	0.05–0.16	0.01–2.2	0.28–1.6	0.09–7.3	0.25–0.95	0.03–2.7	0.053–1.0
Dib	M	0.082	0.032	0.018	0.088	0.073	0.071	0.016	0.019
	S	0.01–0.19	0.005–0.14	0.005–0.19	0.01–0.21	0.01–0.18	0.01–0.19	0.005–0.06	0.008–0.035
Bg	M	0.486	0.143	0.063	0.504	0.425	0.403	0.06	0.095
	S	0.13–1.0	0.02–0.35	0.02–0.13	0.13–1.2	0.1–1.1	0.19–0.58	0.02–0.30	0.05–0.15
Ind	M	0.495	0.15	0.095	0.557	0.433	0.414	0.064	0.103
	S	0.06–0.97	0.02–0.346	0.02–0.44	0.1–1.29	0.11–1.18	0.18–1.28	0.02–0.30	0.055–0.17

Figure 4 plots the spatiotemporal variation in averaged Σ_{15} PAHs in Lake IJssel during 2000–2010. The sites of Amsterdam IJtunnel, Genemuiden, Kampen, and Ketelmeer were heavily contaminated, with higher levels of PAHs. A large number of PAHs from the Amsterdam, capital of the Netherlands, was discharged in the Amsterdam IJtunnel. Genemuiden, Kampen and Ketelmeer, located in a river intersection, received the transported PAHs of big cities along the IJssel River.

The concentration of Σ_{15} PAHs at Amsterdam IJtunnel ranged from 1.96 to 14.32 mg/kg, with a monthly mean of 5.76 mg/kg. The maximum level was found in July 2002, and the minimum was detected in March 2000. Σ_{15} PAHs in particulate phase at Eemmeerdijk varied from 0.61 to 3.91 mg/kg, with a monthly mean of 1.67 mg/kg and standard deviation of 0.63 mg/kg. The maximum concentration was found in February 2001, and the minimum was detected in August 2000. The concentration of Σ_{15} PAHs in SPM at Wolderwijk ranged from 0.43 to 3.16 mg/kg, with a monthly mean of 1.32 mg/kg and standard deviation of 0.43 mg/kg. The maximum concentration was found in October 2006, and the minimum

was detected in December 2000. The particulate Σ_{15} PAHs at Genemuiden ranged from 3.33 to 13.03 mg/kg, with a monthly mean of 6.49 mg/kg and standard deviation of 2.30 mg/kg. The maximum concentration was found in May 2003, and the minimum was detected in August 2003.

The Σ_{15} PAHs in SPM at Kampen ranged from 2.63 to 13.94 mg/kg, with a monthly mean of 5.84 mg/kg. The maximum was found in April 2004, and the minimum was detected in January 2002. Σ_{15} PAHs at Ketelmeer west ranged from 3.13–8.30 mg/kg, with a monthly mean of 5.27 mg/kg and standard deviation of 0.89 mg/kg. The maximum concentration was found in May 2003, and the minimum was detected in April 2007. While Σ_{15} PAHs in SPM at Markermeer and Doove Balg coast ranged from 0.34 to 3.87 mg/kg and 0.58 to 1.85 mg/kg, respectively.

Different PAHs levels were observed in Lake IJssel, reflecting their different sources. The heavy contamination was located in the river mouths. The minimum was shown at Doove Balg coast compared with other sites. The possible cause was that particulate PAHs at Doove Balg coast were mostly affected by marine water as they are connected to the North Sea, and

