Effect of Global Warming on Lacustrine Productivity and Accumulation of PAHs in Lakes, East China

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Abstract

Multiple organic proxies and lipid biomarkers in the sediment core samples collected from Luoma Lake and Hongze Lake in Jiangsu are used to expound the relationships of global warming with lacustrine productivity and depostion of polycyclic aromatic hydrocarbons. Total organic carbon, S2, and hydrogen index in sedimentary organic matter were obtained with the Rock-Eval analysis. Nutrient status such as total phosphorus and total nitrogen was measured in the sediment cores. The source apportionment modeling and statistical analyses demonstrated that algal organic matter and bacteria organic matter showed an increasing trend and an obvious enrichment effect on PAHs, which was also related to the increasing temperature and algal productivity in the lakes. Global warming enhanced the lacustrine productivity and the accumulation of polycyclic aromatic hydrocarbons. The rapidly increasing ecological risks of PAHs in LM and HZ indicated the impact of global warming and human activities in the last 60 years. Therefore, the internal cycling and the input of contaminants and nutrients in the lakes should be controlled to reduce the algal growth in LM and HZ.

Key words: PAHs, biomarkers, Rock-Eval, stable carbon isotope, global warming, aquatic productivity, lake

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) have the characteristic of persistence, bioaccumulation, and toxicity. It can cause potential hazards to the ecosystem and human health (Sun et al., 2022; Zhang et al., 2022). Sediment is one of the most important sinks of PAHs in the environment. The distribution, migration, and transformation of PAHs in the water-sediment interface are controlled by physical and chemical processes such as adsorption and desorption. These processes directly affect the fate and ecological risk of PAHs (Wang et al., 2013; Du and Jing, 2018). Sedimentary organic matters (SOM) are biopolymers with

highly heterogeneous chemical properties and physical structures. PAHs adsorbed on different components of SOM exhibit different adsorption-desorption behaviors, and their bioavailability and ecological risk to organisms are different significantly (Brion and Pelletier, 2005). Thus, different components of SOM should be distinguished in the investigations of the deposition history of PAHs and their ecological risks.

In recent years, some researchers have begun to use sediment cores in lakes to study the impact of historical primary productivity on the migration and enrichment of pollutants, and then analyze the "biological pump" role of phytoplankton. Outridge et al. (2005, 2007) used the Rock-Eval pyrolysis parameters to study the primary productivity history in Arctic lakes, while also analyzing the mercury concentration in the deposition cores. They found that climate warming of algae growth played the role of a "biological pump" on mercury. Stern et al. (2009) investigated some lacustrine systems and also found the effect of algal "biological pump" on mercury concentrations in the sediment cores while emphasizing that historical changes in primary productivity were mainly due to global temperature warming. Carrie et al. (2009) also found the effect of global warming on lake historical productivity, while increased algae acted as a "biological pump" for mercury, enhancing its accumulation in sediments and aquatic fish. Söderström et al. (2000) found large polychlorinated polybenzene (PCB) and dichlorodiphenyltrichloroethane (DDT) sedimentary flux and high PCB concentration on the surface sediment compared with oligotrophic lakes, and most of the transport depended on phytoplankton. Jeremiason et al. (1999) selected a pair of lakes of similar size and catchment area for comparison, and also found large sedimentary fluxes of PCB in lakes with higher nutrition. However, the study of two Swedish lakes by Larsson et al. (1998) found that nutrient-poor lakes instead had higher PCB settlement fluxes, and they attributed this phenomenon to the fact that oligoplankton algae dominated by diatom and green algae contained more lipids and thus could adsorb more hydrophobic organic pollutants. Therefore, the impacts of global warming on the productivity and internal cycling of typical organic pollutants in lacustrine sediments are very important to the aquatic ecological systems. Moreover, lipid biomarkers (alkanes, sterols, fatty acids, etc.) are organic molecules that serve as indicators of the past presence of certain biota, including algae, bacteria, and higher plants (Mayers and Ishiwatari, 1993; Boschker and Middelburg, 2002; Sachse et al., 2012). Furthermore, the aquatic SOM input can be estimated and identified by Rock-Eval analysis and biomarker data (Carrie et al., 2012; Disnar et al., 2003; Duan et al., 2015). Therefore, more investigations on the effects of trophic levels, early diagenesis, preservation of organic matter, and oxidation-reduction processes of lakes are warranted to expound on the relationships of PAHs and algal organic matter with climate warming.

Impacts of climate change include changes in carbon dioxide, temperature, and precipitation, affecting the spatial distribution of phytoplankton, coupling between primary producers and herbivores, and algal respiration (Ratti et al., 2007; Najjar et al., 2010). Theoretical and empirical studies have shown that

temperature affects a range of biological processes, including the rate of growth, respiration, and reproduction, and that the rate of metabolic processes increases with temperature (Brown et al., 2004; Gillooly et al., 2001, 2002; López-Urrutia et al., 2006; Price et al., 2010). Moreover, climate change is expected to further reduce biodiversity (Sala et al., 2000). In addition, biological community and ecosystem services will be affected by regional reduced species diversity, over-fishing, and invasion of alien species (Vitousek et al., 1997; Worm et al., 2006). Thus, it is important to understand the expected and unknown effects of climate change on lake biological community and ecosystem services.

