Historical records of polycyclic aromatic hydrocarbon deposition in a shallow eutrophic lake: Impacts of sources and sedimentological conditions

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Sediment core samples collected from Lake Chaohu were analyzed for 15 priority polycyclic aromatic hydrocarbons (PAHs) to assess the spatial and temporal distributions of the PAHs during lacustrine sedimentary processes and regional economic development. Assessing the PAH sedimentary records over an approximately 100-year time span, we identified two stages in the PAH inputs and sources (before the 1970s and after the 1970s) in the eastern lake region near a village, whereas three stages (before the 1950s, 1950s–1990s and after the 1990s) were identified in the western lake region near urban and industrial areas. Rapid increases in the PAH depositional fluxes occurred during the second stage due to increased human activities in the Lake Chaohu basin. The composition and isomeric ratios of the PAHs revealed that pyrolysis is the main source of PAHs in this lake. Strong positive relationships between PAH concentration and the total organic carbon concentration, sediment grain size (<4 μm), as well as the local population and Gross Domestic Product indicated that the sedimentary conditions impact the depositional characteristics of the PAHs; simultaneously, socioeconomic activities, such as energy consumption and the levels of urban industrialization and civilization, affect both the composition and abundance of the PAHs.

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Keywords: PAHs, Vertical distribution, Flux, Sedimentological impact, Socioeconomic

Introduction

Polycyclic aromatic hydrocarbons (PAHs), a group of ubiquitous organic pollutants listed as priority pollutants by the international environmental protection agencies, have raised significant environmental concern due to their toxic, carcinogenic, and mutagenic characteristics, on regional and global scales (Xu et al., 2005; Wilcke, 2007; Okuda et al., 2010; Li et al., 2012a; Nie et al., 2014). Although they can arise from both natural and anthropogenic sources, the PAHs released into the environment stem mainly from anthropogenic sources, including the incomplete combustion of fossil fuels and biomass, waste incineration, and traffic emissions (Yunker et al., 1996; Leite et al., 2011; Chen et al., 2012; Azoury et al., 2013).

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2013). Previous studies have shown that PAHs correlate well with anthropogenic activities (Liu et al., 2012b); thus, PAHs are treated as a useful geochemical marker to trace the impact of anthropogenic activities, such as socioeconomic changes and energy use (Schneider et al., 2001; Lima et al., 2002; Liu et al., 2012b). Because they are highly hydrophobic and weakly soluble, PAH compounds are typically attached to fine particles in the environment and are eventually incorporated into lake or sea sediment via runoff and atmospheric fallout (Mouhri et al., 2008; Hui et al., 2009; Guo et al., 2011b). However, the PAH pollutants trapped in lake or sea sediments can sometimes return to the water column, causing secondary pollution (Machado et al., 2014). Using dated, segmented sediment core samples is a well-established method for reconstructing the historical records of anthropogenic PAH input into the environment and for assessing temporal environmental changes, such as human population growth and land settlement (Kannan et al., 2005; Ihlo et al., 2010; Arp et al., 2011; Li et al., 2012b). In addition, lake sediments are more efficient in revealing historical contamination than marine sediments due to the more limited post-depositional mixing processes in lacustrine systems (Guo et al., 2010).

Lake Chaohu is one of the five largest freshwater lakes in China and is located in the lower reach of the Yangtze River (Huo et al., 2013). Lake Chaohu plays an important role in supporting the more than 9.1 million people living in Anhui Province, Eastern China (Wang et al., 2013). Several studies have investigated the historical contamination characteristics of different pollutants in relation to human activities in Lake Chaohu, such as eutrophication and pollution by heavy metals (Zan et al., 2011a, 2011b; Wang et al., 2013; Wang et al., 2014). Nevertheless, reports on the sedimentary records of PAHs are rare for Lake Chaohu. During recent decades, China has experienced rapid economic development, especially after the implementation of the Reform and Opening policy in 1978 (Liu et al., 2012b). This social trend resulted in an increasing consumption of energy, particularly the massive combustion of coals, biomass and foils oils, which consequently caused vastly increased emissions of PAHs (Yunker et al., 1996). However, most studies of PAHs have focused on near-shore estuarine areas (Liu et al., 2000, 2005; Zhang et al., 2009), and few studies have examined the influence of socioeconomic development on PAH contamination in inland shallow water lakes in China (Liu et al., 2012b). Because sediment records in the semi-enclosed Lake Chaohu have been well preserved by stratification, using the depositional fluxes and concentrations of PAHs in the sediment can reveal both the historical impact of socioeconomic development and the sedimentological changes in the inland Lake Chaohu.