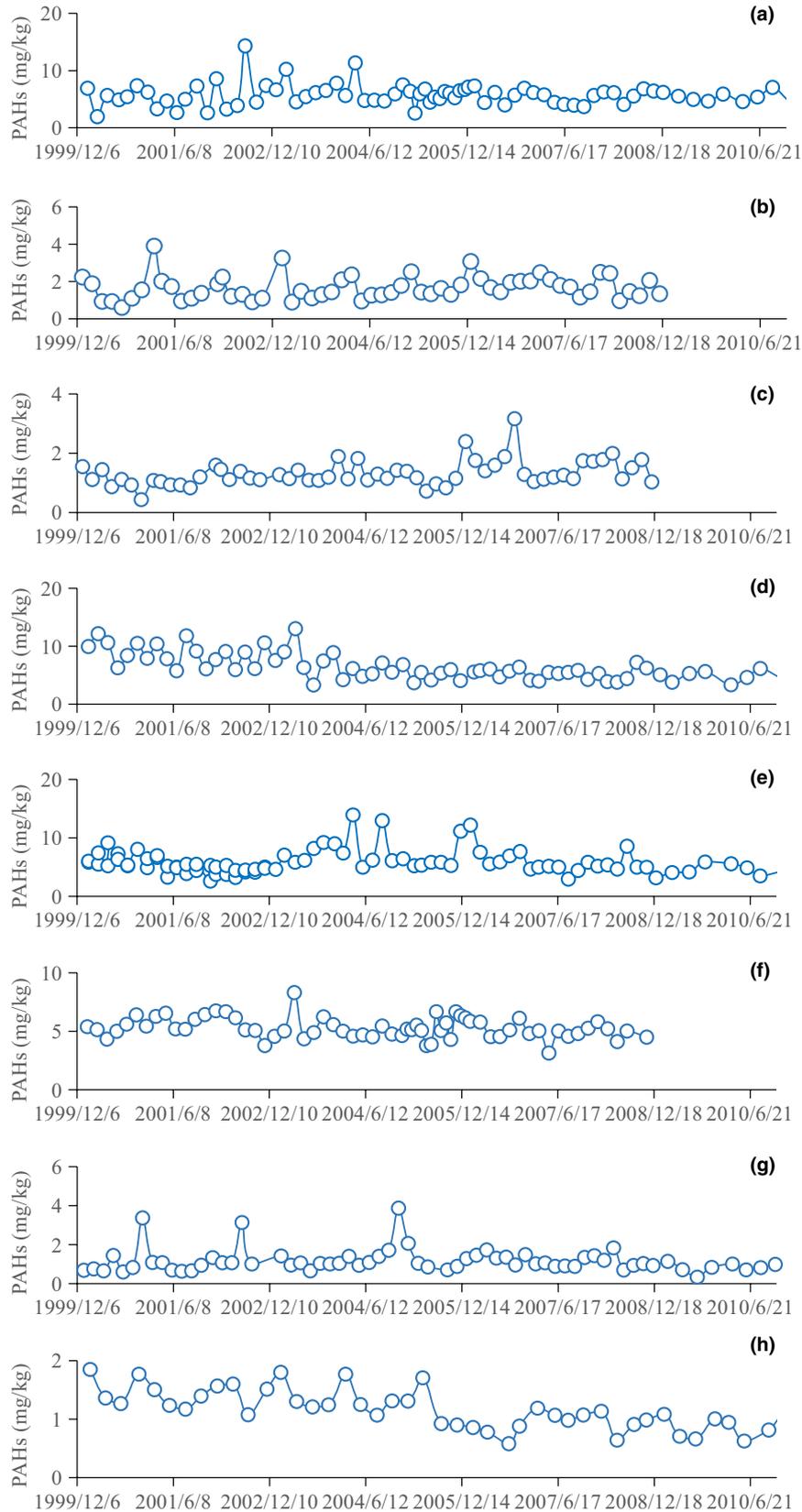


Figure 4. Time-varying change in the sum of 15 particulate PAHs ($\Sigma 15\text{PAHs}$) concentration in Lake IJssel from 2000 to 2010 (a, N1; b, N2; c, N3; d, N4; e, N5; f, N6; g, N7; h, N8).

the organic contaminants could be diluted by the marine water. Thus, lower contaminants were examined.

The particulate PAHs were largely attributed to the SPM properties (Laane et al., 2013; Niu et al., 2018). Figure 5 plots the seasonal dynamics of PAHs levels in Lake IJssel. The monthly mean PAH concentration in the dry season was higher than that in the wet season. The monthly averaged level of Σ_{15} PAHs in the dry season in Lake IJssel was 6.00 mg/kg, 1.88 mg/kg, 1.36 mg/kg, 1.06 mg/kg, 6.34 mg/kg, 5.45 mg/kg, 1.40 mg/kg, and 1.28 mg/kg at sampling sites, respectively, while 5.47 mg/kg, 1.36 mg/kg, 1.22 mg/kg, 6.36 mg/kg, 5.72 mg/kg, 5.08 mg/kg, 1.03 mg/kg, and 1.04 mg/kg in the wet season.

The particulate Σ_{15} PAHs levels in our study were moderately contaminated for a global comparison, as presented in Table 2, ranged from 0.76 to 9.66 mg/kg, with a mean value of 3.584 mg/kg. The concentration was higher than that in Pearl River estuary (mean value of 0.022 mg/kg, Niu et al., 2018), Yellow River Delta (mean value of 0.209 mg/kg, Wang, Yang, Niu, & Wang, 2009), Samo River estuary (mean value of

0.255 mg/kg, Montuori & Triassi, 2012), and lower than that in Tianjin River (mean value of 8.9 mg/kg, Shi et al., 2005), Weihe River (mean value of 20.78 mg/kg, Chen, Jia, & Yang, 2015), and Daliao River estuary (mean value of 6.852 mg/kg, Men, He, Tan, Lin, & Quan, 2009). Thus, the contamination of particulate PAHs in this case was at a moderate level on a large scale.

Spatial and temporal evaluation in PAH composition

Compared with the particulate PAHs, the dissolved PAHs levels were much lower in Lake IJssel. Thus, this following discussion would concentrate on the dynamics of PAHs in SPM. Figure 6 shows the spatiotemporal evaluation of particulate PAH composition. The levels of HMW-PAHs were greatly higher than the LMW-PAHs in this study. As for the composition of particulate PAHs at Amsterdam IJtunnel, Eemmeerdiijk, Genemuiden, Kampen, and Ketelmeer, the Σ 4-ring PAHs (e.g., Fluo, Pyr, Ba, and Chr) contributed the most to the total PAHs and accounted for 45%, 45%, 45%, 39%, and 43%, ranging from 2.12 to 3.14 mg/kg, 0.62 to 1.03 mg/kg, 2.09 to 4.97 mg/kg, 1.75