We aim to estimate the historical input of PAHs in Luoma Lake (LM) and Hongze Lake (HZ) and investigate the effects of algal and microbial organic matter and increasing temperature on the accumulation and ecological risk of PAHs in the sedimentary cores. Two sediment cores were collected. PAHs and lipid biomarkers were analyzed. The relationships among PAHs, organic matter parameters, and temperature will help to illustrate the historic records and ecological risks of PAHs in the sediments under the background of global warming.

2. Materials and Methods

2.1. Study Sites and Sampling

Luoma Lake is one of the four largest lakes in Jiangsu province, China (34°00 - 34°14 N; 118°06 -118°18 E) and is used for water supply, aquaculture, irrigation, navigation, and tourism. The average water depth and a surface water area of Luoma Lake are 3.3 m and 260 km^2, respectively. It is a man-controlled, lightly eutrophic reservoir and a transfer station for South-to-North Water Transfer Project. Luoma Lake was once widely regarded as "clean water" before the establishment of industrial factories (Wang et al., 2021).

Hongze Lake (33°06'-33°40'N, 118°10'-118°52'E) is the fourth largest freshwater lake in China (with an area of about 1577 km^2), located at the end of the middle reaches of the Huaihe River, within the territory of Huai 'an and Suqian, across four counties of Hongze, Siyang, Sihong, and Xuyi. Hongze Lake is 65.0 km in length, 55.0 km in maximum width, 24.3 km in average width, 4.37 m in maximum depth, 1.77 m in average depth, and 27.9 $\times 10^8$ m^3 in storage. Hongze Lake has a rapid water exchange period of about 35 d. The main upstream rivers that enter Hongze Lake are distributed on the west side of the lake, including Huaihe River, Chongtong River, Suihe River, An River, and Weiqiao River, among which the Huaihe River is the largest inflow (Cai et al., 2016; Cao et al., 2017).

We collected each sediment core from Luoma Lake (34°2'N, 118°13'E) and Hongze Lake (33°18'N, 118°43'E) in August 2017, respectively (Fig. 1). These sediment cores were sliced at 2 cm intervals, and these subsamples were imme-diately placed into plastic bags, sealed, stored, and transported at low temper-atures (0-10°C). The sediment samples were stored at -20°C in the laboratory until they were freeze-dried and homogenized for chemical analysis.

2.2. Temperature Data and Chronological Dating

The air temperature data of Luoma Lake and Hongze Lake used in this study are collected from https://www.ncei.noaa.gov and https://rp5.ru/, and the selected station is Xuzhou station for LM and Bengbu station for HZ. The activities of radionuclide were conducted in the Institute of Geochemistry, Chinese Academy of Sciences, Guiyang. The activity of ^{210}Pb was calculated from the peak area of 46.5 KeV-ray spectrum, and the activity of ^{226}Ra was calculated from the peak area of ^{214}Pb spectrum (351.9 KeV), and the activity of ^{137}Cs from the peak area of 661.7 KeV-ray spectrum. The activity of ^{210}Pb$_{ex}$ was the difference value between the specific activity of ^{210}Pb and that of ^{226}Ra. The activity of ^{210}Pb$_{ex}$ was used for the chronological calculation based on a constant rate of supply (CRS) dating model.

2.3 Analysis of C, N, and P and Bulk ^{13}C

Total organic carbon (TOC) and nitrogen (TN) were analyzed with a Vario EL III Elementar analyzer (Germany). Before the analysis, the sediment samples (about 500 mg) were treated with 1 M HCl to remove carbonates. The samples were analyzed in duplicate. The mean deviations of the duplicate samples for C and N were $< 0.05\%$. Total phosphorus (TP) was extracted from sediments with 1 M HCl after ignition at 550°C (2 h), and then determined by an ammonium molybdate spectrophotometry (Aspila et al., 1976).

Bulk stable carbon isotopic compositions were measured on acidified sediment samples. The measurement was performed on a ThermoQuest EA coupled on-line to a Finnigan Mat Delta PlusXLS by a Conflo III system. The values are given in formulation as ^{13}C = [(R$_{sample}$ – R$_{std}$)/ R$_{std}$]*1000, where R equals to the ^{13}C/^{12}C ratio in the sediment sample and the standard, and are reported vs. the Vienna Pee Dee Belemnite (VPDB) standard. We corrected the ^{13}C value (^{13}C$_{corrected}$) for the Suess effect using the polynomial equation for the correction, modeled by Verburg (2007) as follows:

^{13}C$_{atm}$ = 7.77 * 10^{-16} * Y^{6} – 1.22 * 10^{-11} * Y^{5} +7.16 * 10^{-8} * Y^{4} – 2.10 * 10^{-4} * Y^{3} + 3.33 * 10^{-1} * Y^{2} – 274 * Y + 917

With Y = year. The calculated, time-dependent depletion for a given year resulted by subtracting from the measured ^{13}C for each dated sediment section.

