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Nitrated and parent PAHs in the surface water of Lake Taihu, China: Occurrence, distribution, source, and human health risk assessment

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ABSTRACT

Nitrated polycyclic aromatic hydrocarbons (NPAHs) have toxic potentials that are higher than those of their corresponding parent polycyclic aromatic hydrocarbons (PAHs) and thus have received increasing attention in recent years. In this study, the occurrence, distribution, source, and human health risk assessment of 15 NPAHs and 16 PAHs were investigated in the surface water from 20 sampling sites of Lake Taihu during the dry, normal, and flood seasons of 2018. The Σ PAH concentrations ranged from 255 to 7298 ng/L and the Σ NPAH concentrations ranged from not-detected (ND) to 212 ng/L. Among the target analytes, 2-nitrofluorene (2-nFlu) was the predominant NPAH, with a detection frequency ranging from 85% to 90% and a maximum concentration of 56.2 ng/L. The three-ringed and four-ringed NPAHs and PAHs comprised the majority of the detected compounds. In terms of seasonal variation, the highest levels of the Σ NPAHs and Σ PAHs were in the dry season and flood season, respectively. Diagnostic ratio analysis indicated that the prime source of NPAHs was direct combustion, whereas in the case of PAHs the contribution was predominantly from a mixed pattern including pollution from unburned petroleum and petroleum combustion. The human health risk of NPAHs and PAHs was evaluated using a lifetime carcinogenic risk assessment model. The carcinogenic risk level of the targets ranged from 2.09×10^{-7} to 5.75×10^{-5} and some surface water samples posed a potential health risk.

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Introduction

Polycyclic aromatic hydrocarbons (PAHs) comprise various types of ubiquitous global pollutants (Lee et al., 2005; Shi et al., 2005) and are primarily derived from the incom-

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plete combustion of carbon materials at high temperatures (Tobiszewski and Namieśnik, 2012). In the early 1980s, the United States Environmental Protection Agency (US EPA) designated 16 PAHs as priority pollutants in order to control their risk. Subsequently, these pollutants were also classified as possible human carcinogens by the International Agency for Research on Cancer (IARC). In order to better protect human health and the environment, the extensive examination and assessment of both the parent PAHs as well as their derivatives are required. In recent years, nitrated polycyclic aromatic hydrocarbons (NPAHs), which are one type of PAH derivative, have attracted increasing attention. On the one hand, NPAHs are formed by homogeneous or heterogeneous reactions of PAHs with atmospheric oxidants (such as OH, NO₃⁻, and HNO₃) (Keyte et al., 2013; Cochran et al., 2016). On the other hand, NPAHs are emitted by the incomplete combustion of fuel (Bandowe and Meusel, 2017). The water solubility of NPAHs is generally higher than that of their corresponding parent PAHs (Patrolecco et al., 2010). Many kinds of NPAHs have been demonstrated to have mutagenic/carcinogenic effects either directly or via biotransformation. For example, although a 1-nitropyrene (1-nPyr) concentration of only 1 ng/L was found in drinking water, it accounted for 1% of the total genotoxicity (Ohe and Nukaya, 1996). The toxic equivalency factor (TEF) values of NPAHs are much higher than those of PAHs (Wei et al., 2015a). Therefore, NPAHs are considered to be more carcinogenic and mutagenic than their parent PAHs. Due to their carcinogenicity and mutagenicity, NPAHs exert a greater effect on human health than some PAHs (Taga et al., 2005; IARC, 2013). There have been numerous studies across the globe that have monitored PAHs and investigated their toxicity, but there have been few reports concerning NPAHs (Ringuet et al., 2012). Andersson and Achten (2015) pointed out that overdependence on the toxicity evaluation of the 16 PAHs listed by the US EPA often leads to underestimations of the potential toxicity in different environmental matrices. Therefore, the risks of derivatives should also be considered.

Most of the previous studies have focused on NPAH occurrence in the soil and atmosphere (Tsakas et al., 2010; Guidi et al., 2012; Alam et al., 2015; Wei et al., 2015; Zhe et al., 2017; Yadav et al., 2018). The NPAHs in the soil and atmosphere might be transported into the aquatic environment via deposition, erosion, and surface runoff (Qiao et al., 2014). Other potential sources include discharges from industrial plants and wastewater treatment plants and/or in situ formation (Sato et al., 1985; Ozaki et al., 2010; Lübecke-Von et al., 2011; Huang et al., 2014a, b). NPAHs have been widely detected in the environment and are now part of the global pollution problem. Nevertheless, only a few studies have focused on NPAHs in the aquatic environment. Moderate levels of NPAHs in sediments have been reported from Hiroshima Bay, Japan (Ozaki et al., 2010), the Suimon River, Japan (Sato et al., 1985) and the Elbe River Basin, Germany (Lübecke-von Varel et al., 2011). Uno et al. (2017) reported that the highest concentration of 15 NPAHs was 1949 ng/kg near the city of Amagasaki, Japan, and those NPAHs were primarily derived from the exhaust gases of industrial facilities and automobiles. Nassar et al. (2015) found that the total average concentrations of eight NPAHs ranged from 5.2 to 11.2 ng/L and 7.6 to 20.0 ng/L in the Nile River and Ismailia Canal (Egypt), respectively, with

the major sources of PAHs and NPAHs being mixed contamination sources exhibiting a predominance of petroleum at the Nile River sites and pyrogenic sources at the Ismailia Canal in both summer and winter. Yvonne et al. (2013) reported that the total concentration of five NPAHs in the Asano River of Japan was 604 ng/L. In the water samples collected from rivers in Japan, 1-nitronaphthalene (1-nNap), 2-nNap, 1,3-dinitronaphthalene (1,3-dnNap), and 1,5-dnNap have been detected, with concentrations ranging from 1.3 to 11.7 ng/L (IPCS, 2003). It has been observed the NPAH concentrations in the surface water are much lower than those in other environmental matrices. Overall, since little attention has been paid to the source and risk of NPAHs in surface water, we found it necessary to perform the related research.