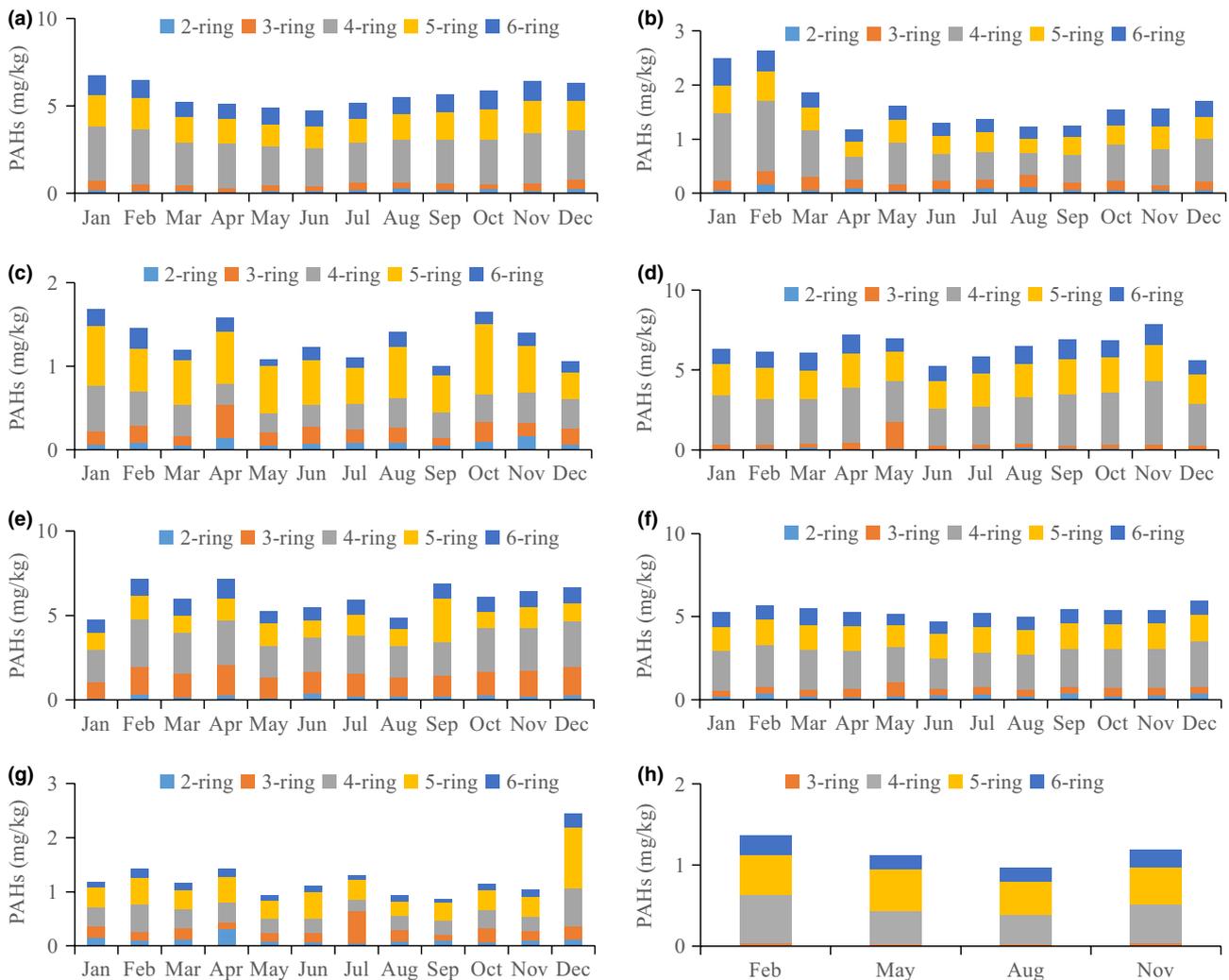


Figure 5. Seasonal dynamics of particulate PAH concentration in Lake IJssel from 2000 to 2010 (a, N1; b, N2; c, N3; d, N4; e, N5; f, N6; g, N7; h, N8).

Table 2. A global comparison of particulate PAHs (expressed in mg/kg) discussed in this study and other zones (*N* indicates the number of PAH compound)

LOCATION	<i>N</i>	MEAN	RANGE	SAMPLE YEAR	STUDY
Daliao River estuary	16	6.852	1.542–20.094	2007	Men et al. (2009)
Daliao River watershed	18	21.724	0.317–238.518	2005	Guo et al. (2007)
Seine River and estuary	11	5	1.0–14.0	1993	Fernandes, Sicre, Boireau, and Tronszynski (1997)
York River estuary	20	0.596	0.199–1.153	1998–1999	Countway, Dickhut, and Canuel (2003)
Tianjin River	16	8.9	0.938–64.2	–	Shi et al. (2005)
Yellow River Delta	16	0.209	0.065–0.675	2007	Wang et al. (2009)
Samo River estuary	16	0.255	0.006–0.779	2008	Montuori and Triassi (2012)
Weihe River	16	20.78	3.557–147.91	2014	Chen et al. (2015)
Pearl River estuary	16	0.022	0.003–0.112	2011	Niu et al. (2018)
Lake IJssel	15	3.584	0.76–9.66	2000–2010	This study

to 2.96 mg/kg, and 1.94 to 2.86 mg/kg, respectively. While for the PAH composition detected at Wolderwijk, Markermeer, and Doove Balg, the Σ 5-ring PAHs (e.g., Bb, Bk, Bap, and Dib) were the dominant and accounted for 44%, 36%, and 41% of the total PAHs, ranging from 0.41 to 0.80 mg/kg, 0.21 to 0.78 mg/kg, and 0.25 to 0.72 mg/kg, respectively.

Of all the samples, the Σ 4-ring and Σ 5-ring PAHs made up a big proportion, excluding the site of Kampen, Σ 4-ring and Σ 3-ring PAHs (e.g., Ace, Acy, Flu, and Ant) were the main contributors. The Σ 2-ring PAHs (e.g., Nap) accounted for a small proportion in Lake IJssel. The role of Σ 6-ring PAHs (e.g., Bg and Ind) followed that of Σ 4-ring and Σ 5-ring PAHs, accounting for 17% of the total (ranging from 0.74 to 1.14 mg/kg), 17% (0.22 to 0.35 mg/kg), 11% (0.07 to 0.29 mg/kg), 16% (0.74 to 1.55 mg/kg), 15% (0.66 to 1.18 mg/kg), 15% (0.67 to 0.89 mg/kg), 11% (0.06 to 0.20 mg/kg), and 18% (0.15 to 0.25 mg/kg) at eight sampling sites, respectively. Additionally, the mean concentrations of Σ 4-ring and Σ 5-ring PAHs in the dry season were higher than that in the wet season during the study period.