2.4 Analysis of Rock-Eval Pyrolysis

Rock-Eval analyses were performed with a Rock-Eval 6 pyrolyzer (Vinci Technologies). About 70 mg of the sediment sample was placed in Incoloy crucibles. The Rock-Eval analytical process consists of two sequential heating steps under different ambient conditions. First, we heated bulk sediment in an inert, O$_2$-free oven (300°C-650°C, 25°C min^{-1}), followed by combustion in an oxidation oven (300°C-850°C, 20°C min^{-1}). When long-chained C-compounds cracked they released HC which was recorded as the S2 fraction. Thermal cracking released the S2 fraction of organic matter between 300°C and 650°C, representing high

molecular weight aliphatic hydrocarbons. The ratio of S2 to TOC is hydrogen index (HI).

2.5 Extraction and Analysis of PAHs

Analysis of Σ16PAHs (Table S1, Supporting Information) was performed through a multi-step procedure including Soxhlet-extracted, chromatographic column purification, and GC-MS analysis. First, about 10 g freeze-dried and ground samples were spiked with 5 deuterated surrogate standards (NaP-d_8, Ace-d_{10}, Phe-d_{10}, Chry-d_{12}, and Per-d_{12}), extracted with dichloromethane by using Soxhlet extraction, and activated copper was added for desulphurization during the extraction. Then, the extracts were concentrated, purified, and consequently fractionated on a silica/alumina column (1 cm i.d.). The PAHs were eluted with 60 ml of hexane: methylene chloride (1:1, V: V), and the final extract volume was reduced to 200 L under a gentle N_2 stream. Before instrumental analysis, hexamethylbenzene was added to each of the extracts as the internal standard, and finally, the extracts were analyzed by Agilent 7890A-5975C GC-MS using a DB-5 MS capillary column (30 m×0.25 mm i.d. with 0.25 m film thickness).

The QA/QC samples included procedural blanks and duplicate samples. The average recoveries of NaP-d_8, Acy-d_{10}, Phe-d_{10}, Chry-d_{12}, and Per-d_{12} were 38.2±7.59%, 65.7±4.82%, 89.9±10.3%, 97.0±8.77%, 96.4±8.22%, respectively, with the relative standard deviations <10%. The NaP contents reported in this study were corrected by the recovery rate of NaP-d_8, and the contents of Ace, Acy, and Flu were corrected by the recovery rate of Ace-d_{10}.

2.6 Extraction and Analysis of Sterols and Fatty Acids

Analysis of sterols and fatty acids was performed through a multi-step procedure including Soxhlet-extracted, chromatographic column purification, derivation, and GC-MS analysis. First, about 4 g of freeze-dried and ground samples were spiked with 2 surrogate standards (nonadecanol and deuterated palmitic acid), extracted with CH_2Cl_2:CH_3OH (93:7, V: V) by using Soxhlet extraction, and activated copper was added for desulphurization during the extraction. The neutral and acids components were isolated from the extracts above by saponification with 0.5 N KOH in 95% methanol/5% water solution. Before derivation, the sterols were purified by silica gel (120°C, 4 h) from neutral components. Before GC-MS analysis, the sterols were derivatized using 50 μL of bis(trimethylsilyl)-trifluoroacetamide and trimethylchlorosilane (99:1) and 50 μL of pyridine (70°C, 1 h), and the fatty acids were derivatized using 500 μL of 10%BF_3 methanol solution (60°C, 2 h). Sterol trimethylsilylation products and fatty acid methyl esters were detected by Agilent 7890A-5975C GC-MS using a DB-5 MS capillary column (30 m×0.25 mm i.d. with 0.25 m film thickness).

2.7 Bayesian mixing model

The MixSIAR model is used to calculate the contribution of different sources of organic matter (e.g., macroplants, plankton, C3 plants, C4 plants, sewage)

to sediments. The end-member values of ^{13}C and C/N from different organic matter sources were input into the MixSIAR model (Version 3.1.12) (Stock et al., 2018) written to identify the contributions of different types of organic matter sources. In this study, ^{13}C values of macrophytes, plankton, C3plants, C4plants, and sewage sources were -23.5±3.5‰, -27.5±4.5‰, -29.8±0.5‰, -15.3±4.2‰, -25.3±2.8‰, respectively; and the C/N values are 20±10, 6.5±1.5, 18±7.3, 15±4.6, 12.5±0.8 (Guo et al., 2020; Duan et al., 2022). The Markov chain Monte Carlo algorithm was set as "normal" and the Gelman-Rubin and Geweke diagnostic tests were used to evaluate the reliability of the output data (Stock and Semmens, 2013). In general, a Gelman-Rubin diagnostic value < 1.05 indicates that the output data is reliable. In this study, we demonstrate that scatterplots of ^{13}C and C/N are reliable for qualitative assessment of OM sources, suggesting that the combination of ^{13}C and C/N can be used to calculate proportional contributions in sediments.