In the present study, four dated sediment cores from different regions of Lake Chaohu were used to (1) reconstruct the PAH contamination history to provide a comprehensive picture of the temporal trends in PAH emissions in a typical inland, shallow lake in Eastern China, i.e., Lake Chaohu; (2) identify the possible sources of PAHs; and (3) evaluate the relationship between PAH pollution and socioeconomic development together with sedimentological changes.

1. Materials and methods

1.1. Study area and sampling

Lake Chaohu, located in Anhui Province, Eastern China (117°16′–117°51′N, 31°25′–31°43′E), has a mean depth of approximately 3.0 m and a surface area of 780 km². Six main rivers, providing approximately 80% of the runoff volume from the catchment area, feed into Lake Chaohu, and the outlet, the Yuxi River, is the only channel linking the lake to the Yangtze River (Fig. 1). The Nanfei River and the Shiwuli River are the principal sources of pollutant inflows into the western lake region (Zan et al., 2012).

The sampling sites were chosen away from lake banks, stream inlets and the lake outlet to diminish any disturbance of the sediment by scouring or re-suspension. Eight cores were obtained in July, 2009 at four sites, C4, C5, C6 (western lake region) and C10 (eastern lake region), with two cores taken at each site. A coring sampler was used to insert an 8 cm inner diameter 50 cm long PMMA tube into the lake sediment. After siphoning overlying water on the sediment-water interface, the sediment in each core (ca. 30 cm) was immediately sectioned at 2-cm intervals. The labeled slices were placed in aluminum foil, which had been prewashed by methylene chloride, and temporarily kept in iceboxes at –4°C. Then, the samples were transferred to the laboratory and stored frozen below –20°C. All the sediment samples were freeze-dried at –50°C, homogenized via grinding with an agate mortar and pestle, and passed through a 100 mesh sieve before analysis.

1.2. Sample preparation and analysis

A detailed description of the analytical methods has been provided in a previous study (Zeng et al., 2012). Briefly, the freeze-dried and homogenized samples (10 g) were Soxhlet extracted with a mixed solvent (200 mL) of hexane and dichloromethane (1:1 by volume) for 48 hr. In addition, a mixture of deuterated PAHs (naphthalene-d10, acenaphthene-d10, phenanthrene-d10, chrysene-d13, and perylene-d12) was spiked as the recovery surrogate. About 2 g of activated copper was added to the extract solvent for desulphurization. The obtained extract was filtered, solvent-exchanged to hexane and then concentrated to less than 1 mL. The purification and fractionation process was performed on a two-layer 3% deactivated alumina/silica gel (1:2 by volume) column. The first fraction, eluted with 15 mL hexane, was collected for another purpose, which is not further discussed here. The second fraction, containing the PAH components, was eluted with a 70 mL mixture of hexane:dichloromethane (7:3, V/V), then solvent-exchanged and concentrated to 0.2 mL under a gentle nitrogen stream. The internal standard hexamethylbenzene (HMB) was added to each sample extract before instrumental analysis.

The identification and quantification of 15 priority PAHs (acenaphthylene (Acy), acenaphthene (Ace), 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), indeno(1,2,3-cd)pyrene (IcdP),

<table>
<thead>
<tr>
<th>Name</th>
<th>Description</th>
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<tbody>
<tr>
<td>Acy</td>
<td>Acenaphthylene</td>
</tr>
<tr>
<td>Ace</td>
<td>Acenaphthene</td>
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<td>Flu</td>
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<td>Phe</td>
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<td>Ant</td>
<td>Anthracene</td>
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<td>Fla</td>
<td>Fluoranthene</td>
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<td>Pyr</td>
<td>Pyrene</td>
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<td>BaA</td>
<td>Benzo(a)anthracene</td>
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<td>Chr</td>
<td>Chrysene</td>
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<td>BbF</td>
<td>Benzo(b)fluoranthene</td>
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<td>BaP</td>
<td>Benzo(a)pyrene</td>
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<tr>
<td>IcdP</td>
<td>Indeno(1,2,3-cd)pyrene</td>
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then hold for 5 min at 295°C. Both the full scan mode and hold for 2 min, increase to 295°C at a rate of 3°C/min, and