Lake Taihu, the third-largest freshwater lake in China, is located in the economically developed region of the Yangtze River Delta. Lake Taihu is a large and shallow eutrophic lake, with a volume of 4.4 billion m³, an area of 2338 km² and an average depth of 1.9 m (Qin et al., 2007). Lake Taihu is located in the subtropical climate zone, experiencing generally mild and humid weather conditions. Affected by the tropical marine air mass in summer, southeast winds prevail, bringing mild and rainy weather; in winter, the conditions are controlled by the predominant high-pressure air mass to the north, with prevailing northerly winds bringing cold and dry weather. The annual average temperature is 16.0–18.0 °C, and the annual precipitation ranges from 1100 to 1150 mm. There are approximately 40 million urban residents living in the Taihu area (Qin et al., 2010). With the rapid development of the national economy, Lake Taihu has become an important drinking water supply source in the basin and plays an important role in supplying water to the surrounding waterworks. The Lake Taihu Basin, one of the most developed areas in terms of industrial and agricultural production, is facing more complex environmental problems than other regions. Due to the deterioration of water bodies in general, it is extremely important to study persistent organic pollutants in Lake Taihu. The occurrence, distribution, and source of organic pollutants in Lake Taihu have gradually aroused public concern. Organic pollutants such as PAHs, organochlorine pesticides (OCPs), polychlorinated biphenyls (PCBs), and polybrominated diphenyl ethers (PBDEs) have been detected in Lake Taihu (Liping et al., 2011; Zhang et al., 2012; Jian et al., 2013; Yu et al., 2013; Wu et al., 2014). Since PAHs have been recorded in the waters of Lake Taihu (Guo and Jia, 2012; Lei et al., 2016), it has become imperative to understand the levels, sources, and potential risks of their derivatives, that is, NPAHs. This study fills the knowledge gap concerning NPAH profiles in Lake Taihu and could thus become the key to the risk assessment and health monitoring of the lake. The definition of each sampling season was based on the seasonal lake level. The flood season is generally defined as the period with a large amount of precipitation during the hot summer that usually manifests as an upward trend of the water level. The dry season refers to the fact that the precipitation during the cold winter is extremely low, which causes a decrease in the water level. The remainder of the year is the normal season, when the lake is at its normal and stable water level. In this study, surface water samples were collected during the dry season in January, the normal season in May, and the flood season in August of 2018 across all of Lake Taihu. The

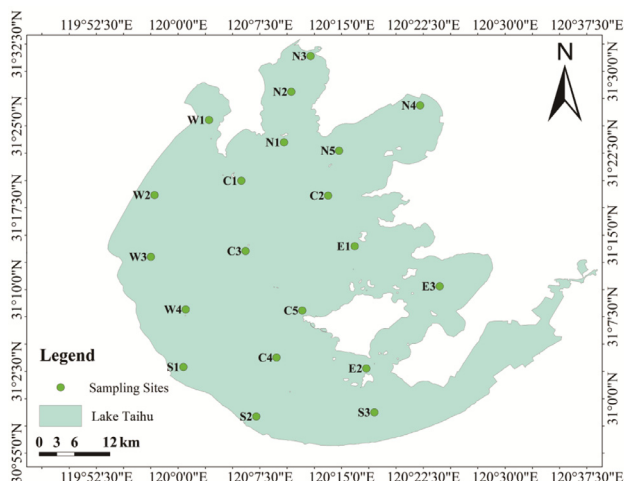


Fig. 1 – Location of sampling sites in Lake Taihu.

objectives of this study were to (1) investigate the occurrence, spatial distribution, and seasonal variation of 31 compounds (15 NPAHs and 16 PAHs) in the surface water of Lake Taihu; (2) identify the possible contamination sources; and (3) assess the human health risks associated with the NPAHs and PAHs ingested by drinking Lake Taihu water.

1. Materials and methods

1.1. Study area and sampling

A total of 20 sampling sites were investigated in Lake Taihu, China, as shown in Fig. 1. For the purpose of sampling, the lake was divided into five different geographical sections, comprising the North waters (N1–N5) near Wuxi in Jiangsu Province; the South waters (S1–S3) near Huzhou in Zhejiang Province; the West waters (W1–W4) near Yixing in Jiangsu Province; the East waters (E1–E3) near Suzhou in Jiangsu Province; and the Central waters (C1–C5). From the 20 sampling sites, 1-liter water samples were collected during the dry season (January 2018), normal season (May 2018), and flood season (August 2018). Latitude, longitude, temperature, pH, dissolved oxygen (DO), and conductivity of all samples were immediately determined in situ. These data concerning the physicochemical properties of the surface water samples are listed in Appendix A Table S1. All the samples were collected from 0 to 50 cm below the water surface and stored in amber glass bottles. Thereafter, all the water samples were transported to a laboratory, filtered with a 0.45 μm cellulose acetate membrane, and stored in a refrigerator (4 °C) in the dark.