2.8 Data Analysis

Pearson's correlation analysis and principal component analysis (PCA) were performed by using SPSS 26.0 (IBM SPSS software). Pearson's correlation analysis was useful in quantitatively assessing the relationship between PAHs and lipid biomarkers. The significant level was set to $p < 0.05$. Pearson's correlation coefficient is a nonparametric rank statistic proposed as a measure of the strength of the association between two variables and is widely used for this purpose (Duan et al., 2015).

3. Results

3.1 Chronological Dating

^{210}Pb, ^{137}Cs, and ^{226}Ra contents in the two sediment cores were analyzed. The activities of ^{210}Pb$_{ex}$ in LM and HZ are 11.9-69.7 Bq · kg^{-1} and 19.7-137 Bq · kg^{-1}, respectively. The activities of ^{137}Cs in LM and HZ are 0.361-3.83 Bq · kg^{-1} and 0.344-1.83 Bq · kg^{-1}, respectively. Ages and sedimentation rates were estimated from the ^{210}Pb (half-life 22.23 ± 0.12 years) activities by using the constant rate of supply (CRS) model (Ontiveros-Cuadras et al., 2012). To check the ^{210}Pb dates, the samples were also analyzed for ^{137}Cs activity (half-life 30.05 ± 0.08 years), of which accumulation peak in sediments in 1963 is considered to be the important time mark (Ritchie & Mchenry, 1990).

It was found that the ages of the sediment cores in LM and HZ range from 1889 to 2012 and from 1947 to 2012, respectively. Sediment accumulation rates (SAR) vary from 0.18 to 0.54 cm yr^{-1} and from 0.19 to 0.50 cm yr^{-1} in the sediment cores at LM and HZ, with mass accumulation rates (MAR) in the ranges of 0.07-0.26 g cm^{-2} yr^{-1}. Figure S1 (Supporting Information) showed an obvious difference in the dating given by ^{210}Pb$_{ex}$ and ^{137}Cs, it may be due to the low ^{137}Cs activities leading to a large error in dating. Thus, we used the result calculated by ^{210}Pb$_{ex}$ in this study.

3.2 Bulk Parameters and Temperature data

TOC, S2, and HI were determined by the Rock-Eval pyrolysis and were presented in Figure S2 (Supporting Information). TOC ranges from 3.15 to 7.05 mg g^{-1} and from 6.41 to 8.60 mg g^{-1} in LM and HZ, respectively. S2 values are in the ranges of 0.15-0.54 mg HC g^{-1} and 0.28-0.52 mg HC g^{-1}, and HI values are in the ranges of 49.3-84.6 mg HC gTOC^{-1} and 45.2-63.7 mg HC gTOC^{-1} in the sediment cores from LM and HZ. The ^{13}C values ranged from -27.1‰ to -25.8‰ with an average of -26.5‰ in LM, and ranged from -25.8‰ to -25.4‰ with an average of -25.6‰ in HZ. The ^{13}C values show a downcore decreasing trend in LM while no obvious downcore trend in HZ is observed. TP contents in LM and HZ vary from 0.34 to 0.49 mg g^{-1} and from 0.66-0.71 mg g^{-1}, respectively. TN contents in LM and HZ are in the range of 0.22-0.84 mg g^{-1} and 0.49-0.74 mg g^{-1}, respectively.

Meteorological data has been obtained from the two stations in the investigated region since 1951. Figure 2 showed the change trends of annual average temperature and five-year-moving annual average temperature (T$_5$) at Xuzhou and Bengbu stations. As the T$_5$ values are easily affected by local heat island and variations, the regression equations between the long-term annual average and time are used. The regression equations are quite good as the regression coefficients are highly significant. The annual average temperatures (T$_{\mathrm{fit}}$) in each of the lakes are estimated from the regression equations.

3.3 PAHs and Lipid Biomarkers Contents and Profiles in Sediment Cores

The distribution pattern of PAHs was different in LM and HZ. The contents of Σ16PAHs in LM and HZ ranged from 131 ng g^{-1} to 468 ng g^{-1} and from 164 ng g^{-1} to 627 ng g^{-1}, respectively. The contents of 16 PAHs in the sediment cores were shown in Table S2 and S3 (Supporting Information). High molecular weight PAHs (HMW-PAHs), including Fla, Pyr, B[a]A, Chry, B[b]F, B[k]F, B[a]P, InP, D[a,h]A and B[g,h,i]P, increased sharply in LM and HZ. Low molecular weight PAHs (LMW-PAHs), including NaP, Acy, Ace, Flu, Phe, and Ant, oscillated in LM and increased in HZ.

