Sedimentary records of polycyclic aromatic hydrocarbons from three enclosed lakes in China: Response to energy structure and economic development[☆]

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ABSTRACT

Historical polycyclic aromatic hydrocarbon (PAH) pollution was explored through the sedimentary records of three lakes: Huguangyan Maar Lake (HGY) in South China, Mayinghai Lake (MYH) in North China, and Sihai-longwan Lake (SHLW) in Northeast China. In these three lakes, the PAH concentrations in sediments are still rising, showing the different trend to lakes in developed countries. PAH pollution in South China occurred from 1850, much earlier than the increases since 1980 observed in North and Northeast China. The temporal trends of PAH concentrations in lake sediments are highly correlated with local economic development. Spatially, although the region where HGY is located has the highest gross domestic product, higher fluxes of PAHs were found in MYH sediments, indicating that atmospheric PAH pollution in North China might be more serious, and that PAH pollution is not fully correlated with economic development. Source analysis suggested that the PAHs in lake sediments are mainly derived from oil leaks, coal and biomass combustion, vehicle emissions, and diagenesis. Positive matrix factorization (PMF) model revealed that the contribution of vehicle emissions and coal combustion to PAHs has increased significantly in the past 40 years. Benzo(a)pyrene equivalent (BaPE) in the surface sediments of MYH and SHLW were similar and higher than in HGY. In HGY, vehicle emissions posed the highest toxic risk, followed by coal combustion. However, in MYH, the toxicity risk of vehicle emissions was close to that of coal and biomass combustion due to the highly developed coal industry in Shanxi Province. In SHLW, the contribution of fossil fuel combustion to BaPE was significantly higher than that of biomass combustion. This study provides important information for understanding PAH pollution affected by anthropogenic activities in the Anthropocene and provides a scientific basis for formulating PAH pollution control strategies.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are organic pollutants with hundreds of homologs (Srogi, 2007; Wilcke, 2000). The concentrations, physicochemical properties, spatio–temporal distribution, and risk to human health of PAHs have received extensive attention due to their persistence and toxicity (Bostrom et al., 2002; Guo et al., 2017; Karp et al., 2020; Maletic et al., 2019; Zhang et al., 2009). There are currently 16 PAHs with significant carcinogenicity, teratogenicity, and mutagenicity, which are listed as priority pollutants by the US Environmental Protection Agency (US EPA) (Gao et al., 2018; Ma et al., 2020; Qian et al., 2017).

During the second half of the last century, developed countries in Europe and North America made great efforts to reduce the emission of PAHs with considerable effects (Guo et al., 2017; Pacyna et al., 2003). PAH concentrations in these countries have shown a downward trend in recent years (Du and Jing, 2018; Guo et al., 2017). Despite this, global PAH emissions continuously increased and peaked in 1995 (Shen et al., 2013), which seems to be related to the increase in PAH emissions from developing countries. As a developing country with rapid economic growth, PAHs pollution is a critical environmental issue in China. It is estimated that in 2007, the emission of 16 US EPA priority PAHs reached

106 Gg in China, accounting for approximately one-fifth of total global PAH emissions (Shen et al., 2013).

PAH sources in the environment can be classified as pyrogenic, petrogenic, or biogenic (Buczyńska et al., 2013; Gao et al., 2018; Walker et al., 2005). Pyrogenic PAHs are produced by incomplete combustion of fossil fuels or biomass. Petrogenic PAHs originate from the slow maturation of organic matter in the strata. Biogenic PAHs are formed in the process of organic matter degradation. PAHs currently in the environment, especially those that cause significant harm to human health, mainly come from pyrogenic sources related to anthropogenic activities, including industrial activities such as coking, metallurgy, wood processing, and waste incineration, as well as emissions from mobile sources such as automobiles and ships (Kim et al., 2008; Ma et al., 2017; Mojiri et al., 2019; Ravindra et al., 2008). This makes the atmosphere an important pathway for the diffusion of PAHs (Abdel-Shafy and Mansour, 2016; Dat and Chang, 2017).

To mitigate the adverse effects of PAH emissions on the ecosystems and human health, it is important to understand the historical variation in PAH concentrations in the environment, as well as the main sources of PAHs. Lake sediments are good natural archives for recording environmental pollutant information. The changes in environmental PAH concentrations over time and information on their sources can be preserved in sediments (Feliciano Ontiveros-Cuadras et al., 2019; Maletic et al., 2019; Xu et al., 2014). Although numerous studies on PAHs in lake sediments have been done and reported, the information is mostly site-specific, and lacks a wider perspective on this issue. Furthermore, there are relatively few studies using sediment record to discuss the long-term trends of atmospheric PAHs because PAHs in many lake sediments were dominantly inputted by runoff and by direct discharge into the lake.

Thus, in this study, sediment cores were collected from three enclosed lakes in different regions of China, including two maar lakes in South and Northeast China, as well as one alpine lake in North China. Maar and remote alpine lakes have small catchment areas and stable sedimentary environments. The long-term variation of atmospheric pollutants can be clearly recorded by lake sediments, making them ideal for reconstructing the trends of atmospheric PAH pollution (Lin et al., 2017; Ortiz et al., 2013; Ruiz-Fernandez et al., 2007). The chronologies of the sediment cores were determined by ^{210}Pb, and the contents of 28 PAHs in sediments were analyzed, including the 16 US EPA priority PAHs. The main objectives of this study are as follows: (1) to provide a wider perspective of the history of PAH pollution through lake sediments in South, North and Northeast China; (2) to identify the possible sources and causes of PAH pollution in the study areas; and (3) to determine the toxicities of the PAHs in sediment and their links with different sources of PAHs.

2. Materials and methods

2.1. Study sites and sampling

Sediment cores were sampled from three lakes, including two maar lakes, Huguangyan Lake (HGY) in Guangdong Province in South China and Sihailongwan Lake (SHLW) in Jilin Province in Northeast China, and an alpine lake, Mayinghai Lake (MYH) in Shanxi Province in North China (Fig. 1). Atmospheric deposition is the main route for pollutant input in these lakes because they are hydrologically closed.