1.2. Reagents and chemicals

The standards of 15 NPAHs, comprising 2-nitronaphthalene (2-nNap), 2-nitrobiphenyl (2-nB), 5-nitroacenaphthene (5-nAce), 2-nitrofluorene (2-nFlu), 9-nitroanthracene (9-nAnt), 9-nitrophenanthrene (9-nPhe), 1-nitropyrene (1-nPyr), 2-nitrofluoranthene (2-nFla), 3-nitrofluoranthene (3-nFla), 2,7-dinitrofluorene (2,7-nFlu), 6-nitrochrysene

(6-nChr), 1,3-dinitropyrene (1,3-dnPyr), 1,6-dnPyr, and 1,8-dnPyr, 6-nitrobenzo[a]pyrene (6-nBaP), along with 16 PAHs, comprising including naphthalene (Nap), acenaphthene (Ace), acenaphthylene (Acy), fluorene (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene (Fla), pyrene (Pyr), benzo[a]anthracene (BaA), chrysene (Chr), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), dibenzo[a,h]anthracene (DahA), benzo[g,h,i]perylene (Bghip), and indeno[1,2,3-c,d]pyrene (IcdP) were purchased from AccuStandard (New Haven, CT, USA). Four types of surrogates (9-Nitroanthracene-d9, 1-Nitropyrene-d9, Phenanthrene-d10, and Pyrene-d10) were purchased from Cambridge Isotope Laboratories (Andover, MA, USA). The concentrations of the stock standard solutions were 1000 $\mu\text{g/mL}$ for the 16 PAHs and 100 $\mu\text{g/mL}$ for the 15 NPAHs in methylbenzene. An intermediate working solution, that is, the master mix, was prepared in acetone containing each of the 15 NPAHs and 16 PAHs at a concentration of 10 $\mu\text{g/mL}$. The acetone was liquid chromatography grade (> 99.8%) and was obtained from Merck (Darmstadt, Germany). All of the intermediate working solutions were stored at 4 °C in the dark. Ultrapure water was generated by the Milli-Q water purification system (Milli-Q System, Millipore, Bedford, MA, USA) in our laboratory.

1.3. Sample pretreatment

The 15 NPAHs and 16 PAHs were pretreated using solid-phase microextraction (SPME). A 100 μm PDMS fiber was used to extract the 16 PAHs, and a 65 μm PDMS/DVB fiber was used to extract the 15 NPAHs (Supelco, Bellefonte, PA, USA). The SPME procedure utilized for the NPAHs and PAHs was detailed in our previous study (Kong et al., 2018). Briefly, 15 mL of the filtered sample was poured into an amber glass bottle. The fiber (with a length of 1 cm) was directly immersed into the sample for 35 min at 55 °C at a stirring speed of 1150 r/min. After extraction, the fiber was removed and thermally desorbed at 260 °C for 3 min. Four surrogates were added to the aqueous solutions to probe the matrix effect and extraction efficiency in order to reduce handling errors.

1.4. Instrumental analysis

All of the samples were separated and detected using the TSQ Quantum GC–MS/MS system (Thermo Fisher Scientific, Waltham, MA, USA) with a negative chemical impact (NCI) source for the NPAHs and an electron impact (EI) source for the PAHs under full scan mode and selective reaction monitoring (SRM) mode. The collision energy in the collision-induced dissociation (CID) chamber was 50 eV. A 30 m \times 0.25 mm \times 0.25 μm DB-5MS column was used to separate the targets. The carrier gas was high-purity helium (99.999%) at a column flow rate of 1.0 mL/min. The oven temperature for the NPAHs varied as follows: 50 °C (held for 1 min) initially, then increased to 280 °C at a rate of 10 °C/min, and held for 10 min. The oven temperature for the PAHs varied as follows: 50 °C (held for 1 min) initially, increased to 160 °C at a rate of 10 °C/min, and then finally increased to 290 °C at a rate of 4 °C/min and held for 5 min. The transfer line temperature was maintained at 280 °C and the injector temperature was

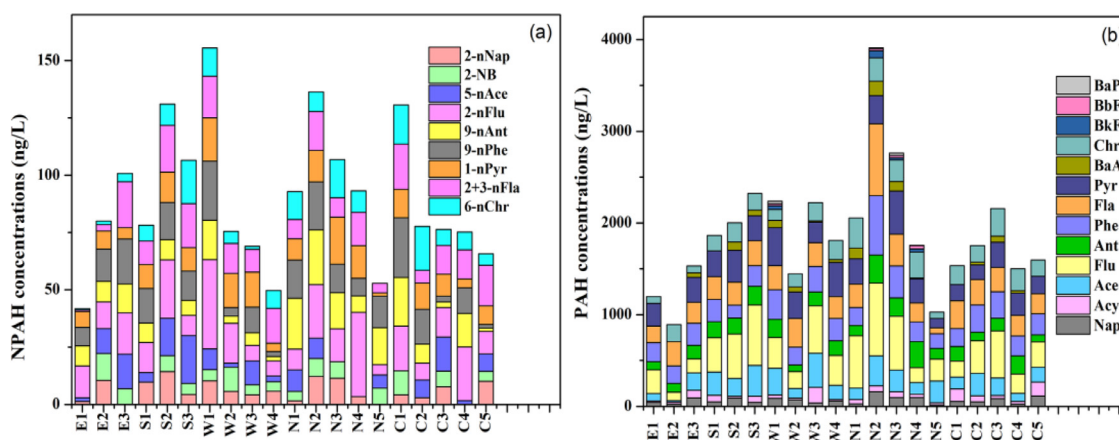
Table 1 – Ranges, means, median concentrations, and detection frequencies of NPAHs in surface water of Lake Taihu (ng/L) during three seasons.