4. Discussion

4.1 Ecological Risk Assessment and Sources of PAHs

In order to reasonably assess the potential hazards of PAHs in the sediments, effective assessment methods have been proposed. Among them, the effects range-low (ERL) and the effects range-median (ERM) values have become typical ecological risk assessment methods for PAHs, and are widely used in sediments (Qiao et al., 2006). Moreover, high-cyclic PAHs have higher carcinogenic and mutagenic risks, and the total toxic B[a]P equivalent (TEQ) and the total mutagenic B[a]P equivalent (MEQ) of 8 PAHs (B[a]A, Chry, B[b]F, B[k]F, B[a]P, InP, D[a,h]A and B[g,h,i]P) can be calculated to evaluate the health risks of PAHs in the aquatic environment (Rogula-Kozlowska et al., 2013; Nisbet et al., 1992). Table S4 (Supporting Information) lists the PAH content ranges in this study in comparison with ERL and ERM values. Table S5 (Supporting

Information) lists the total toxic B[a]P factor (TEF) and the total mutagenic B[a]P factor (MEF) of 8 PAHs. The formula for calculating the concentration is presented as follows:

$TEQ = \Sigma C_i * TEF$ (1)

$MEQ = \Sigma C_i * MEF$ (2)

The results showed that, except for the Flu contents in the surface sediments, which were higher than the effective low value, the rest of the PAHs were lower than the ERL values, indicating that the overall ecological risks of PAHs in the sediments from LM and HZ were still at a low level. However, as shown in Figure 3, the TEQ and MEQ showed a trend of gradual increase, indicating that the health risk in sediments was increasing. In addition, the TEQ and MEQ of PAHs in LM and HZ showed a trend of rapid increase from 1960, which is later than the time of rapid increase in the deposition records of PAHs in global lake sediments (Wang et al., 2021). The modern human activities during urbanization and industrialization are the main driving force leading to the increasing deposition flux of PAHs. However, the time of China's economic development lags behind that of developed countries, and the starting point of the rapid growth of PAHs is later than that of developed countries. The sedimentary records of PAHs in Luoma Lake and Hongze Lake reflect this difference. As shown in Figure 3, the content of PAHs in sediments increased rapidly during the 20 years after 1960, indicating that human activities had a significant impact on the record of PAHs content in sediments.

Yan et al. (2019) reviewed the concentrations of airborne particulate PAHs in China, and their results showed that the concentrations of PAHs showed a decreasing trend since 2000. This may be related to the possibility of effective mitigation measures (Wang et al., 2007; Zhuo et al., 2017; Duan et al., 2015). In addition, strict and mandatory legislation has been implemented to control air pollution in some cities with heavy smog (Zhuo et al., 2017). However, Figure 3 shows the continuous increase of TEQ and TMQ in sediments from Luoma Lake and Hongze Lake since 2000, suggesting that anthropogenic emission is not the major factor, but the bioaccumulatioj of PAHs in the lakes also led to the increase of PAHs in the sediments.

PCA was used to further identify the sources of PAHs in LM and HZ (Figure S3, Supporting Information). Previous studies found that individual PAHs indicated different combustion sources (Ravindra et al., 2008). Based on the individual PAH contents for LM, two principal components were extracted: PC1 and PC2. The percentages of these components were 65.2% and 28.1% of the total variance in the PAH contents, respectively. PC1 included PAHs with three to six rings (including Fla, Pyr, B[a]A, Chry, B[b]F, B[k]F, B[a]P, InP, D[a,h]A, and B[g,h,i]P) and relatively low loading for NaP, Acy, Ace, Flu, Phe and Ant. Thus, PC1 indicates vehicle emissions, natural gas combustion, and coal and wood combustion are the predominant PAH sources, and PC2 indicates coal and wood combustion sources. As for HZ, the percentages of PC1 and PC2

were 61.7% and 35.4% of the total variance in the PAH contents, respectively. PC1 included PAHs with three to six rings (including Phe, Ant, Fla, Pyr, B[a]A, Chry, B[b]F, B[k]F, B[a]P, InP, D[a,h]A, and B[g,h,i]P) and relatively low loading for NaP, Acy, Ace, and Flu. It showed similar PAH sources to those of LM. The factor score plots displayed increasing trends in PC1 after 1960 in LM and HZ. Therefore, the sediment cores from LM and HZ contain the deposits of PAHs derived from mixed sources of vehicle emissions, natural gas combustion, and coal and wood combustion (Ravindra et al., 2008).

4.2 SOM

Aquatic and terrestrial organic matter are the two major sources of SOM. The ^{13}C composition is often used to distinguish the sources of SOM (Meyers, 1997; Cerling and Harris, 1999). Previous studies have shown that algae in the lake are rich in protein and have lower cellulose contents, and their C/N values are generally between 4 and 10. But terrestrial vascular plants have rich cellulose contents and lower protein content, and their C/N values are generally higher than 20 (Meyers, 1997). Moreover, the HI values derived from the Rock-Eval analysis reflect the proportion of high molecular weight aliphatic hydrocarbons (pyrolysis products between 300-650°C) in the aquatic SOM fractions. But the HI value of terrestrial SOM is lower than that of leaf wax, and is much lower than that of algae (Talbot and Laerdal, 2000). Hence the comprehensive analyses of ^{13}C, C/N, and HI can more accurately identify the sources of SOM.