For the mean concentration of individual PAHs in SPM, the proposition of 15 individual PAHs is shown in Figure 6i. The 4-ring PAHs accounted for the most of the total, almost the half (41%), followed by the composition of 5-ring and 6-ring PAHs, 29% and 15%. Naphthalene accounted the least, 4%, only one-tenth of the 4-ring PAHs.

DISCUSSION

This section stated different contributions of environmental factors (e.g., SPM, water temperature, and salinity) to particulate PAHs due to their internal properties. And the potential risk sources were apportioned using a statistical-based method of principal component analysis.

Environmental controls of particulate PAHs

How the ecosystem responding to physical–chemical properties was always the researcher's concern (Jing, Chen, Zhang, Zheng, & Liu, 2014; Kannan et al., 2005), especially the contaminants. The PAH patterns could be explained by the internal properties

of sediment, salinity, water temperature, precipitation, biological cycles, and water currents (Laane et al., 2013; Liu et al., 2017; Moeckel et al., 2014). The SPM contributed to a large proportion of PAHs in water column, especially for the coarse particle samples and played an important role in transporting the PAHs (Sun, Soltwedel, Bauerfeind, Adelman, & Lohmann, 2016; Wang et al., 2016). The grain size of the suspended sediment corresponded to different adsorption levels of PAHs. The salinity gradients may affect the mixing process, which could influence the vertical distribution of PAHs (Niu et al., 2018). In the shallower water zones where phytoplankton were relatively abundant, the concentration of PAHs was reduced due to the uptake by phytoplankton (Wan, Jin, Hu, & Jin, 2007). PAH input in the top layers was linked to air–water exchange, deposition, and runoff, while in the bottom layers, it closely correlated with water masses. Hereby, the roles of SPM, water temperature, and salinity were examined, and the contributions from other environmental factors (e.g., discharge, precipitation, waves, wind, and biological cycles) are left to future investigations.

The spatiotemporal dynamics of individual/total PAHs were linked to the variations of environmental factors. The trends of SPM, salinity, and temperature in Lake IJssel are provided in Figure 2. Using linear and nonlinear statistical models, the levels of total PAHs (e.g., Σ 2-ring, Σ 3-ring, Σ 4-ring, Σ 5-ring, Σ 6-ring, and Σ_{15} PAHs) were found to be significantly or moderately correlated with SPM and water temperature (Table 3). Σ 2-ring PAHs were negatively with temperature and SPM in Lake IJssel.

As for the site of Amsterdam IJtunnel, PAH compounds (Σ 3-ring, Σ 4-ring, Σ 5-ring, Σ 6-ring, and Σ_{15} PAHs) were positively and strongly correlated with SPM and temperature; the coefficient *r* values with SPM were 0.58, 0.76, 0.83, 0.77, and 0.99, respectively; the coefficient *r* values with temperature were 0.68, 0.68, 0.78, 0.72, and 0.99, respectively. The significant correlation between PAHs and SPM could be explained from their binding to the particles and low solubility. Water temperature had a greater effect than the environmental factors of salinity, precipitation and water discharge (Niu et al., 2018). Temperature influenced water solubility (Schwarzenbach et al.,