Season		2-nNap	2-NB	5-nAce	2-nFlu	9-nAnt	9-nPhe	1-nPyr	2,3-nFla	6-nChr
Dry Season	Range	< LOD–31.4	< LOD–31.7	< LOD–44.7	< LOD–56.2	< LOD–42.4	< LOD–54.6	< LOD–57.7	< LOD–52.5	< LOD–42.1
	Mean	10.2	9.9	13.5	15.8	16.4	20.3	15.1	16.4	14.3
	Median	9.5	9.6	8.7	14.3	14.1	21.6	12.5	15.2	11.0
	DF	70	55	65	65	75	75	85	75	70
Normal Season	Range	< LOD–12.6	< LOD–8.5	< LOD–35.5	< LOD–23.7	< LOQ–31.2	< LOD–23.5	< LOD–16.5	< LOD–25.2	< LOD–11.4
	Mean	3.1	0.5	3.9	12.9	6.4	9.1	6.9	6.9	3.9
	Median	0.4	ND	ND	12.5	5.1	7.5	7.4	5.0	4.5
	DF	55	10	25	85	90	85	75	70	80
Flood Season	Range	< LOD–21.4	< LOD–21.4	< LOD–27.5	< LOD–41.3	< LOD–32.1	< LOD–37.7	< LOD–34.0	< LOD–45.6	< LOD–23.6
	Mean	4.6	4.8	5.0	17.3	9.5	9.2	11.2	14.2	7.3
	Median	2.3	ND	ND	13.0	7.9	7.6	7.4	12.0	3.4
	DF	55	40	45	90	70	60	85	80	65

LOD: Limit of detection.

ND: Not detection.

DF: Detection frequency (%).

**Fig. 2 – Average of (a) NPAH and (b) PAH concentrations of collected samples during the three different seasons.**

kept at 260 °C. The ion source temperature was maintained at 220 °C. The injection mode was splitless. The detailed analytical parameters of each compound (retention time, precursor ion, and product ion) are listed in Appendix A Tables S3 and S4.

1.5. QA/QC and data analysis

A solvent blank and a method blank were detected every 10 samples. The standard mixture solution (50 ng/L for the NPAHs and 200 ng/L for the PAHs) was checked every 10 injections to ensure analysis stability. Samples were analyzed in triplicate. The glass bottles were cleaned using ultrapure water and methanol and then baked in a muffle furnace at 500 °C for 6 hr prior to use. During the sampling process, the field blanks of pure water were transported together with the real samples. Milli-Q-purified water was used as the blank sample in which no target compounds were detected thus indicating there was no potential contamination. As detailed in Appendix A Table S5, the spike recoveries of the NPAHs and PAHs ranged from 72.5% to 108% and from 73.6% to 108%, respectively. The average recoveries of the surrogates ranged from

79.4% to 102%, and the precision levels of the four surrogates were < 8.2%. The limit of detection (LOD) was defined as the concentration that was three times the signal-to-noise ratio (S/N). The LODs were 0.17–7.8 ng/L for the NPAHs and 0.12–0.63 ng/L for the PAHs. Among the targets, since 2-nFla and 3-nFla cannot be separated using this analytical method, these targets were treated as a single variable (2 + 3-nFla).

1.6. Health risk assessment

People are exposed to NPAHs and PAHs in the water environment primarily through drinking water. Lake Taihu is an important drinking water source, which supplies water to the surrounding waterworks. Therefore, an incremental lifetime carcinogenic risk (ILCR) assessment model was used to quantify and evaluate the lifetime carcinogenic risk caused by the NPAHs and PAHs in Lake Taihu (EPA, 2001; Chen and Liao, 2006). Toxic equivalent (TEQ) values were first calculated and the ILCR was then assessed, based on Eqs. (1) and (2). The values of the toxic equivalency factors (TEFs) are presented in Appendix A Table S6. Eqs. (1) and (2) for calculating the ILCR model are as follows:

[illegible]

$$\text{ILCR} = \left(\frac{\text{TEQ (BaP)} * \text{DR} * \text{CSF} * \text{EF} * \text{ED}}{\text{BW} * \text{AT} * 10^6} \right). \quad (2)$$

In these equations, TEQ (BaP) is the sum of the benzo[a]pyrene equivalent concentration; C (ng/L), of the PAHs or NPAHs; TEF is the toxicity equivalency factor; DR (2 ng/L) is the daily water intake rate; CSF (ng/L) is the carcinogenic slope factor (7.3 mg/kg/day) (EPA, 2001); EF is the exposure frequency (365 days/year); ED is the exposure duration for adults (43 a) (Xia et al., 2010); BW is the body weight of an adult (70 kg); and AT is the average life span exposure (for carcinogens, $AT = 70 \times 365 = 25,550$ days) (EPA, 2001; Chen and Liao, 2006; Liao and Chiang, 2006). According to the recommendation of the US EPA, an ILCR value $< 10^{-6}$ indicates a negligible health risk, a value between 10^{-6} and 10^{-4} is considered to be a potential risk, and an ILCR value $> 10^{-4}$ indicates a high risk (Szu-Chich and Chung-Min, 2006). Moreover, the maximum acceptable risk level is $5.0 \times 10^{-5}/a$, according to the International Commission of Radiation Protection (ICRP).