On 13 August, 15 September, and September 25, 2020, a gravity sampler was used to collect sediment cores from the center of HGY, MYH, and SHLW lakes. Two sediment cores were collected from each lake, one of which was used for chronology determination and the other for PAHs analysis. The cores were sectioned at 1.0 cm intervals immediately after collection, and each sample was sealed in pre-cleaned centrifuge tubes. Then, samples were transported to the laboratory, freeze-dried at −80 °C, ground to a powder and stored at −20 °C until further treatment.

2.2. Chronology

The chronologies of sediment cores were determined by excess ^{210}Pb (^{210}Pb$_{ex}$). In brief, the activities of ^{210}Pb and ^{226}Ra were tested by a multi-channel spectrometer (GX6020, CANBERRA, USA). The activity of ^{210}Pb was determined from gamma emissions at 46.5 keV, and ^{226}Ra activity was determined from gamma emitted by its progeny isotope (^{214}Pb) at 295 keV and 352 keV. ^{210}Pb$_{ex}$ was calculated by subtracting the ^{226}Ra activity from the measured ^{210}Pb activity. The chronologies of sediment cores were calculated using the constant flux and constant sedimentation rate (CFCS) model (Appleby and Oldfield, 1978). Mass
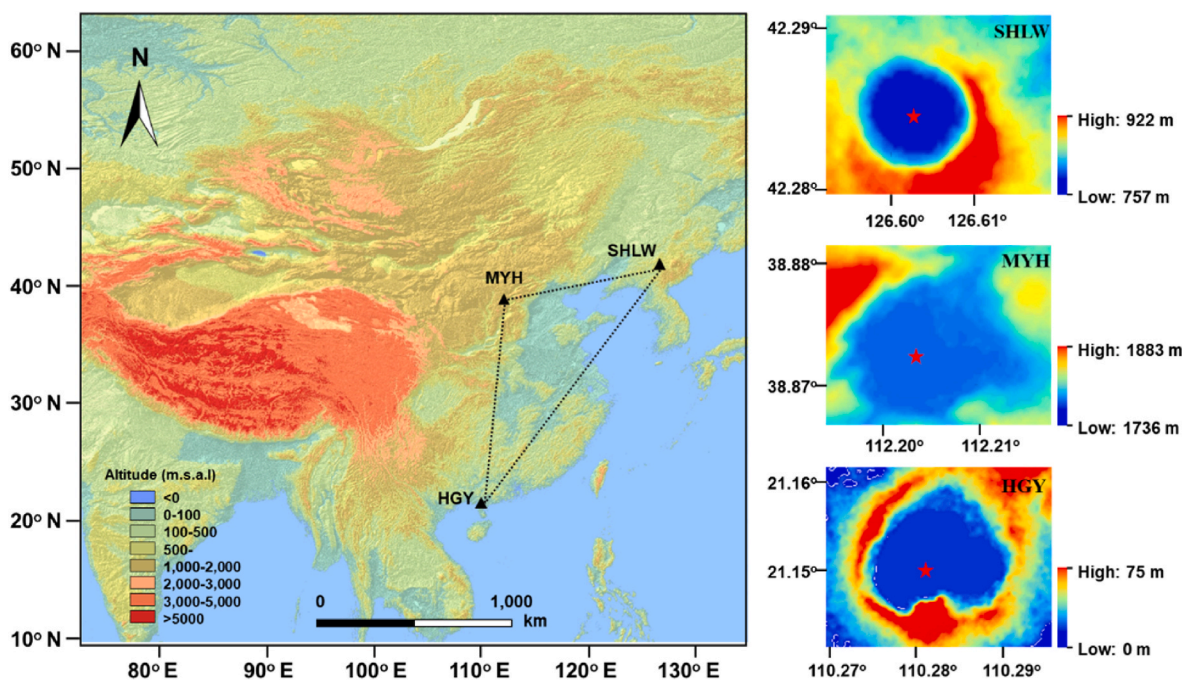

Fig. 1. Map of the study area and location of the sampling site.

depth (g cm^{-2}) was used to replace the depth (cm) in the calculation of sediment accumulation rate because sediment cores usually have higher porosity in the upper section. Mass depth M(a) at depth a can be described as:

$$M(a) = \int_0^a \rho(x)dx \qquad (1)$$

where $\rho(x)$ denotes the dry bulk density of sediment at depth x.

2.3. Geochemical analysis

Soxhlet extraction was used for sample extraction (Guo et al., 2010; Xu et al., 2014). Deuterated PAHs, including naphthalene-d8, ace-naphthene-d10, phenanthrene-d10, quinone-d12 and perylene-d12, were added to sediment as recovery surrogates, and then Soxhlet extracted with a 200 mL mixture of hexane and acetone (1:1, v/v). After Soxhlet extraction for 48 h, the extracts were filtered, concentrated, and the solvent was then replaced with hexane. An alumina/silica gel chromatography column was used for the cleanup and fractionation of the extract. The chromatography column was firstly eluted with hexane, then eluted with a mixture of hexane and dichloromethane (7:3, v/v) to collect the aromatic fraction. The collected eluent was concentrated to 0.5 mL, and the internal standards (1,1-difluorobiphenyl, p-terphe-nyl-d14, dibenzo[a,h]anthracene-d14) were then added before the instrumental analysis.

PAH analysis was conducted using a gas chromatography-mass spectrometer (GCMS-QP2010, Shimadazu, Japan). The chromato-graphic column was DB-5 (60 m × 0.25 mm × 0.10 μm). Ultrahigh purity He (99.999%) was used as the carrier gas, and the flow rate was set at 1 mL/min. The GC oven temperatures were programmed from 60 °C to 200 °C at a rate of 10 °C/min, increased to 220 °C at a rate of 2 °C/min (remaining for 5 min), and finally increased to 290 °C at a rate of 8 °C/min (hold for 30 min).

The following 28 PAHs were quantified, including 16 US EPA priority PAHs, 2-methylnaphthalene (2-MNAP), 1-methylnaphthalene (1-MNAP), biphenyl (BP) 2,6-dimethylnaphthalene (2,6-DNAP), 2,3,5-tri-naphthalene (2,3,5-TNAP), 2-methylphenanthrene (2-MPHE), 1-methyl-phenanthrene (1-MPHE), 2,6-dimethlyphenanthrene (2,6-DPHE), 11H-benzo(b)fluorene (11H-BbF), benzo(e)pyrene (BeP), perylene (PER), and 9,10-diphenylanthracene (9,10-DPA).