The GC oven temperature was programmed to start at 70°C, low recovery rates in measurements (Tao et al., 2006). The detectable PAHs are most likely ascribed to the sociopolitical changes in the 1940s may reflect World War Two (1937–1945) or the Chinese Civil War (1946–1949) (Guo et al., 2011b; Liu et al., 2012a). The resulting focusing factors for the western lake region (1.97 for cores C4, C5 and C6) were significantly different between the western region (C4, C5 and C6) and the eastern region (C10) in Lake Chaohu. Focusing factor, defined as the ratio of unsupported 210Pb inventory to atmospheric deposition of 210Pb activity, was used to measure the degree of sediment focusing (Zhu and Hites, 2005; Liu et al., 2012a). The resulting focusing factors for the western lake region (1.97 for cores C4, C5 and C6) were greater than that for the eastern lake region (0.97 for core C10). The PAH concentrations accumulated in cores C4, C5 and C6 from the western lake region exhibited three different stages (Fig. 2): a rather slow growth period prior to the 1940s, a sharp increase from the 1950s to the 1990s, and a significant decline from the 1990s to the present. During the first stage (before the 1940s), these relatively low and constant levels of PAHs may be due to the emissions from domestic wood combustion in the economically underdeveloped period (Chen et al., 2013) or the atmospheric deposition from the rapid development of natural gas industries abroad (Lima et al., 2002; Guo et al., 2006). The first obvious increase observed in the 1940s may reflect World War Two (1937–1945) or the Chinese Civil War (1946–1949) (Guo et al., 2011b; Liu et al., 2012b). During the second stage, the increasing trends of total PAHs are most likely ascribed to the sociopolitical changes.

dibenzo(a,h)anthracene (DBahA), and benzo(g,h,i)perylene (BghiP) were performed with a Gas Chromatograph–Mass Spectrum (QP 2010, Shimadzu Corporation, Japan) equipped with a DB-5MS fused silica capillary column (30 m x 0.25 mm i.d. with a 0.25 μm film thickness; Agilent Technologies) to separate the individual PAHs. Naphthalene (Nap) and the recovery surrogate naphthalene-d8 were not quantified due to their tendency for high volatility and low recovery rates in measurements (Tao et al., 2006). The mass spectrometer was operated in electron impact mode. The GC oven temperature was programmed to start at 70°C, hold for 2 min, increase to 295°C at a rate of 3°C/min, and then hold for 5 min at 295°C. Both the full scan mode and selected ion mode (SIM) were used for qualitative analysis.

1.3. Quality assurance and control

A series of standard spiked blanks, a procedural blank, a standard-spiked matrix, and a random duplicate sample were processed for every 15 analyzed samples as quality control measures. PAH recoveries of the standard-spiked blanks and the matrix-spiked samples ranged from 74.4%–110.6%. The average recoveries of the surrogate standards were 69.7% ± 9.1% for acenaphthene-d10, 80.6% ± 12.2% for phenanthrene-d10, 85.4% ± 13.8% for chrysene-d12, and 94.5% ± 14.9% for perylene-d13. The detection limits for each PAH ranged from 0.03 to 0.21 ng/g dry weight. Only trace levels of PAHs were detected in the procedural blanks, and all were below the detection limits. Each of the duplicate samples had a relative standard deviation of less than 15%. All the PAH individual peaks were corrected with the mass, area and retention time of the corresponding spiked standard.