2.1. Occurrence and concentrations of NPAHs and PAHs in Lake Taihu

Ten NPAHs (2-nNap, 2-NB, 5-nAce, 2-nFlu, 9-nAnt, 9-nPhe, 1-nPyr, 2-nFla, 3-nFla, and 6-nChr) and 13 PAHs (Nap, Acy, Ace, Flu, Ant, Phe, Fla, Pyr, BaA, Chr, BkF, BbF, and BaP) out of the 31 targeted compounds were detected in the surface water of Lake Taihu. Summaries of the concentration and frequency data for the compounds detected in the Lake Taihu surface water during the dry season, normal season, and flood season are presented in [Tables 1](#) and [2](#). The mean (range) of the Σ NPAHs in Lake Taihu was 132 ng/L (46.6–212 ng/L) in the dry season, 53.6 ng/L (ND–135 ng/L) in the normal season, and 79.6 ng/L (18.1–181 ng/L) in the flood season, whereas the mean (range) of the Σ PAHs was 1226 ng/L (255–2177 ng/L) in the dry season, 1762 ng/L (831–2425 ng/L) in the normal season, and 2613 ng/L (1352–7298 ng/L) in the flood season. [Fig. 2](#) shows the average NPAH and PAH concentrations in the three different seasons at each sampling site.

Among the 15 NPAHs, 2-nFlu had the highest detection levels in the normal and flood seasons, with means as high as 12.9 ng/L and 17.3 ng/L, respectively. Although 2-nFlu (18.0 ng/L) was not the compound with the highest concentration in the dry season, it exhibited the highest detection frequency (85%). The NPAH 9-nPhe had the highest detection level in the dry season, with its mean reaching as much as 20.3 ng/L, and a detection frequency of 75%. In addition, the detection frequencies of 9-nAnt and 2 + 3-nFla were also high ($\geq 70\%$), indicating the ubiquitous occurrence of these compounds in the surface water of Lake Taihu. The concentrations of 2-NB and 5-nAce were relatively low compared with those of the other NPAHs in all sampling seasons, although their detection frequencies were relatively high in the dry season, with values of 55% and 65%, respectively. Five NPAHs (2,7-

Table 3 – Comparison of NPAH concentrations in Lake Taihu with those in other countries.

	Location	Year	Compounds	Water samples	ΣNPAH concentrations (ng/L)	Reference
1	Nile River and Esmailia canal (Egypt)	September 2011 and February 2012	8 NPAHs	Surface water samples	5.2–20 ng/L	Nassar et al., 2015
2	Asano River in Kanazawa city (Japan)	/	5 NPAHs	River water samples	604.03 ng/L	Yvonne et al., 2013
3	Japan	/	4 NPAHs	River water samples	17.9 ng/L	IPCS, 2003
4	Meichuan River and Luchuan River (China)	/	7 NPAHs	River water samples	5.2–7.5 ng/L	Hung et al., 2012
5	Gasoline stations (Japan)	October, 1981–August, 1982	2 NPAHs	Gas station wastewater	nd–25,600 ng/mL (1-nPyr)	Manabe et al., 1984
6	Paraguaçu River in Cachoeira City (Brazil) and Salvador City (Brazil)	/	27 NPAHs	Surface water samples and groundwater samples	8.96 and 22.80 ng/mL	Santos et al., 2017
7	Taihu Lake (China), Changzhou Industrial plant (China) and Changzhou sewage treatment plant (China)	May 2017, July 2017, and, July 2017	10NPAHs	Lake water samples, wastewater samples, and domestic sewerage samples	0.008–0.243, 0.609–1.456, and 1.446–1.741 ng/mL	Kong et al., 2018
8	San Luis Province (Argentina)	/	4 NPAHs	Drinking water samples and lake water samples	1.07 and 15.95 ng/mL	Guíñez et al., 2018
9	Lake Taihu (China)	January 2018, May 2018, and August 2018	15 NPAHs	Surface water samples	nd–212 ng/L	This study

nFlu, 1,3-dnPyr, 1,6-dnPyr, 1,8-dnPyr, and 6-nBaP) were not detected in any sampling season. A comparison of our results with those of previous studies from other areas revealed that 1-nPyr had a relatively high detection frequency. The level of 1-nPyr in our study (6.9–11.4 ng/L) was lower than that in the Asano River of Japan (49.5 ng/L) (Yvonne et al., 2013) and slightly higher than that in the Meichuan River (5.4 ng/L) and Luchuan River (6.2 ng/L) of China (Hung et al., 2012). In addition to the surface water, NPAHs have also been detected in the neutral fraction of crankcase oil, which is used in diesel engines, with 1-nPyr and 1,6-dnPyr levels of 349 ng/mL and 31 ng/mL, respectively (Manabe et al., 1984). Two NPAHs, 1-nPyr and 9-nAnt, have also been detected in domestic sewerage at levels as high as 634 ng/L and 623 ng/L, respectively (Kong et al., 2018). The NPAH concentrations in Lake Taihu are compared with those in other countries in Table 3. Among the 16 PAHs, Flu exhibited the highest detection levels in the dry season (266 ng/L), normal season (430 ng/L), and flood season (395 ng/L) in Lake Taihu. Meanwhile, Bghip, DahA, and IcdP were not detected in any of the studied seasons. To better understand the PAH levels in Lake Taihu, the results were compared with those of other reports on the surface water from other countries and parts of China. The PAH concentrations in Lake Taihu (255–7298 ng/L) were approximately one order of magnitude less than those measured in the Daliao River of China (946–13,450 ng/L) (Guo et al., 2007). Our levels were higher, however, than those detected in the Luanhe River of China (9.80–310 ng/L) (Li et al., 2006). The PAH concentrations in the Sarno River of Italy (23.1–2670 ng/L) (Montuori and Triassi, 2012), the Songhua River of China (164–2746 ng/L) (Xuesong et al., 2014), and the northern bays of Taihu Lake (1582–3030 ng/L) (Lei et al., 2016) were not much different from

those in our study. In summary, the NPAHs and PAHs in the surface water of Lake Taihu are moderately high compared with other water bodies within China and abroad.