The surrogate recoveries in all samples were 71.3 ± 17.5% for naphthalene-d8, 79.4 ± 7.4% for acenaphthene-d10, 94.1 ± 17.5% for phenanthrene-d10, 83.6 ± 16.7% for chloroquine-d12, and 85.0 ± 15.7% for perylene-d12. The PAH concentrations in duplicate samples varied by less than 15%. Only minimal concentrations of target com-pounds were found in blank samples and were subtracted.

2.4. Receptor models for source identification

Positive matrix factorization (PMF) model is a multivariate factor analysis method based on the weighted least squares method, and is commonly used to identify the sources of environmental pollutants (Paatero and Tapper, 1994; Reff et al., 2007; Uchimiya et al., 2011). This model only needs input of the concentration and uncertainty of the target pollutant to complete the calculation.

In this study, 20% of the concentration was taken as the uncertainty data. PMF analysis was performed using PMF version 5.0 developed by the US EPA. More details and evaluation of PMF model results are provided in Text S1.

3. Results and discussion

3.1. Sediment cores dating

The dating process of the sediment core of HGY can be found in a previous study (Wu et al., 2022). The $^{210}Pb_{ex}$ activity in sediment cores of HGY, MYH, and SHLW decreased exponentially with increasing mass depth (Fig. S1). Considering the large variation in the sediment accu-mulation rate of lake sediments in different regions, and the higher uncertainty of $^{210}Pb_{ex}$ in the lower part of the core, the sediment accu-mulation rates in HGY, MYH, and SHLW were determined by using the $^{210}Pb_{ex}$ data above 30, 16, and 10 cm, respectively. Although this might mean that the age of sediment in the lower part cannot be accurately calculated, it likely has little influence on the main conclusions as variation of PAHs in sediment cores mostly occurs in the upper part.

The obtained chronologies are shown in Fig. S1. The sediment accumulation rates of HGY, MYH, and SHLW were 0.0576, 0.2178, and 0.0225 g/(cm^2·a), respectively. These values are similar to previous studies (Guan et al., 2012; Li et al., 2021; Zhan et al., 2019). The sedi-ment accumulation rates of HGY, MYH, and SHLW were not consistent with their annual precipitation (Table S1), which might be related to the degree of vegetation cover around the lake. Although the annual pre-cipitation in MYH is the lowest of the studied lakes, the lower degree of vegetation cover increase soil erosion in the catchment, resulting in a higher sediment accumulation rate in this lake (Mu et al., 2021; Yang et al., 2018).

3.2. Historical trends of ΣPAH concentrations in sediment cores

The concentrations and fluxes of PAHs in lake sediments in devel-oped countries such as the USA and Europe mostly peaked in 1950s and 1980s or even earlier, and then began to decline (Du and Jing, 2018; Guo et al., 2017). In some lake sediments in China, such as in Baiyangdian Lake in North China and Dianchi Lake in Southwest China, PAHs showed a similar trend, with PAH concentrations peaking in 1990 and 2004, respectively, and then declining (Guo et al., 2011; Ma et al., 2020). However, these decreases do not appear to be due to the reduc-tion of atmospheric PAH emissions, but were more likely the result of the formulation and implementation of strict water protection policies in China in the past few decades, which have caused a substantial reduc-tion in pollutants from rivers to these lakes (Guo et al., 2017; Guo et al., 2011). In our study, the concentrations and fluxes of PAHs in sediment cores of HGY, MYH, and SHLW were still rising (Fig. 2 and S2), indi-cating that atmospheric PAH emissions in these regions are increasing.

The total concentrations of 28 PAHs (ΣPAHs$_{28}$) and 16 the US EPA priority PAHs (ΣPAHs$_{16}$) in HGY sediment cores ranged from 261 to 1750 ng/g (average 1000 ng/g) and 14.2 ng/g to 840 ng/g (average 157 ng/g), respectively. Before the Industrial Revolution (pre-1850), there was no obvious increase in ΣPAHs$_{28}$ and ΣPAHs$_{16}$, but the fluctuation in ΣPAHs$_{28}$ was significantly greater than that of ΣPAHs$_{16}$. This fluctuation is mainly due to the inclusion of PER in the calculated ΣPAHs$_{28}$. PER is widely distributed in lake and marine sediments, mainly from early diagenesis, as only a small amount of PER is produced during the combustion process (Luo et al., 2006; Silliman et al., 1998). The con-centration of PER is often higher in the lower section of sediment cores. From 1850 to 1980, ΣPAHs$_{28}$ and ΣPAHs$_{16}$ in HGY sediments began to increase slowly, which might be related to the industrial development in China at that time. After 1850, western countries established numerous factories in coastal cities in China. Meanwhile, China pursued a series of reforms since 1860 to promote industrial development, and Guangdong was one of the earliest regions to carry out these reforms (Lee et al., 2008; Wu et al., 2022). After 1980, with the implementation of the Reform and Opening-Up Policies, the economy and industry in various regions of China developed rapidly (Fig. 3), and ΣPAHs$_{28}$ and ΣPAHs$_{16}$ in HGY sediment also increased significantly, especially in the past two decades during which time ΣPAHs$_{16}$ increased by nearly 3.7-fold.

In MYH, ΣPAHs$_{28}$ and ΣPAHs$_{16}$ in sediment cores ranged from 380 to 1070 ng/g (average 562 ng/g) and 32.3–578 ng/g (average 126 ng/g), respectively. Similar to HGY, the variation of ΣPAHs$_{28}$ in MYH sedi-ments fluctuated more than ΣPAHs$_{16}$. In terms of historical changes, although the sediment core of MYH only covered the period of

1940–2018 due to the higher sediment accumulation rate and shorter length of the core, it can be speculated that the PAH concentrations in MYH sediments did not increase significantly from the Industrial Revolution to 1980. Firstly, the PAH concentrations were relatively lower and varied slightly from 1940 to 1980 (Fig. 2). Secondly, in addition to PAHs, anthropogenic activities such as vehicle emissions and coal combustion also often increase the concentration of heavy metal in the environment, but a previous study showed that Pb concentrations in MYH and nearby lake are low and only experienced slightly increased from 1950 to 1980 (Wan et al., 2020). From 1980 to 2000, with the Reform and Opening-Up, economic and industrial development caused the atmospheric PAH pollution in this region, and ΣPAHs$_{16}$ in sediments began to increase (Figs. 2 and 3). After 2000, with further industrial intensification, the ΣPAHs$_{16}$ concentrations in MYH sediments increased nearly six-fold.