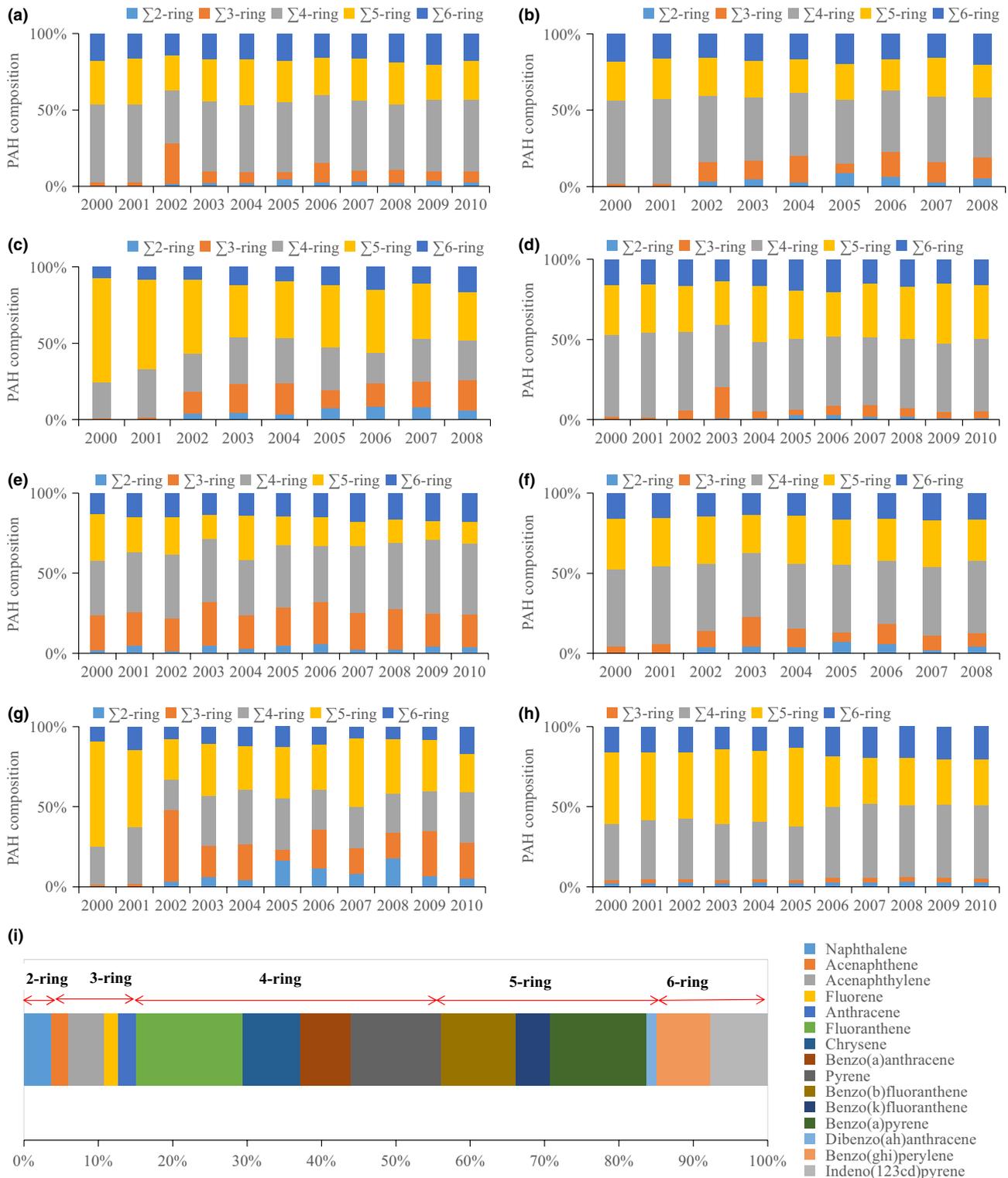


Figure 6. Spatiotemporal distribution of particulate PAH composition in Lake IJssel from 2000 to 2010 (a, N1; b, N2; c, N3; d, N4; e, N5; f, N6; g, N7; h, N8); and mean concentrations of individual PAHs in SPM (i).

2005); thus, the concentration of PAHs varied as temperature changed.

At the sites of Markermeer and Doove Balg coast, a big difference was found compared with that at Amsterdam IJtunnel.

PAHs were negatively correlated with the environmental factors (e.g., SPM and temperature). Of which, water temperature influenced the Σ 4-ring PAHs, Σ 6-ring PAHs, and Σ_{15} PAHs, with a negative sign at Markermeer ($r = -0.60, -0.66,$ and $-0.64,$

Table 3. Pearson correlations (r) between the particulate PAHs and hydrological factors in Lake IJssel (p , significance level; T , water temperature; SPM, suspended particulate matter)

PAHS	N1				N7				N8					
	T		SPM		T		SPM		SALINITY		SPM		T	
	R	P	R	P	R	P	R	P	R	P	R	P	R	P
Σ 2-ring	-.25	.51	-.18	.64	-.27	.43	-.48	.13	-	-	-	-	-	-
Σ 3-ring	.68	.02	.58	.06	-.18	.59	-.09	.78	.01	.10	-.49	.12	-.93	.06
Σ 4-ring	.68	.02	.76	.01	-.60	.05	-.03	.92	-.04	.90	-.42	.20	-.98	.01
Σ 5-ring	.78	.01	.83	.01	-.25	.47	.87	.00	.16	.63	-.56	.05	-.42	.58
Σ 6-ring	.72	.01	.77	.01	-.66	.03	-.04	.91	-.12	.72	-.36	.27	-.96	.04
Σ_{15} PAHs	.99	.00	.99	.00	-.64	.04	.28	.41	.09	.79	-.55	.04	-.99	.01

^aBold values: Correlation is significant at the 0.05 level (2-tailed).

respectively); while SPM was closely correlated with Σ 5-ring PAHs, with a positive sign ($r = 0.87$). At Doove Balg coast, SPM was negatively influenced the PAHs, correlation coefficient defining as -0.49 , -0.416 , -0.562 , -0.363 , and -0.548 for Σ 3-ring, Σ 4-ring, Σ 5-ring, Σ 6-ring, and Σ_{15} PAHs, respectively. Several researchers reported a close correlation between salinity and PAHs (Jing et al., 2014), but others suggested little correlation (Ou et al., 2009).

Figure 7 plots the environmental correlations between PAHs levels and environmental factors (e.g., water temperature, salinity, and SPM) in Lake IJssel (N1, N4, N7, and N8), based on monthly/yearly data during 2000–2010. Positive correlations between PAHs and temperature were detected at Amsterdam IJtunnel and Genemuiden, while a negative correlation was detected at Markermeer. Changes in temperature can affect the amount of total PAHs. Temperature can also improve the adsorption of PAHs onto particles. The HMW-PAHs were greatly influenced by temperature. In this case, no significant correlation between salinity and sum of PAH compound was found ($r = 0.01$ – 0.16).

It can be concluded that SPM and temperature played different roles in PAH composition and concentration. SPM was an important carrier, and PAHs accumulated in the sediments via sinking/binding. In this study, SPM and water temperature were considered to be the determining factors (Pearson's correlation, linear regression analysis) controlling the distribution and fate of PAHs in the water column in Lake IJssel. PAHs levels varied as temperature changed because temperature influenced water solubility. Salinity, representing the tidal currents, had less effect in the particulate PAHs than the dissolved PAHs due to water solubility. SPM was mainly originated from river discharge. Therefore, the influence of riverine input was responsible for transport of particulate PAHs.

Source apportionment of particulate PAHs

The PAH sources originate mainly from incomplete combustion and petroleum leakage (e.g., wood burning, coke combustion, forest burning, petroleum pollution, and oil spills) (Lima, Farrington, & Reddy, 2005; Mai et al., 2003; Tobiszewski & Namiesnik, 2012). The statistical methods of PCA and diagnostic ratios have widely been studied to identify the PAH sources in water column (Lima et al., 2005; Liu et al., 2017;

Yunker et al., 2002). In this study, PCA using varimax rotation with Kaiser Normalization was performed to explore the differences and similarities of 15 priority individual PAHs in SPM. Based on the monthly variation of the individual PAHs, principal components (PCs) were identified according to the criteria of eigenvalue > 1 , as shown in Table 4, accounting for 73%, 71%, 67%, 77%, 70%, 71%, 74%, and 92% of the total variances at eight sampling sites, respectively. Figure 8a1–h1 depicts the target diagram of the first two PCs using the component scores of individual PAHs each month. Components between each other were independent. PC1 correlated more with other factors than PC2, and so on.