As shown in Figure S4 (Supporting Information), the HI values in the LM sediments are slightly higher than from HZ, but their values are much lower than the reported data for some eutrophic lakes, but are similar to those for mesotrophic lakes (Bechtel and Schubert, 2009). *Chlorophyta*, and *Diatomeae* are the dominant phytoplankton species in LM and HZ (Yang and Hu, 2010). Moreover, the phytoplankton biomass in Hongze Lake was reported higher than that in Luoma Lake (Peng et al., 2010). But the HI values in Figure S4 (Supporting Information) are lower than those in LM, which might be related to the different inputs of terrestrial organic matter. The C/N average of HZ is around 15, indicating mixed aquatic and terrestrial organic matter input. However, the C/N average in LM is generally lower than 10, which indicates that algal organic matter input is the major SOM component in LM. However, due to the wide ranges of C and N sources of SOM and the influences of sediment particle size distribution and mineral composition, we analyzed the stable carbon isotope composition to further determine the origin of SOM. The ^{13}C values of terrestrial C4 plants range from -15‰ to -10‰, those of C3 plants range from -30‰ to -24‰, and those of organic matter from aquatic algae range from -30‰ to -25‰ (Meyers, 1997). Due to the increase in human activities in recent years, CO_2 emissions from fossil fuel burning will change the ^{14}C and ^{13}C composition of CO_2 in the atmosphere (the Seuss effect) (Verburg, 2007). Recent studies have shown that it is necessary to carry out Seuss correction for the ^{13}C of SOM in lakes, especially for the reconstruction of lake primary productivity. Therefore, we corrected ^{13}C for the Seuss effect in LM and HZ, which is shown in Figure

S5 (Supporting Information). The corrected ^{13}C values ranged from -26‰ to -22‰, indicating that the current SOM sources of LM and HZ were a mixture of terrestrial and aquatic sources. The ^{13}C values in LM showed a gradually increasing trend after the correction, which was consistent with the variation trends of TOC and HI. The ^{13}C values after the correction in HZ showed a continuously increasing trend after 1960. In general, the SOM fractions in LM and HZ showed mixed sources from terrestrial and aquatic organic matter, but the SOM fractions in LM showed a high portion derived from aquatic organic matter.

According to the scatter diagram of ^{13}C vs. C/N, the contribution of plankton sources accounted for 50% and 11% of SOM sources in Luoma Lake and Hongze Lake (Fig. 5). The contribution ratios of macrophytes, plankton, C3plants, C4plants and sewage were 4.5±0.2% and 27.5±0.4%, 6.1±0.2% and 13.6±0.3%, 3.4±0.1% and 12.8±0.5%, 54.0±2.1% and 11.3±0.2%, and 32.0±1.6% and 34.8±0.6% in LM and HZ (Tab. S6. Supporting Information), respectively. By multiplying the contribution of plankton source in each layer by the corresponding TOC, the historical changes of plankton source organic carbon in lake sediments were obtained. They all showed a trend of gradual increase, indicating that the plankton source organic matter in the sediments was gradually increasing. Algae is an important part of lake plankton, and the increase of organic matter from plankton indicates the gradual increase of lake primary productivity.

The use of lipid biomarkers to distinguish the sources of organic matter has been widely used in lake SOM studies (Tuo et al., 2011; Randlett et al., 2017; Arnold et al., 2019). Compared with the apportionment of organic matter by using C/N, ^{13}C, and HI, recent studies mainly focus on certain aquatic organic matter derived from *Cyanobacteria*, *Diatomeae*, and bacteria (Bridous et al., 2011; Zhang et al., 2017). Organic matter of different biological origins can be distinguished according to the special components (sterols, fatty acids, alkanes, etc.) in cell membranes or cell walls of organisms (Rotani and Volkman, 2003; Volkman, 2005). Therefore, brassicasterol in the diatom cell membrane and *iso-/ anteiso-*C$_{15:0}$ / C$_{17:0}$ fatty acids in Gram-positive bacteria cell membrane has been widely used to study the contribution of diatom and bacteria to SOM in sediments. In this investigation, brassicasterol and branched fatty acids (*iso-* and *anteiso-*C$_{15:0}$, *iso-* and *anteiso-*C$_{17:0}$) were detected in LM and HZ. The contents of brassicasterol were in the range of 0.08-0.59 µg g-1 in LM and 0.11-0.55 µg g-1 in HZ. The contents of branched fatty acids were in the range of 0.76-2.85 µg g-1 in LM and 0.61-1.25 µg g-1 in HZ. As shown in Figure S6 (Supporting Information), the trends of brassicasterol contents in LM and HZ were quite similar. However, there were few reports on the contents of brassicasterol in lake sediments in China, which mainly dealt with those in lake sediments in the Tibetan Plateau, and in estuarine, coastal, and marine sediments (Xing et al., 2011; Chen et al., 2017; Pu et al., 2017). The contents of brassicasterol in LM and HZ were similar to those in the coastal muddy area of Zhejiang province and the sediment of the East China Sea (Chen et al., 2017).

The diatom in LM and HZ increased gradually since 1960, which is similar to the variation trends of TOC and HI, indicating that phytoplankton productivity also increased gradually in recent years. The contents of branched-fatty acids as bacterial biomarkers also showed a similar trend, suggesting that heterotrophic bacteria utilizing algal organic matter may be the major contributor of bacterial organic matter in LM and HZ.