In SHLW, ΣPAHs$_{28}$ and ΣPAHs$_{16}$ ranged from 143 to 1800 ng/g (average 589 ng/g) and 50.4–1510 ng/g (average 267 ng/g), respectively. Similar to MYH, ΣPAHs$_{28}$ and ΣPAHs$_{16}$ in SHLW sediments were relatively low and showed no significant variation before 1980. Therefore, it seems that PAH pollution in South China occurred earlier than in the North and Northeast. With economic and industrial development (Fig. 3), PAH concentrations in SHLW Lake sediments increased more rapidly than HGY and MYH lakes, and were the highest among the three lakes. After 1980, ΣPAHs$_{16}$ in SHLW Lake sediments increased from 108 ng/g to 1510 ng/g, an almost 14-fold increase. However, although PAH concentrations of surface sediments in SHLW Lake were higher than in HGY and MYH lakes, the sedimentation fluxes of PAHs in SHLW Lake were lowest due to its lower sediment accumulation rate (Fig. S2). In fact, the highest sedimentation fluxes of PAHs were found in MYH Lake, indicating that the atmospheric PAH pollution in the MYH area might be more serious than in HGY and SHLW.

It should also be noted that although the temporal trends of PAH pollution in different lakes are highly correlated with the development of local economic and industry, this correlation is not obvious in the spatial distribution. Guangdong is the most economically developed region among the provinces where the lakes are located (Fig. 3), but the
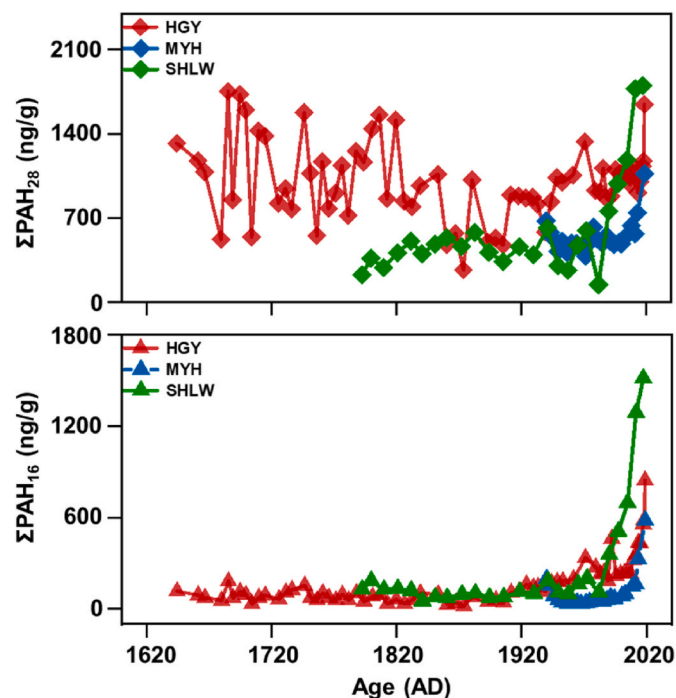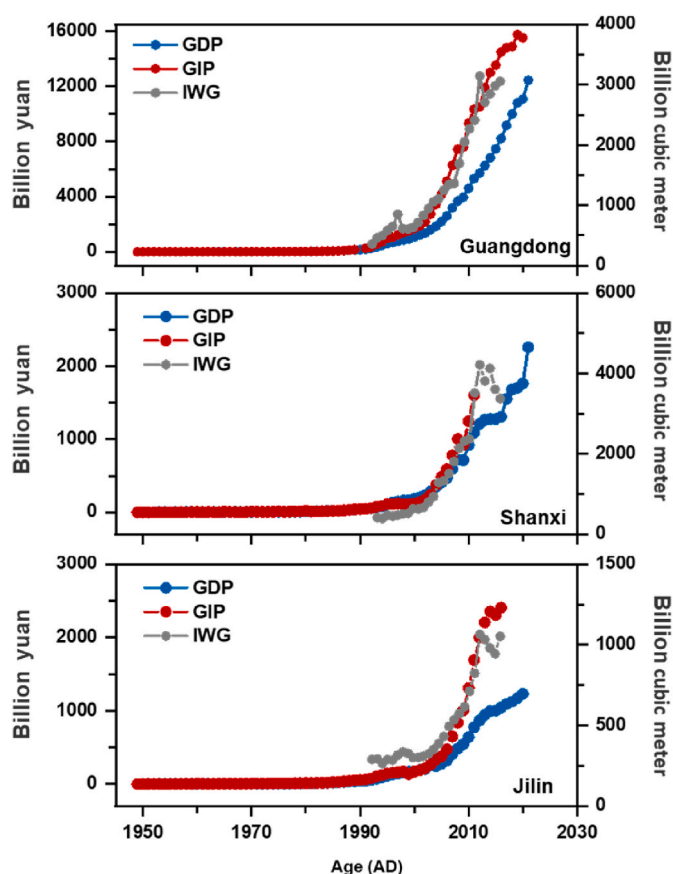

Fig. 3. Gross domestic product (GDP), gross industrial product (GIP), industry waste gas (IWG) emission in Guangdong, Shanxi and Jilin Province.

sedimentation fluxes of PAHs in MYH are much higher than HGY. This might be because Shanxi is the one of the centers of China's coal industry, so its economic growth is more dependent on the mining and consumption of coal, compared with Guangdong. Therefore, local economic structure, consumption of fossil fuels, and development of cleaner technologies might be the more important factors influencing spatial distribution of atmospheric PAH pollution.