1.4. Dating of the sediment cores

Geochronological dating of the sediment cores in Lake Chaohu was performed using the 137Cs activities combined with the 210Pb activities. In brief, the 137Cs activities were determined using γ-spectrometry on a multi-channel spectrometer mated to a coaxial detector (efficiency 50%) with γ-emission of 661.6 keV. The 137Cs peaks in the sediment cores corresponded to the maximum atmospheric fallout due to the nuclear testing conducted in the mid-1960s. The activity of 210Pb was obtained by subtracting the 226Ra activity from the total 210Pb activity (Wan et al., 1987). The 210Pb activities were determined based on α-radioactivity on a Canberra S-100 multi-channel spectrometer with a PIPS Si detector, and the 226Ra activity was determined by gamma-spectrometry on a Canberra S-100 multi-channel spectrometer mated to a GCW3022 H-PR Ge well detector. In this study, constant rate of supply dating models was used to determine the ages based on 210Pb (Zan et al., 2011b), which assumes that the sediment interface receives a constant flux of unsupported 210Pb, and the cumulative dry weights were used to correct for the sediment compaction (Helm et al., 2011). Despite the absence of a longer, more contemporary 210Pb record, both the 210Pb estimated age and the 137Cs peak were consistent in assigning an age of 1963 to the 16–17 cm layer in the C4 and C10 cores. The detailed dating results were previously reported in Zan et al. (2011b), and the average sedimentation accumulation rates were 0.224 g/(cm²-year) for the C4 core and 0.242 g/(cm²-year) for the C10 core. The timing of PAH deposition at sites C5 and C6 was estimated by comparing the concentration-depth profiles of the PAHs at site C4.

2. Results and discussion

2.1. Vertical profiles of PAHs

Based on the isotope dating of sediment cores C4 and C10 (C5 and C6 were located in the western region and were dated according to C4), nearly 100 years of the vertical distributions of PAH concentrations were investigated, as displayed in Fig. 2. Although the sediment chronology was of low resolution and involved uncertainties, it provided an understanding of the general history of the lake and revealed the historical records of anthropogenic PAH input. The total concentrations of PAHs deposited in the four sediment cores were significantly different between the western region (C4, C5 and C6) and the eastern region (C10) in Lake Chaohu. Focusing factor, defined as the ratio of unsupported 210Pb inventory to atmospheric deposition of 210Pb activity, was used to measure the degree of sediment focusing (Zhu and Hites, 2005; Liu et al., 2012a). The resulting focusing factors for the western lake region (1.97 for cores C4, C5 and C6) were greater than that for the eastern lake region (0.97 for core C10). The PAH concentrations accumulated in cores C4, C5 and C6 from the western lake region exhibited three different stages (Fig. 2): a rather slow growth period prior to the 1940s, a sharp increase from the 1950s to the 1990s, and a significant decline from the 1990s to the present.
that led to the development of the economy during this period in China (Guo et al., 2006). After the establishment of the People’s Republic of China, and especially after the implementation of the Reform and Opening policy in 1978, China’s economy developed quickly, and this rapid industrialization and urbanization resulted in a huge consumption of energy (Liu et al., 2012a). The growing use of coal as a dominant source of energy consequently resulted in increasing emissions of PAHs. In addition, underdeveloped facilities and technologies, together with the low efficiency of energy consumption and outdated emission mitigation measures, also led to higher PAH emissions during this period (Shen et al., 2013). During the third stage, the continuous, rapid development of the economy did not cause any further increases in PAH contamination in recent years, reflecting China’s awareness of the deterioration caused by PAHs and its consequent commitment to reducing emissions of PAH contaminants (Guo et al., 2010). Moreover, the dramatically increasing energy consumption finally generated change in the energy structure through a switch from a single fuel (primarily coal) to multiple fuels (coal, oil and natural gas) (Guo et al., 2006, 2011b).

The PAH accumulation in core C10 from the eastern lake region only exhibited two different stages (Fig. 2): before the 1970s and after the 1970s. Before 1970, the PAH concentrations remained fairly stable, followed by a rapid increase to the present level. The PAH increase in the eastern lake region occurred much later than that did in the western lake region, perhaps due to the different levels of development between the western urban area and the eastern rural area. Moreover, different sedimentation rates may also have caused this difference (Liu et al., 2005). In addition, the total PAH content in the western lake region was much higher than that in the eastern lake region. This difference occurred because the western lake region directly received a large amount of pollutants from the upstream rivers and catchment in the vicinity of the developed capital city of Anhui Province, Hefei.