The proportions of NPAH and PAH concentrations were calculated for all three sampling seasons and are presented in Appendix A Fig. S1. Overall, the ΣPAHs and ΣNPAHs accounted for 95.4% and 4.6% of the sum of the targets detected, respectively. Among the 15 NPAHs, 2-nFlu was the most abundant (13.7% in the dry season, 28.5% in the normal season, and 21.6% in the flood season), followed by 9-nPhe (15.4% in the dry season, 15.3% in the normal season, and 11.4% in the flood season), and 2 + 3-nFla (13.2% in the dry season, 9.9% in the normal season, and 15.7% in the flood season). Likewise, Flu, Fla, and Pyr were the most abundant PAHs. The target compounds were insoluble in water and as their molecular weight increased, the hydrophobicity of the benzene hydrocarbons increased. The compounds with a large number of rings (five-ringed and six-ringed) enriched the suspended matter and sediment more easily (McGroddy and Farington, 1995; Chiou et al., 1998). In addition, for the low-ringed compounds (two-ringed), the volatile targets could enter the water directly via water-air exchange (Park et al., 2002; Baker and Eisenreich, 1990). For these reasons, the three-ringed and four-ringed NPAHs and PAHs constituted the majority of the detected compounds.

2.2. Distribution patterns and seasonal variations of NPAHs and PAHs in the surface water of Lake Taihu

The distribution patterns and seasonal variations of the target NPAHs and PAHs in Lake Taihu are illustrated in Fig. 3. It was discovered that the highest ΣNPAH concentrations were

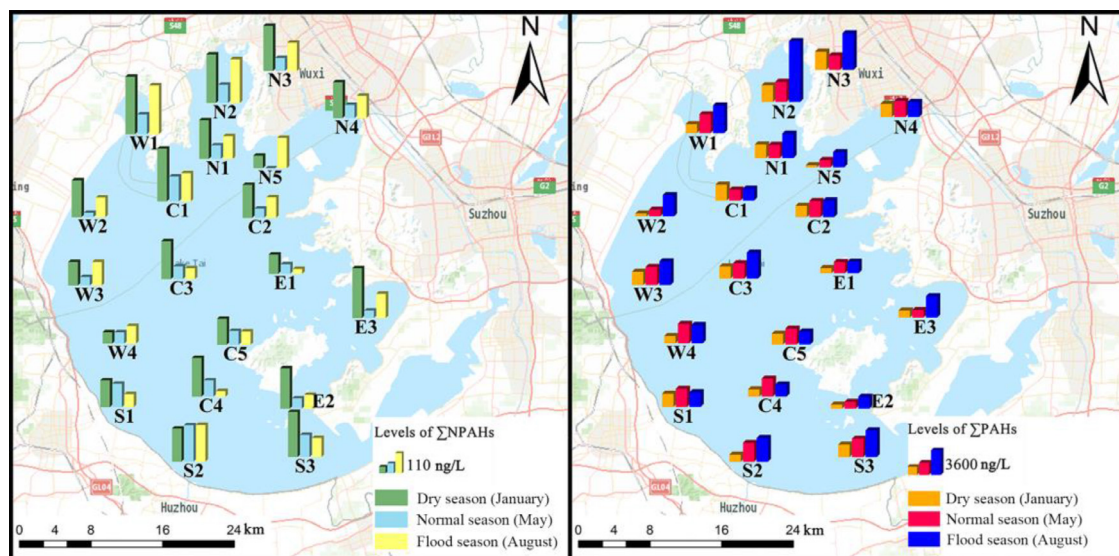


Fig. 3 – Distribution patterns and seasonal variations of NPAHs and PAHs in surface water of Lake Taihu.

measured at W1 (212 ng/L) in the dry season, S2 (135 ng/L) in the normal season, and W1 (181 ng/L) in the flood season. Furthermore, the highest Σ PAH concentrations were observed in the northern part of the lake in all seasons. These maxima were 2177 ng/L at site N3 in the dry season, 2425 ng/L at site N2 in the normal season, and 7298 ng/L at site N2 in the flood season. NPAHs were not detected at all of the sampling sites in Lake Taihu, whereas PAHs were found at all of the sites. The concentrations at the sampling sites decreased initially from north to south and then increased. This was perhaps due to the fact that the pollution levels in the Wujin district of Changzhou and in Wuxi (both northern cities in Jiangsu Province) were relatively serious, which is related to excessive human activities and rapid economic development (Zhao et al., 2017). Higher concentrations have been observed at the northern sites over the years, which has been attributed to the river inflow (Li et al., 2019).