3.3. Identifying PAHs sources

Diagnostic ratios (DRs) of PAHs have been widely used to study the sources of PAHs in the environment (Guo et al., 2010; Jia and Batterman, 2011; Lin et al., 2020). Commonly used DRs include ANT/(ANT + PHEN), BaA/(BaA + CHRY), FLA/(FLA + PYR), IcdP/(IcdP + BghiP), BaP/(BaP + BeP), BaP/BghiP, BbF/BkF, and RET/(RET + CHRY) (Guo et al., 2017). Compared with other ratios, FLA/(FLA + PYR) and IcdP/(IcdP + BghiP) are more conservative (Lin et al., 2020; Tobiszewski and Namiesnik, 2012), therefore these ratios were used to explore the sources of PAHs in this study. In general, higher values of these two ratios imply larger relative contributions from pyrogenic sources, while lower ratios indicate relatively higher petrogenic inputs (Gao et al., 2018; Jautzy et al., 2015).

As shown in Fig. 4, pyrogenic sources were important contributors of PAHs in HGY, MYH and SHLW lakes. Specifically, the ratios of FLA/(FLA + PYR) and IcdP/(IcdP + BghiP) of most HGY samples were all greater than 0.5, indicating coal and biomass combustion sources. However, both FLA/(FLA + PYR) and IcdP/(IcdP + BghiP) of HGY sediments have decreased over the past 100 years (Fig. 4), indicating that the PAHs derived from petroleum combustion increased. The FLA/(FLA + PYR) ratios of most MYH samples were greater than 0.5, while the IcdP/(IcdP + BghiP) ratios were between 0.3 and 0.5. Since 1980,

Fig. 2. Historical changes in the concentrations of the sum of 28 PAHs (ΣPAH$_{28}$) and 16 priority control PAHs (ΣPAH$_{16}$) in the sediment cores of HGY Lake, MYH Lake and SHLW Lake.
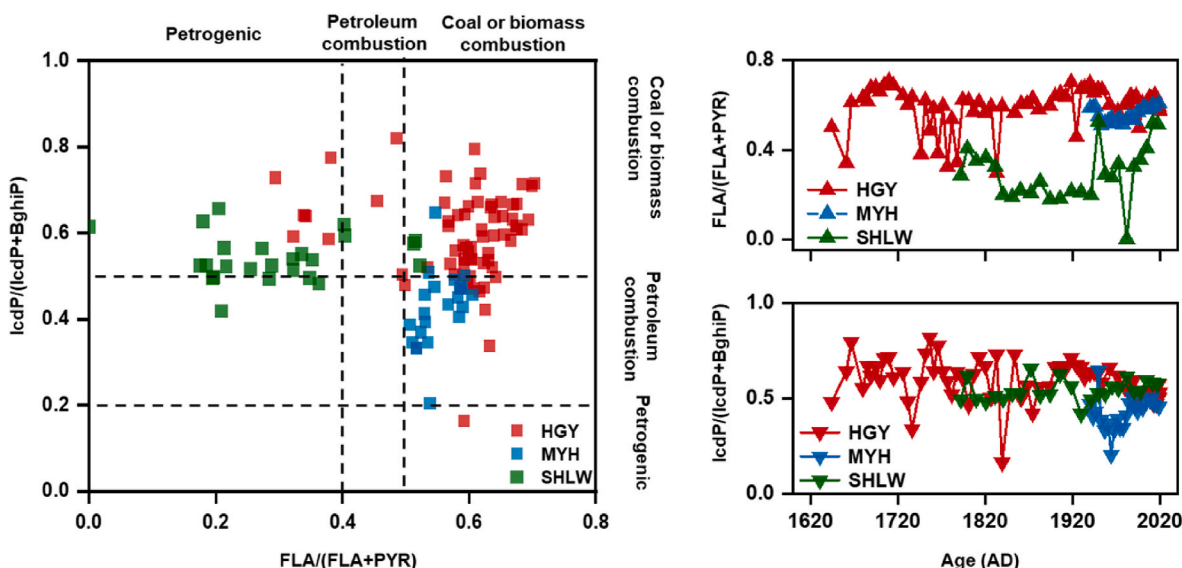
Fig. 4. Diagnostic ratios of PAHs in lake sediments.

FLA/(FLA + PYR) and IcdP/(IcdP + BghiP) increased (Fig. 4), indicating the contribution of biomass and fossil fuel combustion sources increased. The IcdP/(IcdP + BghiP) of most SHLW samples were greater than 0.5, while the FLA/(FLA + PYR) of most samples in the lower part of the cores were lower than 0.4, but in the surface samples they were higher than 0.4 (Fig. 4), indicating that the contribution of pyrogenic sources increased from the bottom to the surface.

The sources of PAHs in lake sediments were further analyzed by the PMF model. Four factors/sources were identified in HGY (Fig. 5a). Factor 1 was characterized by the prominence of NAP, 2-MNAP, 1-MNAP, BP, 2,6-DNAP, and FLO. The volatilization or leak of crude oil