2.2. Deposition fluxes and mass inventories of PAHs

PAH accumulation in sediment cores is dependent not only on direct source emissions but also on the sedimentary rates and sedimentological conditions (Lima et al., 2002). Therefore, PAH depositional fluxes are more meaningful than PAH concentrations alone (Fernández et al., 1999; Guo et al., 2010; Liu et al., 2012b). The PAH deposition fluxes (F) were calculated using the following Eq. (1):

\[
F = C_i \gamma_i \rho_i
\]

where, \(C_i\) (ng/g), \(\rho_i\) (g/m²) and \(\gamma_i\) (cm/year) refer to the PAH concentration, the sediment dry mass density and the sedimentation rate, respectively, for slice \(i\). The variation tendencies of depositional fluxes were consistent with the corresponding changes of PAH concentration profiles for each sediment core. The higher depositional fluxes in the sediment cores of the western lake region were mainly attributed to the high emission factors, such as the high frequency combustion of coal, wood or petroleum (Yunker, 2002; Machado et al., 2014). The record of depositional fluxes can facilitate calculation of the gradient rate at which depositional flux changes occurred in Lake Chaohu (Azoury et al., 2013). In the western lake region, low PAH deposition fluxes with a slow and uniform exponential increase in accumulation (Appendix A Fig. S1) were exhibited after the establishment of the People’s Republic of China. A relatively low first-order rate of growth in PAH flux was identified before the 1950s, with a rising rate of 0.021 year⁻¹ (\(n = 5, R^2 = 0.53\), 0.019 year⁻¹ (\(n = 6, R^2 = 0.62\)) and 0.033 year⁻¹ (\(n = 6, R^2 = 0.90\)) for C4, C5 and C6, respectively. Then, a sudden increase in the PAH depositional flux was observed in the years between the 1950s and the 1990s. During this period, China experienced rapid economic development, and the depositional fluxes increased 2–8 times faster in this period than they did prior to the 1950s (0.060 year⁻¹, \(n = 7, R^2 = 0.97\); 0.095 year⁻¹, \(n = 6, R^2 = 0.98\) and 0.045 year⁻¹, \(n = 7, R^2 = 0.97\) for C4 C5 and C6, respectively). However, in the top layers of the sediment cores in the western lake region, no clear trends were found in the PAH depositional fluxes due to the coexistence of both PAH generation processes and the controlled measurements of PAHs in this period after 1990. Large differences in PAH depositional fluxes, as well as flux changes, were observed between the eastern lake region and the western lake region (Appendix A Fig. S1). Only two stages were observed in the eastern lake region, and the sharp rise in the PAH flux began later, at the beginning of the 1970s, with a relatively low first-order rate of 0.031 year⁻¹ (\(n = 7, R^2 = 0.92\)), which was two times faster than the rate before the 1970s (0.0169 year⁻¹, \(n = 8, R^2 = 0.80\)). The similarities between the flux chronologies and concentration records in the sediment cores in Lake Chaohu verified the changes in anthropogenic input to this system over the last century (Xuo et al., 2011).

While sediment is an important sink for PAHs, it is also an important potential source of accumulated PAH release into the aquatic environment (Guo et al., 2010). Thus, mass inventories were used to evaluate the potential sources of PAHs in Lake Chaohu. The mass inventories of the total PAHs were separated according to the natural stages of each core, which are listed in Table 1. The mass inventories in the eastern region were fairly low compared to those in the
western region, indicating a somewhat latent secondary pollution. In addition, after the years 1950 and 1970, the inventories in C4 and C10, respectively, accounted for over 81%–91% of the total PAH inventories over the entire 100-year period, further confirming that the PAH contamination in Lake Chaohu is mainly due to recent input related to increased anthropological activities.

2.3. Impacts of sedimentary conditions

Grain size distributions can provide information on hydrological changes because the ability to transport grains of different sizes is related to hydrodynamic intensity. Certain researchers have shown that a negative correlation exists between the water current velocity and fine particle levels (<8 μm) (Molinaroli et al., 2009), and coarser grains may indicate strong currents, which are able to transport fine particles out of the lake to the Yangtze River (Chen et al., 2011).

As shown in Fig. 3, the grain size showed a large change before and after the construction of the Chaohu Dam in 1963. Before the dam development in Lake Chaohu, the annual average water exchange volume with the Yangtze River was more than 50% of the mean volume of the lake. Hence, a mass of fine particles was transported out of the lake, and coarser grains were deposited in the lake (Molinaroli et al., 2009). Since the construction of the dam, the annual exchange of water between Lake Chaohu and the Yangtze River has decreased from 13.6 × 10^8 m^3 to 1.6 × 10^8 m^3, which represents 45% and 5% of annual runoff from the whole catchment area, respectively, and almost all of the natural water handling capacity was lost (Zan et al., 2012). Once the sedimentological conditions had stabilized, the deposition of fine grains in the lake accelerated (Fig. 3). A general trend can be observed that the fraction of fine grains (<8 μm) in both cores gradually increased with decreasing age; on the contrary, from 1963 onward, the relative content of coarser grains gradually decreased.