As for the individual PAHs at Amsterdam IJtunnel, the first three components were extracted to represent the total variances. PC1, with an eigenvalue of 8.117, accounting for 54% of the total variance, was heavily contaminated by HMW-PAHs, including Pyr, Bk, Chr, and Ba. Researchers have identified Pyr, Chr, and Ba as indicators of coal combustion sources (Duval & Friedlander, 1981; Larsen & Baker, 2003; Simcik, Eisenreich, & Lioy, 1999). Thereby, PC1 was due to a coal combustion source. PC2, with an eigenvalue of 1.77, highly weighted by 3-ring PAHs, including Ace and Flu, was responsible for 12% of the total variance. Flu was used as a tracer of coke oven emissions (Duval & Friedlander, 1981; Khalili, Scheff, & Holsen, 1995). Therefore, PC2 represented a coke oven source. PC3, with an eigenvalue of 1.07, highly weighted by Acy, was responsible for 7.13% of the total variance, which was identified as having a coke oven source (Khalili et al., 1995).

As for the individual PAHs at Eemmeerdijk, the first three components were extracted, with eigenvalues of 6.90, 2.73, and 1.02, and accounting for 46.01%, 18.20%, and 6.78% of the total variance, respectively. PC1 was heavily contaminated by HMW-PAHs, including Fluo, Chr, Ba, Pyr, Bb, and Bk, which was as an indicator of a coal combustion. PC2 was mainly contributed by LMW-PAHs, including Nap, Ace, and Flu. According to Tolosa, Bayona, and Albaigés (1996), petroleum-derived residues contained a relatively greater amount of LMW PAHs such as 2-ring and 3-ring PAHs. Therefore, PC2 could be considered as a petroleum source. PC3 was dominated by Dib. Dib used as a marker of vehicle emission (Harrison, Smith, & Luhana, 1996; Larsen & Baker, 2003). Thus, PC3 was identified as a vehicular emission source.

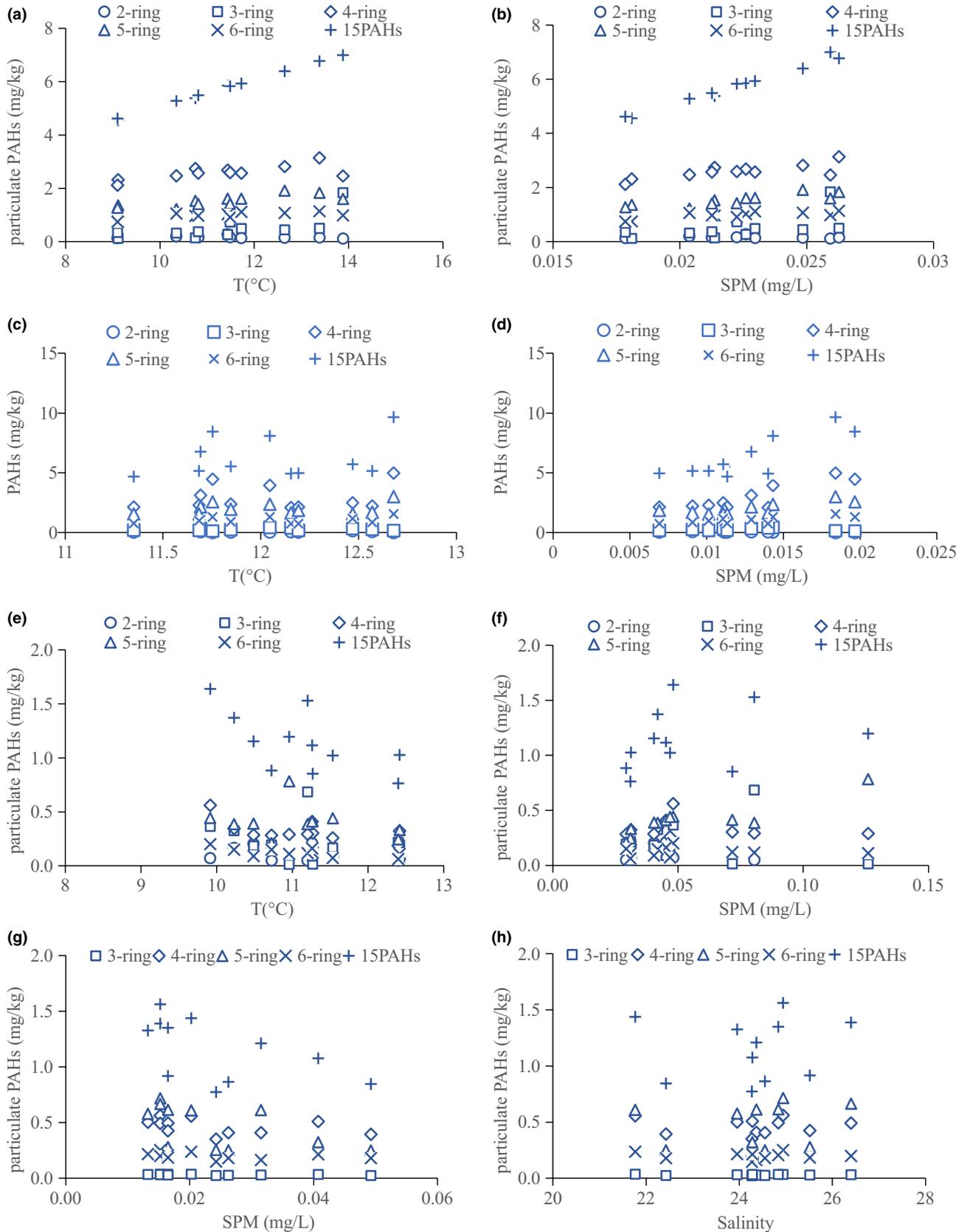


Figure 7. Environmental controls of annual-averaged particulate PAHs in Lake IJssel at Amsterdam IJtunnel (a,b), Genemuiden (c,d), Markermeer (e,f), and Doove Balg coast (g,h).