4.3 Relationship between PAHs and Aquatic SOM

Previous studies have shown that PAHs in tropical reservoir sediment were enriched by algal organic matter (Duan et al., 2015), and demonstrated that the algal organic matter affected the transport and accumulation, and the fate of PAHs in the sediments. Temperature and nutrient status are the important factors that affect lacustrine algae growth and will have direct effects on the distribution of PAHs.

To illustrate the relationships of PAHs with aquatic organic matter derived from diatoms and bacteria in LM and HZ, the Pearson's correlation analyses among the LMW-PAHs, HMW-PAHs, and the SOM parameters (TOC, HI, S2, C/N, $^{13}C_{corrected}$), TN, TP, T_{fit}, and diatom and bacteria biomarker contents were performed (Table 1).

In LM, there were significant positive correlations between PAHs and TOC, TN, TP, HI, S2, diatoms, and bacteria. In addition, diatoms and bacteria also had significant positive correlations with TOC, TN, TP, HI, and S2. These results indicated that the increase of algal organic matter in the SOM of LM had an important influence on the lacustrine SOM, and can enrich PAHs. Moreover, the algal organic matter had a very significant positive correlation with bacteria biomarkers, which suggested that bacterial organic matter is mainly composed of bacteria utilizing algal organic matter. No significant correlations among $^{13}C_{corrected}$, C/N, and LMW-PAHs were found. To explore the impacts of these factors on individual PAHs, we conducted a linear correlation analysis of TOC, HI, S2, diatom, and bacteria with individual PAHs, respectively. The analysis results were shown in Figures S7-S11 (Supporting Information). The correlations of individual PAHs with these influencing factors were significant. Only Ace, Flu, and Phe congeners showed some exceptions as their data were more variable in the sediment core. Algae can remove PAHs from water through enrichment (Hou et al., 2016), Kirso and Irha (1998) studied the B[a]P by several typical algae in fusobacteria, Rhodophyta, Chlorophyta, and Rhodophyta. The results showed that different algae had different effects on the bioenrichment of B[a]P, but all had important effects on the behavior of B[a]P in the environment. Most PAHs in the sediments have a significant positive correlation with total nitrogen, but only low-cyclic PAHs have a significant correlation with total phosphorus, which may be due to the similar source between organic carbon and total nitrogen in the sediments of Luoma Lake (Liu et al., 2021), thus showing an accumulation feature similar to the enrichment of total organic carbon.

In HZ, positive correlations of PAHs with TOC, S2, $^{13}C_{corrected}$, and bacteria

proxy were significant (Table 1). There was also a significant positive correlation between bacteria and diatom, indicating that the bacterial organic matter in HZ was mainly heterotrophic bacteria that digested and consumed algae. But PAHs showed no significant positive correlation with diatom proxy. Previous investigations showed that the priority algal phytoplankton species still predominantly consisted of Bacillariophyceae, Chlorophyta, and cyanobacteria, but diatom cell abundance and biomass were lower than those of cyanobacteria and Chlorophyta (Yang and Hu, 2010). As a result, the diatom organic matter in the sediment was not the major component of the algal organic matter and did not play a major role in the enrichment of PAHs in HZ. Unlike LM, TN and HI did not show significant positive correlations with PAHs, which may be because the TN sources are complex, and the HI reflects the S2 ratio to TOC. As demonstrated above, SOM is mixed with aquatic and terrestrial sources. However, as the organic matter from algae represented by S2 did not account for the main component of the total organic matter, no significant positive correlation between HI and PAHs was observed. In addition, a significant positive correlation between PAHs and S2 also confirmed the enrichment effect of aquatic organic matter on PAHs. Similarly, to investigate the response of individual PAHs to different productivity factors, we conducted linear correlation analysis among TOC, S2, $^{13}C_{corrected}$, bacteria, and the individual PAHs, respectively. The analysis results were shown in Figure S12-S15 (Supporting Information). Although 16 kinds of PAHs were not related to HI, which may be related to the low HI values in Hongze lake sediments, S2 showed a significant correlation with PAHs, which was similar to that of the total organic carbon, Hence algae organic matter in Hongze Lake also played a role in the bioaccumulation of PAHs in sediments. The above facts indicated that the enrichment effect of aquatic SOM on PAHs was significant.

Climatic change has been observed in this region. As shown in Figure 2, the annual average temperature has risen by 1.5-2.0°C. Thus, the data support overall warming over the past 70 years. In both Luoma Lake and Hongze Lake, a significant positive correlation between temperature and adjusted stable carbon isotopes was observed, suggesting that rising temperature promoted the increase of lake productivity. Moreover, a very significant positive correlation between temperature and PAHs in HZ was observed. It is noted that a significant positive correlation between temperature and HMW-PAHs in LM was also observed, which indicated that the increasing temperature promoted the accumulation of HMW-PAHs in the lake. Figure 4 showed the PCA analysis among PAHs, biomarkers, organic matter parameters, nutrients, and T_{fit} in LM and HZ. The proxies of lake productivity, including TOC, HI, and S2, were represented by PC1, which accounted for about 60% of the total variance. Because LM Lake has undergone several large-scale man-made transformations, the impact of temperature on the lacustrine productivity is relatively small. Moreover, the T_{fit} parameters in HZ were not only closely related to the lacustrine productivity, but they also had a strong correlation with PAHs. The PC1 score plot of HZ had a significant increasing trend between 1970 and 2000, which was highly

consistent with the temperature change trend (Fig 3). This suggested that PC1 represented the effect of climate warming on the lacustrine productivity in HZ Lake.