According to the Pearson correlation analysis on the PAH compounds and the grain size in sediment cores C4 (western lake region) and C10 (eastern lake region), significant positive correlations were observed at the 99.9% or 99.5% confidence level between all PAH compounds (especially the predominant high molecular weight compounds with 4–6 ring PAHs) and particles less than 4 μm in size, while strong negative correlations existed between the PAH compounds and the particles ranging in size from 8 to 64 μm (Table 2). Moreover, a sudden drop in median grain size and a marked rise in sediment PAH concentrations and fluxes after damming support this finding. Consequently, the changes in the sedimentary conditions significantly affected the PAH accumulation in the sediments of Lake Chaohu. In the Yangtze River floodplain region, hundreds of lakes of oxbow or riverine types located in the Yangtze floodplain had open hydraulic connections with the Yangtze river before the 1950s. However, the massive construction of dams in these lakes resulted in significant changes in hydrological conditions, which accelerated the accumulation of contaminants, such as PAHs, heavy metals and nutrients (Chen et al., 2011, 2013).

Furthermore, strong significant positive correlations between the total organic carbon (TOC) and PAHs according to PAH ring number (R² = 0.914 and 0.864 for the 2–3 ring, 4 ring and 5–6 ring PAHs, respectively, p < 0.01) were observed in the sediment cores (Table 2). These results indicate that organic matter plays an important role in the retention of PAHs in Lake Chaohu (Shi et al., 2007; He et al., 2009). Another possible interpretation of these results is that the TOC and PAHs were co-emitted with wastewaters or originated from non-point sources in the catchment (Liu et al., 2013).

2.4. Assessment of local sources and impacts of socioeconomic development

The levels of individual PAH species and diagnostic ratios have been widely used to provide valuable information on the sources and deposition behaviors of PAHs in the environment (Yunker et al., 1996; Yunker, 2002; Kannan et al., 2005). The calculated PAH proportions over time in all the sediment cores are shown in Fig. 4. The low molecular weight PAHs (2–3 ring), which mainly originated from low- or moderate-temperature combustion processes (such as domestic coal burning or biomass burning) (Guo et al., 2010), were the dominant components in the deeper sediment layer in Lake Chaohu, especially near the highly populated area in the western lake region. The proportion of high molecular weight PAHs (5–6 rings), which were generated from high-temperature combustion processes (such as industrial coal combustion and vehicular exhaust) (Harrison et al., 1996; Mai et al., 2002), has been increasing gradually in recent years. The change in PAH emission patterns resulting from the transition from a traditional single fuel to multiple fuels, especially in the developed area (C5 and C6), was closely related to local socioeconomic development.

The diagnostic ratios of PAHs with similar molecular weights can also help in identifying PAH sources (Yunker, 2002). Despite the fact that the ratios are semi-quantitative since numerical apportionment cannot be provided (Huang et

Table 1 - Fluxes and inventories of total PAHs deposition in the dated sediment cores at different stages.

<table>
<thead>
<tr>
<th>Core site</th>
<th>C4 in western lake region</th>
<th>C10 in eastern lake region</th>
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<tbody>
<tr>
<td>Fluxes (ng/(cm²·year))</td>
<td>4.1–12.1</td>
<td>24.1–163.3</td>
</tr>
<tr>
<td>Inventories (ng/cm²)</td>
<td>455.4</td>
<td>2629.2</td>
</tr>
</tbody>
</table>