and petroleum products is considered the main source of environmental NAP (Liu et al., 2009; Wang et al., 2016), while the combustion of straw also produces a high volume of NAP (Jia and Batterman, 2011; Zhang et al., 2008). The combustion of wood is an important emission source of FLO (Ma et al., 2020). Therefore, factor 1 was identified as an oil leak/biomass combustion source. Factor 2 was strongly characterized by 2-MPHE, 1-MPHE, ANT, PHE, FLA and PYR. These compounds are usually formed in the coal combustion process (Cao et al., 2017; Ma et al., 2020; Wang et al., 2018), therefore factor 2 was considered to represent coal combustion source. Factor 3 demonstrated relative higher concentrations for IcdP, BghiP, BaP, BeP, BkF, and BbF. Previous studies
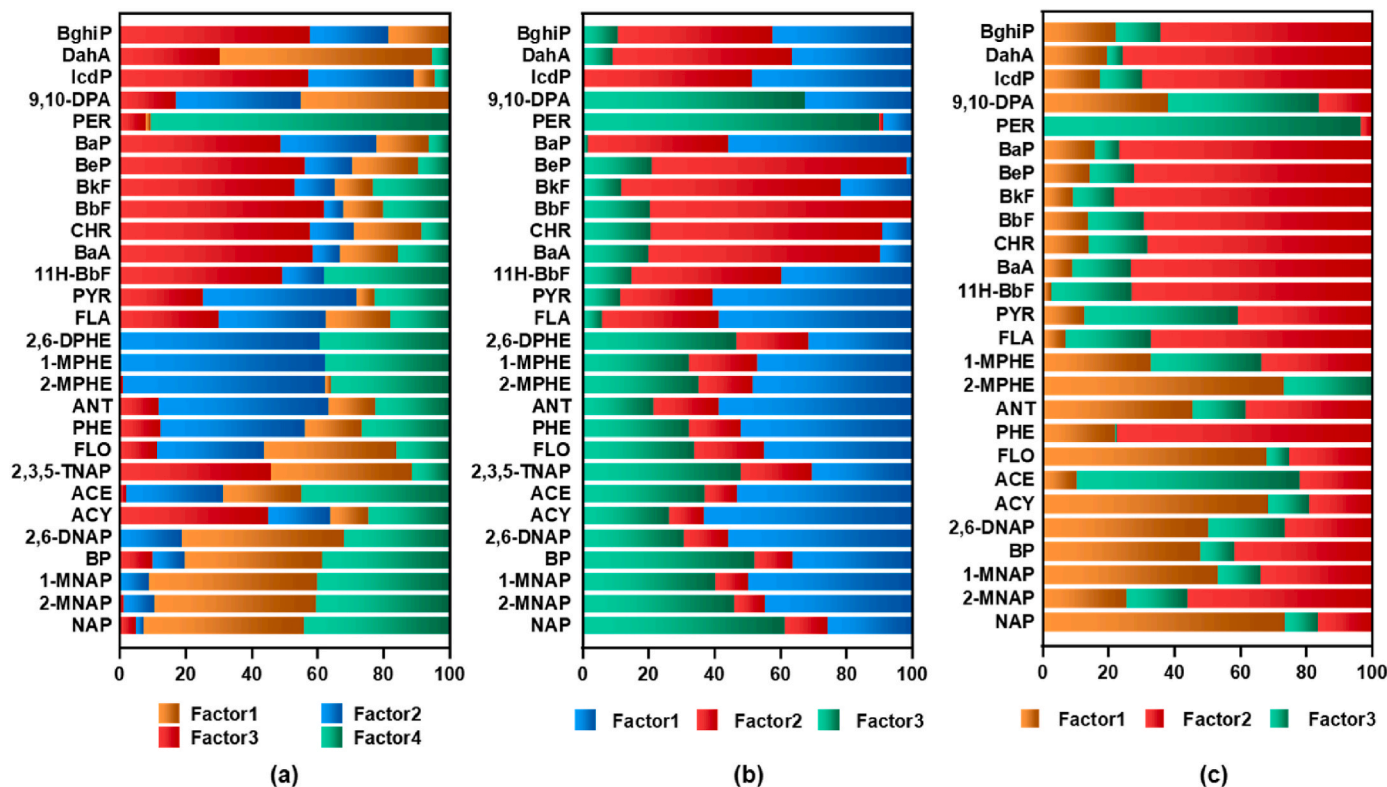

Fig. 5. Main sources components of sedimentary PAHs obtained using a positive matrix factorization (PMF) model for HGY Lake (a), MYH Lake (b) and SHLW Lake (c).

5

have suggested that high molecular weight PAHs such as IcdP, BbF, BkF, BaP, and BghiP are mainly produced from gasoline or diesel engine emissions (Duodu et al., 2017; Liu et al., 2017; Wu et al., 2021; Xu et al., 2014). Therefore, factor 3 was interpreted as vehicle emissions. Factor 4 was strongly characterized by PER. As mentioned previously, PER in lake sediments is mainly generated from diagenesis (Han et al., 2015; Luo et al., 2006), therefore factor 4 was interpreted as a diagenesis source.

Three factors/sources were identified in MYH (Fig. 5b). Factor 1 got relative higher concentrations for ANT, FLA, PYR, ACY, and BaP, while FLO loading was also relatively high. Some studies have shown that the coal coking process can emit a high volume of ACY (Wang et al., 2018), so factor 1 was interpreted as coal and biomass combustion source. Factor 2 was characterized by BeP, BkF, BbF, BaP, IcdP, and BghiP. Therefore, factor 2 was considered as representing vehicle emissions. Factor 3 was strongly characterized by PER and got relative higher concentrations for NAP, therefore, factor 3 was identified as oil leak and diagenesis source.

Similar to MYH, three factors/sources were identified in SHLW (Fig. 5c). Among these, factor 1 was strongly characterized by NaP and

FLO, so factor 1 was identified as an oil leak/biomass combustion source. Factor 2 mainly comprised IcdP, BghiP, BaP, BeP, BkF, BbF, FLA, and PHE, therefore factor 2 was identified as a fossil fuel combustion source. Factor 3 was strongly characterized by PER, so factor 3 was identified as a diagenetic source.