Generally, the concentrations of NPAHs and PAHs will increase during the dry season (winter) due to the direct emissions of combustion. In addition, PAHs and/or NPAHs also originate from direct discharge sources such as urban runoff and atmospheric deposition, urban and industrial wastewater, and oil leakage (Shi et al., 2005; Jiang et al., 2007; Li et al., 2010). The seasonal variation results revealed that the Σ NPAH levels during the dry season were higher than those in the flood and normal seasons at most of the sampling sites. This may be due to the fact that household heating in winter leads to the increase of fossil fuel and biomass combustion, resulting in the increase of NPAHs (Du et al., 2018). In addition, the thermal degradation and photodegradation of these compounds are reduced due to the lower temperatures, decreased radiation, and lower oxidant concentration (Bandowe et al., 2014; Alves et al., 2017). The general pattern of higher NPAH levels in winter was in accordance with previous studies (Li et al., 2015; Alves et al., 2017; Chen et al., 2017; Zhuo et al., 2017). Meanwhile, the Σ PAH levels in the flood and normal seasons were higher than the levels during the dry season in most of

the surface water (Fig. 3). This may be due to the resuspension of sediments, precipitation, and water current erosion in the flood season (Van Metre et al., 2000). In our study, the NPAH concentrations were higher in the winter, whereas the PAH concentrations were higher in the summer. The reasons for this result were as follows. A greater contribution of photochemical reactions is expected during the flood (warm) season than during the dry (cold) season due to the additional light and higher temperatures (Tomaz et al., 2017). NPAHs are more affected by temperature and light than PAHs (Lan et al., 2014). Intense light accelerates the processes of photodegradation, which decreases the concentrations of Σ NPAHs in the normal and flood seasons. In addition, the high temperatures during the flood season favor the upwelling of pollutants from sediments into water (Xuesong et al., 2014). The large amount of water flow in the flood season also increases the release of PAHs and NPAHs from sediments to water. The concentration of PAHs in sediments is much higher than that of NPAHs, however, which provides the higher contribution of PAHs from sediments to water in the summer flood season (August in our study).

2.3. Potential sources of NPAHs and PAHs in Lake Taihu

NPAHs are mainly formed by the direct combustion of fossil fuels as well as photochemical reactions (Bandowe and Meusel, 2017). Different kinds of isomers are produced by different reaction pathways, which are often used to evaluate the NPAH sources at varying concentrations. At present, many researchers use the 2-nFla/1-nPyr ratio as the basis for assessing the dominant source (Zielinska et al., 1989; Bamford and Baker, 2003), since 1-nPyr is a typical direct combustion product whereas 2-nFla is mainly produced by photochemical transformation. In this study, we used 2 + 3-nFla instead of 2-nFla to evaluate the NPAH sources. Gao et al. (2018) also evaluated NPAH sources with this method. When the 2 + 3-nFla/1-nPyr ratio is > 5, NPAHs are mainly produced by photo-

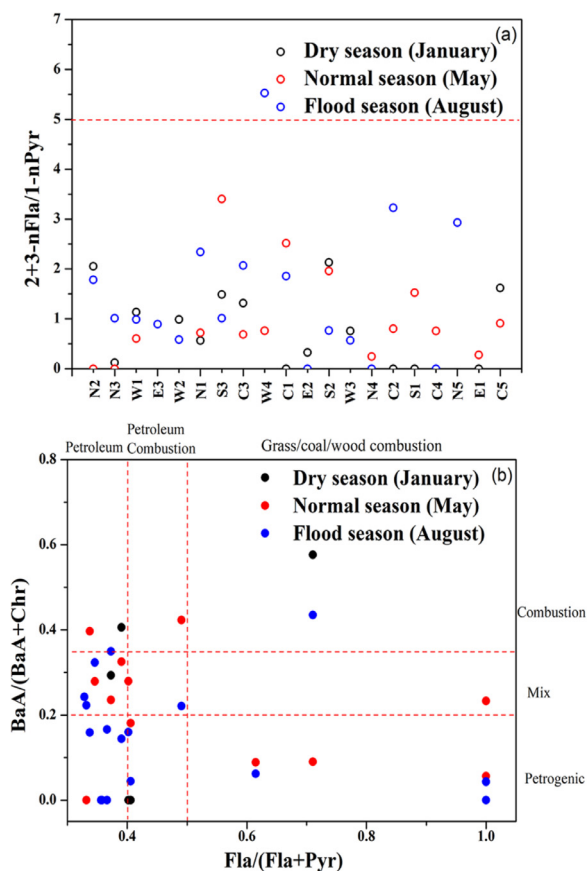


Fig. 4 – Diagnostic NPAH and PAH ratios in the surface water of Lake Taihu.

chemical transformation (Reisen and Arey, 2005; Keyte et al., 2013; Feilberg and Nielsen, 2015). Conversely, direct combustion is the main contributor if the ratio is < 5 . As shown in Fig. 4(a), most of the $2 + 3-n\text{Fla}/1-n\text{Pyr}$ ratios for the three seasons were < 0.5 . If the value of $2 + 3-n\text{Fla}/1-n\text{Pyr}$ is < 5 , then $2-n\text{Fla}/1-n\text{Pyr}$ must also be < 5 . Overall, the high concentrations in the dry season were mostly contributed by the direct combustion source. Although the ratios gradually increased after the dry season (that is, in the normal and flood seasons), they did not exceed the value of 5; hence, combustion was the main source in all seasons.