Table 4. Eigenvalue analysis and variances of individual PAHs explained from principal component analysis (PCA)

SITE	PCS	EIGENVALUE	VARIANCE (%)	SITE	PCS	EIGENVALUE	VARIANCE (%)
N1	PC1	8.117	54.115	N5	PC1	9.045	82.224
	PC2	1.766	11.776		PC2	1.076	9.783
	PC3	1.070	7.132	N6	PC1	9.043	60.284
N2	PC1	6.902	46.014		PC2	1.537	10.244
	PC2	2.730	18.201	N7	PC1	6.496	43.304
	PC3	1.018	6.785		PC2	1.875	12.499
N3	PC1	6.852	45.682	N8	PC3	1.192	7.946
	PC2	2.208	14.721		PC4	1.036	6.905
	PC3	1.030	6.869		PC1	8.595	57.299
	PC4	1.022	6.815	PC2	1.899	12.659	
N4	PC1	4.950	32.998	PC3	1.023	6.817	
	PC2	2.820	18.803				
	PC3	1.238	8.251				
	PC4	1.112	7.412				

As for the individual PAHs at Wolderwijk, the first four components were extracted to represent the most variance. PC1, with an eigenvalue of 4.95, was heavily weighted by Ace and Ant, which was considered as a petroleum source. PC2, with an eigenvalue of 2.82, was heavily contaminated by Pyr, which was used as a coal combustion. PC3, with an eigenvalue of 1.24, was heavily weighted by Bb, which was considered as a coal combustion. PC4, with an eigenvalue of 1.11, was heavily weighted by Acy, which was considered as a petroleum source.

As for the individual PAHs at Genemuiden, the first three components were extracted, with eigenvalues of 8.59, 1.90, and 1.02, and accounting for 57.30%, 12.66%, and 6.82% of the total variance, respectively. PC1 was heavily weighted by HMW-PAHs, including Chr, Ba, Bb, and Pyr, which was considered as a coal combustion source. PC2 was heavily contaminated by Ace, which was used as a petroleum source. PC3 was heavily weighted by Acy, which was considered as a petroleum source.

As for the individual PAHs at Kampen, two components were extracted. PC1, with an eigenvalue of 9.04, accounting for 60.28% of the total variance, was heavily contaminated by HMW-PAHs, including Fluo, Chr, Ba, Bb, and Bk, which was taken as a coal combustion source. PC2, with an eigenvalue of 1.54, accounting for 10.24% of the total variance, was heavily contaminated by Ace, which was considered as a petroleum source.

As for the individual PAHs at Ketelmeer west, the first four components were extracted to represent the most variance (71%). PC1, with an eigenvalue of 6.50, was heavily weighted by HMW-PAHs, including Chr, Ba, and Bk. Thus, PC1 was considered as a coal combustion source. PC2, with an eigenvalue of 1.87, was heavily contaminated by LMW-PAHs, including Ace and Flu, which was used as a petroleum source. PC3, with an eigenvalue of 1.19, was heavily weighted by Bap. Bap has been considered as a coal combustion source (Duval & Friedlander, 1981). PC4, with an eigenvalue of 1.04, was heavily weighted by Dib and Ind. These compounds were correlated with vehicle emission sources (Larsen & Baker, 2003).

As for the individual PAHs at Markermeer, the first four components were extracted to represent the most variance. PC1, with an eigenvalue of 6.85, accounting for 45.68% of the total variance, was heavily weighted by Chr and Ba. Thus, PC1 was considered as a coal combustion source. PC2, with an eigenvalue of 2.21, accounting for 14.72%, was heavily contaminated by Ace, which was used as a petroleum source. PC3, with an eigenvalue of 1.03, accounting for 6.87%, was heavily weighted by Acy. Thus, PC3 was considered as a petroleum source. PC4, with an eigenvalue of 1.02, accounting for 6.81%, was heavily weighted by Bap, which was considered as a coal combustion source.

As for the individual PAHs at Doove Balg coast, the first two components were extracted, accounting for 92% of the total variance. PC1, with an eigenvalue of 9.04, accounting for 82.22%, was heavily contaminated by HMW-PAHs, including Fluo, Chr, Ba, Bb, Ind, and Bk, which was taken as a coal combustion source. PC2, with an eigenvalue of 1.08, accounting for 9.78% of the total variance, was heavily contaminated by Dib, which was considered as a vehicle emission source.

Additionally, source diagnostic ratios were also provided to apportion the potential sources of PAHs, as displayed in Figure 8a2–h2, including $Ba/(Ba + Chr)$ versus $Ind/(Ind + Bg)$ (Yunker et al., 2002) and a plot of $Fluo/(Fluo + Pyr)$ could help provide more accuracy (Lima et al., 2005). A value of $Fluo/(Fluo + Pyr) < 0.4$ indicated the source was from petroleum emissions and a value >0.5 implied a combustion source, while a value between 0.4 and 0.5 indicated petroleum combustion. A value of $Ind/(Ind + Bg) < 0.2$ indicated the PAH source was from petroleum emissions, and a value >0.5 implied the main source was combustion, while a value between 0.2 and 0.5 implied petroleum combustion. A value of $Ba/(Ba + Chr) < 0.2$ indicated the main source was from petroleum emissions, while a value >0.35 implied a combustion source (Yunker et al., 2002). In this study, $Fluo/(Fluo + Pyr)$ at a range [0.4, 0.6] and $Ind/(Ind + Bg) > 0.2$ suggested a mixture of combustion source and petroleum emission; values of $Ba/(Ba + Chr) > 0.35$ implied a combustion source.