Fig. 6 shows the historical contributions of each source to PAHs in lake sediments. For HGY Lake, PAHs derived from oil leak/biomass combustion began to show a slow increasing trend around 1850, and then increased rapidly after 1970, and declined after 1990. In 2005, the contribution of oil leak/biomass combustion sources to PAHs in lake sediments increased rapidly, which might be mainly due to the rapid increase of local tourism in recent years, which has increased cruise ships in the lake, and the subsequent fuel leaks from ships. PAHs originating from coal combustion have been increasing since the early 20th century, later than oil leak/biomass combustion. After 1970, PAHs contributed by coal combustion sources increased rapidly. Similar to coal combustion sources, the contribution of vehicle emissions to lake sediment PHAs has increased since the early 20th century. The decline in the contribution of mobile-source PHAs from 1960 to 1980 might be influenced by the instability of economic policies during this period,
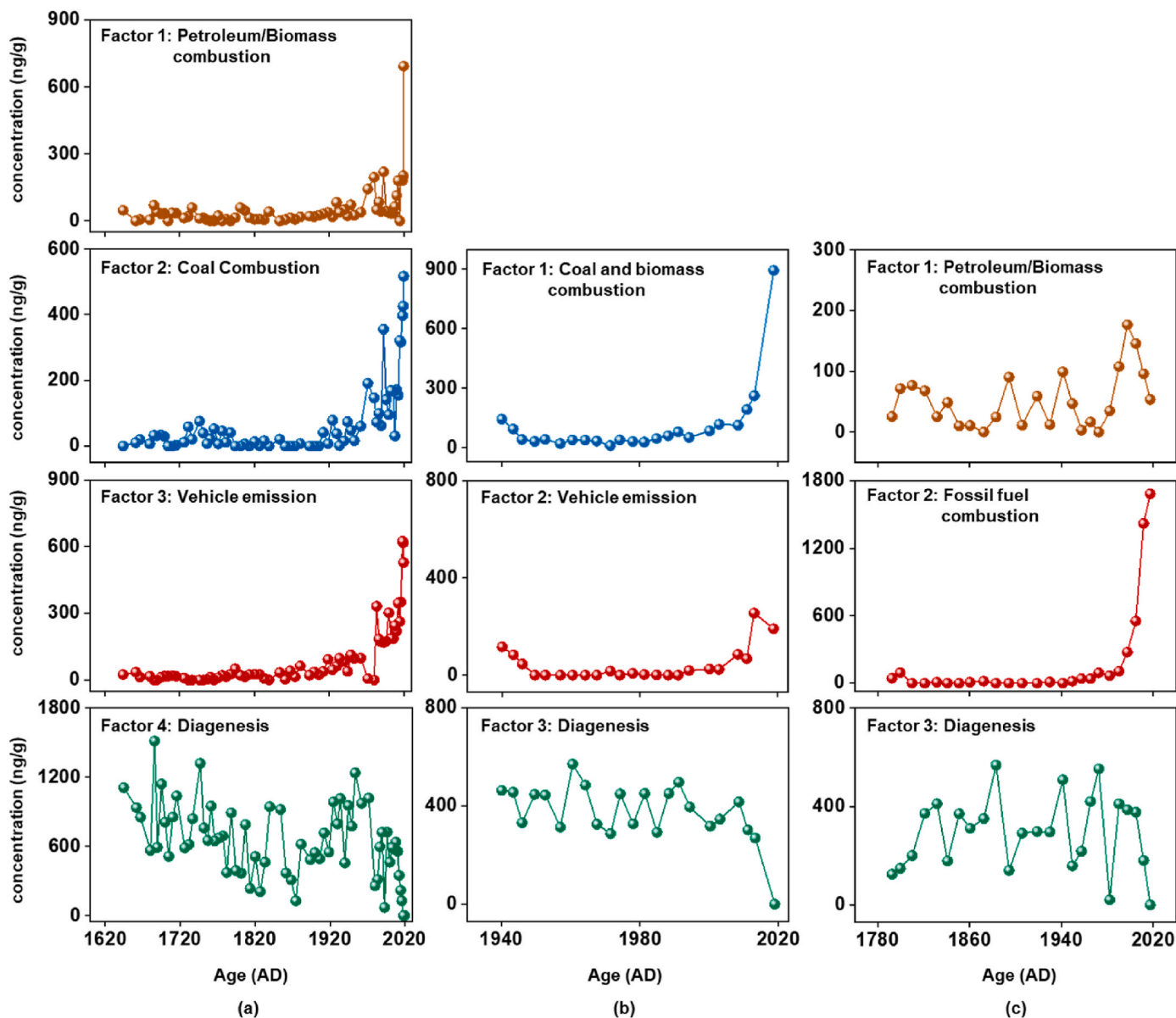

Fig. 6. Temporal contributions of different factors obtained using the positive matrix factorization (PMF) model for HGY Lake (a), MYH Lake (b) and SHLW Lake (c).

which hindered the development of the petroleum industry. After 1980, with the implementation of the Reform and Opening-Up Policy in China, industry developed rapidly and PAHs from vehicle emissions increased significantly. The contribution of diagenesis to PAHs in sediments mainly occurred below a certain depth, and was significantly lower in surface sediments.

Similar to HGY, the contribution of diagenesis to PAHs in the upper sediments of MYH was significantly low, being higher in the middle and lower parts of the sediment core (Fig. 6b). The contribution of vehicle emissions to sediment PAHs began to increase in the 1990s and increased rapidly after 2000. The contribution of biomass and coal combustion to PAHs has increased since 1980, earlier than vehicle emissions. After 2000, PAHs derived from coal and biomass combustion also increased significantly. The variation in the contribution of vehicle emissions, as well as coal and biomass combustion sources, to PAHs were consistent with the growth of GDP and IWG in Shanxi (Fig. 3).

In SHLW, before 1980, PAHs mainly originated from diagenesis and oil leak/biomass combustion (Fig. 6c). After 1980, with the continuous development of economy and industry (Fig. 3), the contribution of fossil fuel combustion to PAH pollution increased rapidly.

3.4. Risk assessment

Benzo(a)pyrene equivalent (BaPE) is an effective tool to evaluate the potential toxicity of PAHs in the atmosphere and aquatic environments. It can be calculated as follows (Xu et al., 2014; Zhang et al., 2012):

$$BaPE = BaA \times 0.06 + BbF \times 0.07 + BkF \times 0.07 + BaP + DahA \times 0.6$$
$$+ IcdP \times 0.08 \tag{2}$$

Similar to the variation in $\Sigma PAHs_{16}$, BaPE values of the three lakes increased from the bottom to the surface sediments (Fig. 7). In surface sediments (<5 cm), the BaPE of HGY, MYH, and SHLW was 20.1–59.3 ng/g (average 33.5 ng/g), 38–80.6 ng/g (average 65.5 ng/g), and 11.6–118 ng/g (average 60.9 ng/g), respectively. Therefore, PAHs in MYH and SHLW may be more harmful than those in HGY.