Although the contents of PAHs were lower than the ecological risk limit values, their health risks increased by more than 4 times in the last six decades. The algal organic matter had a significant enrichment effect on PAHs. Due to the enrichment effect, the internal cycling and input of nutrients should be controlled to prevent the rapid growth of algae in the lakes. It was observed that global warming enhanced the accumulation of aquatic SOM and PAHs. This paper only analyzed the biomarkers of diatoms and bacteria, and the follow-up investigation should use other algal and microorganism biomarkers, so that we can better understand the algae and microorganism community changes and their effects on the enrichment of PAHs.

5. Conclusions

This study investigated the PAHs, brassicasterol, and branched fatty acids, as well as the application of Rock-Eval pyrolysis technology to explore the composition and source of SOM. The source apportionment model, correlation analysis, and principal component analysis were also used to identify the sources of PAHs and SOM. The air temperature in Luoma Lake and Hongze Lake increased significantly in the past 70 years. TOC, HI, S2, and $^{13}C_{corrected}$ increased under the background of global warming, suggesting that global warming promoted the accumulation of aquatic organic matter and the increasing lake productivity in LM and HZ. The algal organic matter in Luoma Lake and Hongze Lake controlled the deposition of PAHs in the sedimentary environment. The potential risk of PAHs in the sediments is still at a low level. However, since 1960, both TEQ and MEQ of PAHs show a trend of a rapid increase due to the bioaccumulation of algal organic matter and the impact of human activities, indicating the potential ecological risks in lake sediments were rapidly increasing. It is necessary to reduce the emission and input of PAHs to reduce their ecological risks.

Supporting Information:

Methods for the instrumental analysis of PAHs, sterols, and fatty acids, data tables of polycyclic aromatic hydrocarbon contents, and plots of linear correlation analysis among PAHs, organic matter parameters, and nutrients are presented.

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Tables

Table 1. Correlations between SOM parameters, TN, TP, T$_{fit}$, lipid biomarkers, and PAHs in LM and HZ.

Figures

Figure 1. Sampling sites and weather stations.

Figure 2. Annual average temperature (T), five-year-moving annual average temperature (T$_5$), and the annual average temperature is calculated by the regression equation of the annual average temperature (T$_{fit}$) at Xuzhou and Bengbu stations.

Figure 3. Historical changes in TEQ and MEQ from LM and HZ.

Figure 4. PCA loadings and factor scores plots of PAHs, biomarkers, organic matter parameters, nutrients, and T$_{fit}$ in LM and HZ.

Figure 5. Scatterplots of ^{13}C vs. C/N ratios, plankton OM record, and the proportional contributions of OM from different end members for sediments in LM and HZ.

Table 1. Correlations between SOM parameters, TN, TP, T$_{fit}$, lipid biomarkers, and PAHs in LM and HZ.

	TOC	TN	TP	HI	S2	C/N	^{13}C$_{corrected}$	T$_{fit}$	Diatoms	Bacte
LM										
TOC	1.000	.963**	.911**	.884**	.980**	-0.082	0.092	0.394	.677*	.799**
TN		1.000	.849**	.914**	.969**	-0.338	0.121	0.504	.727**	.811**
TP			1.000	.808**	.888**	-0.014	0.088	0.414	0.436	.627*
HI				1.000	.954**	-0.265	0.340	.697*	.728**	.767**
S2					1.000	-0.160	0.207	0.520	.727**	.815**
C/N						1.000	0.009	-0.388	-0.242	-0.157
^{13}C$_{corrected}$							1.000	**.707***	0.056	-0.149
T$_{fit}$								1.000	0.202	0.188
Diatoms									1.000	**.903***
Bacteria										1.000
LMW-PAHs										
HMW-PAHs										
HZ										
TOC	1.000	0.488	.632*	0.342	.851**	0.463	.769**	.774**	0.251	.639*

TN	1.000	0.008	0.166	0.417	-0.537	0.106	0.190	-0.013	0.151
TP		1.000	0.313	0.615	0.595	.861**	.885**	0.582	.672*
HI			1.000	.782**	0.221	0.373	0.408	-0.102	-0.078
S2				1.000	0.422	.725*	.745*	0.138	0.396
C/N					1.000	.651*	0.584	0.174	0.399
$^{13}C_{corrected}$						1.000	**.973****	0.321	0.467
T_{fit}							1.000	0.344	0.504
Diatoms								1.000	.817**
Bacteria									1.000
LMW-PAHs									
HMW-PAHs									

*Significant correlation at $p < 0.05$ (Two-tailed); **Significant correlation at $p < 0.01$ (Two-tailed).