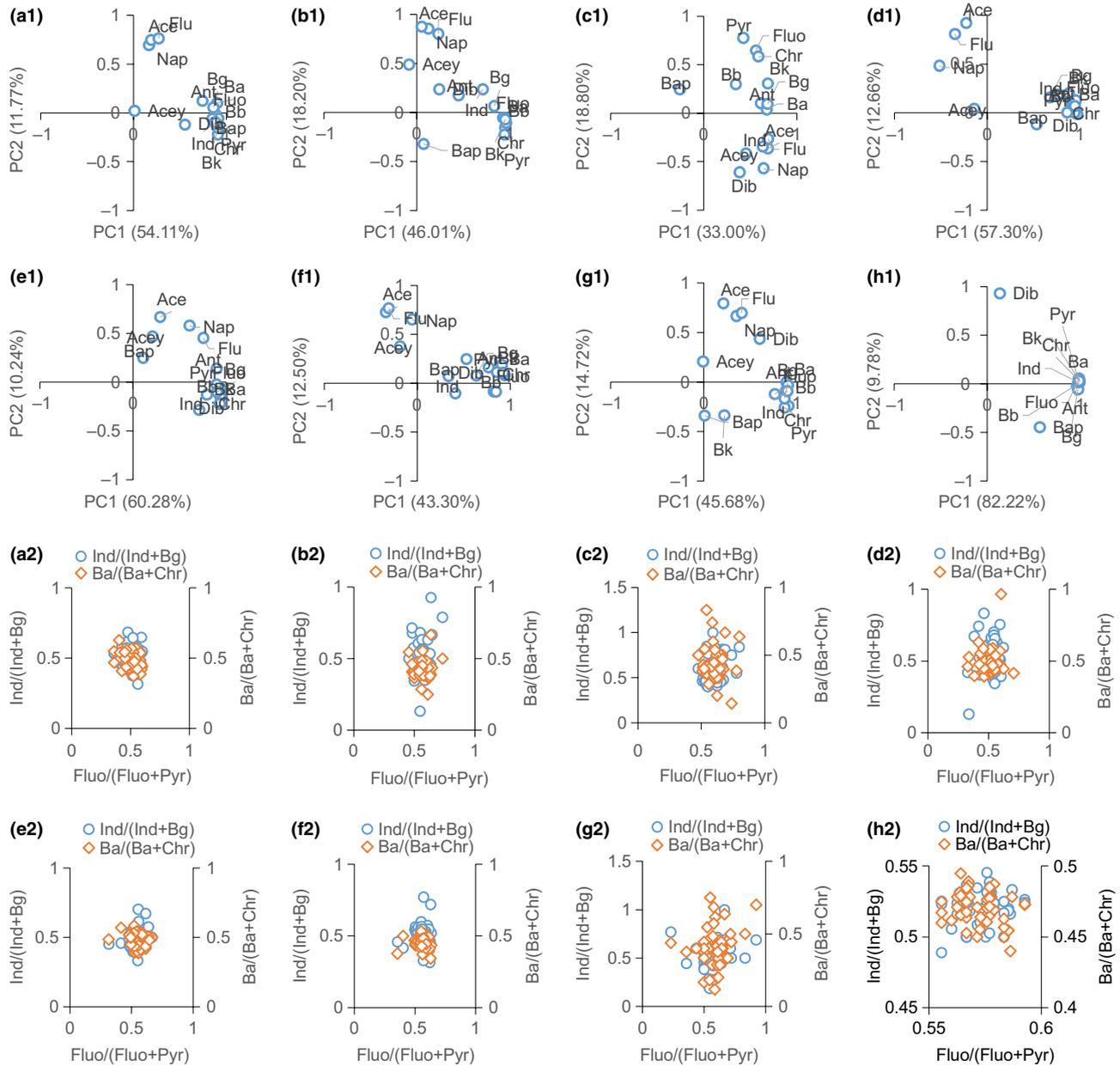


Figure 8. Statistical methods of PCA (a1–h1) and diagnostic ratios (a2–h2) to identify the PAH sources in Lake IJssel from 2000 to 2010 (a, N1; b, N2; c, N3; d, N4; e, N5; f, N6; g, N7; h, N8).

It was summarized that the PAH sources in Lake IJssel were mainly originated from coal combustion source and petroleum source. The coal combustion source made up the largest contribution, accounting for 54.11%, 46.01%, 27.05%, 57.30%, 60.28%, 51.25%, 52.50%, and 82.22% at eight sampling sites, respectively, followed by the contribution of a petroleum source and vehicle emission source. The role of coke oven source was only appeared at Amsterdam IJssel, originated from the city of Amsterdam.

CONCLUSIONS

This study set out to examine the abundance of 15 priority PAHs from 2000 to 2010 in Lake IJssel. Significant variations

in PAH concentration and composition reflected the differences in sources and environmental controls. HMW-PAHs were the predominant instead of LMW-PAHs in the water column because of their high hydrophobicity and absorption onto the SPM. Heavy contamination was found at the river mouth (e.g., Genemuiden), originated from terrestrial emissions along the IJssel River and decreased with the distance. The sinking or binding effect of SPM was strong for the particulate PAHs, revealing the influence of riverine input. However, the dilution of marine waters has a less effect on PAHs. Human contamination sources of coal combustion, petroleum emissions, vehicular emissions, and coke ovens were considered to be the potential risk sources of PAHs in Lake IJssel. Additionally, the

effects of water masses or biogeochemical cycles on PAHs will warrant further investigation.

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