Combining the PMF model with BaPE, the contributions of different sources to BaPE were estimated (Fig. S3) (Xu et al., 2014; Zhang et al., 2012). Although diagenesis contributed a lot to the total concentration of PAHs (Fig. 6), the contribution of diagenesis to BaPE was significantly lower than that of pyrogenic sources, especially after the Reform and Opening-Up in China, when rapid industrial development led to a corresponding increase in the consumption of fossil fuels. Among various pyrogenic sources in HGY, vehicle emissions contributed the most to BaPE. During 1980–2020, mobile sources contributed 8–29.5 ng/g (average 14.5 ng/g) to BaPE, followed by coal combustion sources, which contributed 1–16.7 ng/g (average 6.9 ng/g). Oil leak/biomass combustion contributed the least (0–18.9 ng/g; average 3.8 ng/g). In MYH, the contribution of vehicle emissions to BaPE was comparable to that of coal combustion/biomass combustion sources due to the highly developed coal industry in Shanxi. During 1980–2020, the average contribution of vehicle emissions to BaPE was 10.4 ng/g, while that of coal/biomass combustion source was 9.7 ng/g.

In SHLW, the contribution of fossil fuel combustion to BaPE was much higher than that of oil leak/biomass combustion sources, ranging from 4 to 100 ng/g (average 40.8 ng/g) from 1980 to 2020, respectively. The contribution of oil leak/biomass combustion sources was only 1.5–7.4 ng/g (average 4.3 ng/g).

4. Conclusions

Historical polycyclic aromatic hydrocarbons (PAHs) pollution was explored through the sedimentary records of three lakes: Huguangyan Maar Lake (HGY) in South China, Mayinghai Lake (MYH) in North China, and Sihailongwan Lake (SHLW) in Northeast China. Unlike developed countries in Europe and North America, PAH concentrations
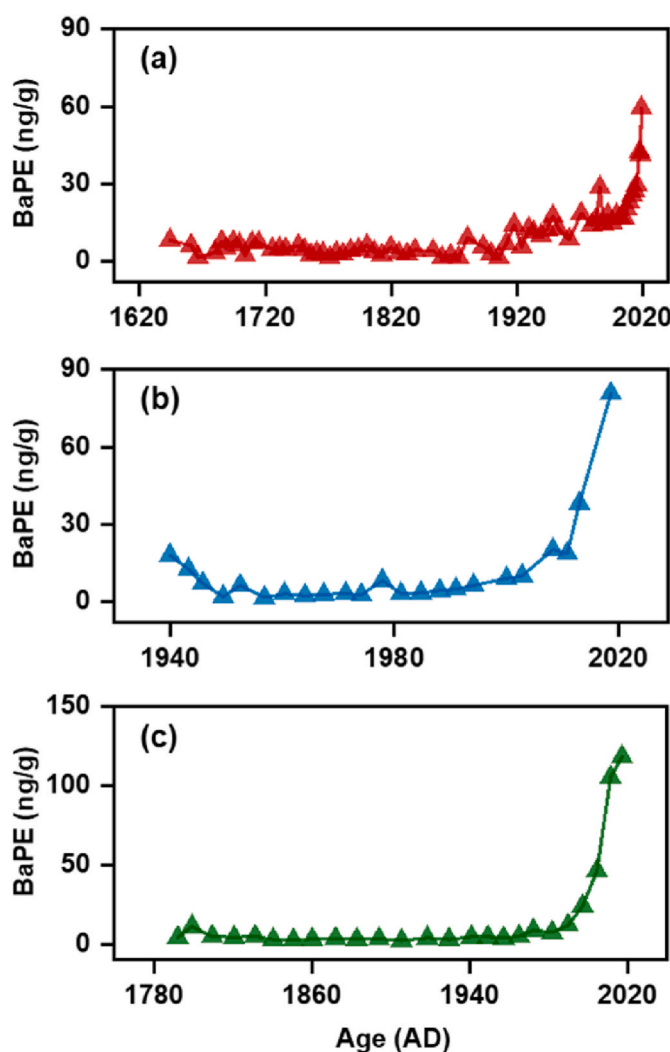

Fig. 7. Temporal trends of the BaPE for HGY Lake (a), MYH Lake (b) and SHLW Lake (c).

in the three studied lakes are still rising, indicating increasingly serious PAH pollution. Affected by the early industrialization in southern China, PAH pollution in South China has been increasing since 1850, much earlier than in North and Northeast China. Sediment records of MYH and SHLW implied that PAH pollution in North and Northeast China has occurred since 1980, and PAH pollution increased rapidly with local economic and industrial development. Compared with HGY and SHLW, the PAH concentrations in MYH sediments were lower, but PAH fluxes were higher, indicating that atmospheric PAH pollution in the North China might be more serious. Although the temporal trends of PAH pollution in different lakes are highly correlated with the development of local economic and industry, this correlation is not obvious in spatial distribution. Economic structure, consumption of fossil fuels, and development of cleaner technologies might be the more important factors influencing the degree of PAH pollution in different regions. Analysis of PAH sources by diagnostic ratios and PMF showed that the PAHs in the three lakes mainly derived from oil leaks, coal and biomass combustion, vehicle emissions, and diagenesis. The contribution of vehicle emissions and coal combustion to PAHs has greatly increased in the past 40 years. The BaPE risk assessment showed that BaPE in the surface sediments of MYH and SHLW were similar and both higher than in HGY. In HGY, vehicle emissions posed the highest toxic risk, followed by coal combustion. While in MYH, the toxicity risk of vehicle emissions was close to that of coal and biomass combustion due to the highly

developed coal industry in Shanxi Province. In SHLW, the contribution of fossil fuel combustion to BaPE was significantly higher than that of biomass combustion.

The concentrations, fluxes, and toxicity risk of PAHs in HGY, MYH, and SHLW sediments are currently still increasing, and it is not clear when the turning point will be. Therefore, it is necessary to conduct long-term monitoring and control PAH concentrations in lakes and the atmosphere in these regions. Due to the refractory and persistent nature of PAHs, they might accumulate or be bio-amplified in aquatic ecosystems, and the subsequent biological effects require further study.

Credit author statement

Hongchen Wu: Investigation, Formal analysis, Writing – original draft, Writing – review & editing. **Jingfu Wang:** Conceptualization, Methodology, Funding acquisition, Writing – review & editing. **Jianyang Guo:** Conceptualization, Methodology, Investigation, Formal analysis, Data Formal analysis. **Xinping Hu:** Investigation, Formal analysis, Data Formal analysis. **Jingan Chen:** Supervision, Funding acquisition, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The data during the current study are not publicly available as they are part of larger study that is currently on–going but are available from the corresponding author on reasonable request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envpol.2022.120929.

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