A general method for analyzing the sources of PAHs is the diagnostic ratio. The ratios of different PAHs represent different sources due to their relative stability (Yan et al., 2010). In this work, $\text{Fla}/(\text{Fla}+\text{Pyr})$ and $\text{BaA}/(\text{BaA}+\text{Chr})$ were applied to analyze the PAH pollution sources as they are the most widely used indicators. If the ratio of $\text{Fla}/(\text{Fla}+\text{Pyr})$ is < 0.4 , the PAHs mainly originated from unburned petroleum products. If $\text{Fla}/(\text{Fla}+\text{Pyr})$ falls within the range of 0.4–0.5, the main source was the combustion of liquid fossil fuels. If it is > 0.5 , the PAHs originated from biomass combustion (grass, wood, or coal) (Magi et al., 2002). As shown in Fig. 4(b), most of the $\text{Fla}/(\text{Fla}+\text{Pyr})$ ratios during all the three sampling seasons were < 0.4 , indicating a strong contribution from unburned petroleum pollution. In the case of $\text{BaA}/(\text{BaA}+\text{Chr})$, a ratio < 0.2 implies petrogenic sources, a ratio > 0.35 indicates

pyrolytic sources, and a ratio ranging from 0.2 to 0.35 suggests petrogenic and/or pyrolytic sources (Soclo et al., 2000). As shown in Fig. 4(b), most of the $\text{BaA}/(\text{BaA}+\text{Chr})$ ratios for the three seasons were < 0.35 , indicating that the PAHs apparently originated from a mix of petrogenic and pyrogenic sources. In summary, the PAH sources in the surface water of Lake Taihu may be primarily derived from a combination of unburned petroleum pollution and petroleum combustion. Hu et al. (2017) and Yang et al. (2013) also drew a similar conclusion. Ship traffic on Lake Taihu could also represent a considerable source of PAHs in the surface water, since the wastewater generated from ships may contain various contaminants, including PAHs. Additionally, there is a risk of petroleum spillage from ships as they consume large amounts of petroleum for propulsion. Therefore, it is necessary to strengthen the management of waterway transportation in order to reduce the unintentional spillage of hazardous chemicals. In addition, the PAH and NPAH source analysis revealed that they both included combustion sources. The PAHs originated primarily from petroleum combustion, whereas the NPAHs were mainly from the indoor combustion of coal and wood during the winter expelled into the outdoor environment (Chen et al., 2017). In particulate matter, the NPAH concentrations were higher in winter, whereas the PAH concentrations were higher in summer. The NPAH concentrations in winter were lower than those in summer due to the increase of indoor coal and wood combustion, whereas the PAH concentrations in winter were higher than those in summer. This finding was consistent with the seasonal variation results.

2.4. Evaluation of human health risk assessment

Lake Taihu is an important drinking water source, which supplies water to the surrounding waterworks. Based on the ILCR model, we used the NPAH and PAH concentrations to calculate the values of TEQ (BaP) and ILCR (Appendix A Table S7). The estimated lifetime carcinogenic risk from the NPAHs and PAHs in the collected surface water samples from Lake Taihu ranged from 2.09×10^{-7} to 5.75×10^{-5} . During the dry season, only one site (N3) in dry season exhibited ILCR values above the maximum acceptable risk levels ($5.0 \times 10^{-5}/\text{a}$) recommended by the ICRP. The health risk due to the NPAHs and PAHs in the lake water did not surpass the maximum acceptable risk levels ($1.0 \times 10^{-4}/\text{a}$) recommended by the US EPA, although most sites had a potential risk, especially during the dry season. The highest risk levels were mainly observed at site N3 (dry season), site N2 (normal season), and site S2 (flood season). These sites are highly polluted and need to be continually monitored in the future. Of all the detected compounds, 6-nChr was the most carcinogenic substance based on the TEQ values. Of the three seasons, the ILCR values during the dry season were higher than the values in the normal and flood seasons due to the carcinogenic strength coefficient of 6-nChr. These results indicate that the NPAHs and PAHs in the surface water of Lake Taihu may pose a human health risk, thus making it necessary to focus on the removal of NPAHs and PAHs, especially during the pretreatment of drinking water, in order to reduce any potential harm to human health.

3. Conclusions

In this work, the occurrence and spatiotemporal variations of 15 NPAHs and 16 PAHs in the surface water of Taihu Lake, China, were investigated. The potential sources were estimated using diagnostic ratio analysis, while the human health risk assessment was evaluated based on the ILCR model. The results of this study demonstrated that the concentration of the Σ NPAHs is an order of magnitude lower than that of the Σ PAHs. The highest concentrations among the Σ NPAHs were observed during the dry season (with a maximum of 212 ng/L at site W1), whereas the highest Σ PAH concentrations were recorded during the flood season (with a maximum of 7298 ng/L at site N2). Flu was the most abundant parent PAH in all seasons, whereas in the case of NPAH, 2-nFlu (normal and flood seasons) and 9-nPhe (dry season) were the most abundant. The prime source of NPAHs was direct combustion, whereas the source of PAHs was predominantly from a mixed pattern including pollution from unburned petroleum and petroleum combustion. In this study, the ILCR values of the PAHs and NPAHs were estimated to range from 2.09×10^{-7} to 5.75×10^{-5} , and the human health risk assessment of drinking water exposure revealed that some surface water samples posed a potential health risk. Therefore, it is necessary to concentrate on the removal of NPAHs and PAHs, especially during the pretreatment of drinking water.

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Appendix A Supplementary data

Supplementary material associated with this article can be found, in the online version, at [doi:10.1016/j.jes.2020.09.025](https://doi.org/10.1016/j.jes.2020.09.025).

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