*”(0)“ mean value of deposition fluxes.*
China has undergone a critical period of energy use during its burning sources (Guo et al., 2010; Liu et al., 2012a). Although indicating a mixture of liquid fossil fuel combustion and coal inP/(BghiP + InP) decreased to between 0.2 and 0.5, while the ratios of Fla/(Fla + Pyr) and IcdP/(IcdP + BghiP) were used to identify the PAH sources. The ratios of Fla/(Fla + Pyr) (<0.4, 0.4–0.5, >0.5) and IcdP/(IcdP + BghiP) (<0.2, 0.2–0.5, >0.5) suggested that the PAH sources were petroleum leakage and the combustion of petroleum, coal, and wood/grass (Yunker, 2002). The Fla/(Fla + Pyr) and InP/(BghiP + InP) ratios were generally higher than 0.5 before the 1930s, indicating sources from the combustion of grass, wood and domestic coals in this less-developed region (Appendix A Fig. S2). A peak value appeared in the 1940s in the Fla/(Fla + Pyr) ratio, which was attributed to the contribution of pyrogenic sources during wartime (Liu et al., 2012b). During the period of reconstruction and rapid development from 1950 to 1990, most ratios of InP/(BghiP + InP) decreased to between 0.2 and 0.5, while the lower ratios of Fla/(Fla + Pyr) were still higher than 0.5, indicating a mixture of liquid fossil fuel combustion and coal burning sources (Guo et al., 2010; Liu et al., 2012a). Although China has undergone a critical period of energy use during its transition from an agricultural to an industrial economy (Guo et al., 2006), biomass burning and domestic coal combustion are still the predominant energy sources in China and are the top two emission sources of PAHs (Xu et al., 2005). In general, the PAHs in Lake Chaohu over the 100-year study period predominantly originated from pyrogenic sources, including the burning of biomass, such as coal or wood combustion, and a mixture of liquid fuel. Although PAH diagnostic ratios are useless in quantitative terms and have some limitations, they still consistently identified the major contributors of the pyrogenic sources, which are identical to the previous source apportionment studies in lake Chaohu, showing that coal combustion, vehicle emission, and wood combustion were the major sources of PAHs for the Lake Chaohu sediment (Qin et al., 2014).

The PAHs generated through human activities are usually used as a proxy to trace the impact of anthropogenic activities (Lima et al., 2002; Elmquist et al., 2007; Machado et al., 2014). Lake Chaohu has undergone significant social and economic development since the founding of the People’s Republic of China. Many studies have reported that the local population size, industrialization activities, the gross domestic product (GDP), the consumption of local energy and the number of vehicles significantly impact PAH generation (Hafner et al., 2005; Liu et al., 2005). In this study, PAH contents in the sediment cores were significantly affected by the sedimentation conditions, as has been verified above. To eliminate the grain size effect, PAH concentrations were normalized to TOC for further correlation analysis with the local socioeconomic data (population/GDP) (Bakhtiari et al., 2009). According to the results of normalization data of PAH to TOC, a linear correlation analysis was conducted on the normalized PAH content and the local socioeconomic data (population/GDP) as illustrated in Fig. 5, thus revealing the impact of economic development on PAH emissions. The socioeconomic data only extend back to the 1950s, and the relevant analysis was conducted for the period from the 1950s to the present. Consequently, no obvious correlation was observed between the population/GDP and the normalized PAH content during the entire period (1950–2010). However, from 1950 to 1990, strong positive correlations were found between the normalized PAHs and the population ($R^2 = 0.89, p < 0.01$), as well as the GDP ($R^2 = 0.70, p < 0.01$), demonstrating that the accumulation of PAH content in the lake sediment was accompanied by the growth of the local population and social economy.

### Table 2 – Correlation between PAH species and the different grain sizes in the sediment cores

<table>
<thead>
<tr>
<th>PAHs species</th>
<th>Organic matter</th>
<th>Fine size</th>
<th>Medium size</th>
<th>Coarse size</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>TOC &lt;4 µm</td>
<td>4–8 µm</td>
<td>8–16 µm</td>
<td>&gt;16 µm</td>
</tr>
<tr>
<td>2-3 ring</td>
<td>0.935**</td>
<td>0.848**</td>
<td>0.784**</td>
<td>−0.358**</td>
</tr>
<tr>
<td>4 ring</td>
<td>0.914**</td>
<td>0.879**</td>
<td>0.801**</td>
<td>−0.599**</td>
</tr>
<tr>
<td>5-6 ring</td>
<td>0.864**</td>
<td>0.871**</td>
<td>0.781**</td>
<td>−0.605**</td>
</tr>
<tr>
<td>∑PAH</td>
<td>0.897**</td>
<td>0.877**</td>
<td>0.794**</td>
<td>−0.501**</td>
</tr>
</tbody>
</table>

** Correlation is significant at the 0.01 level (2-tailed).
However, the normalized PAH contents showed an opposite declining trend relative to socioeconomic data after the 1990s, which should be due to the related implementation of PAH emission control programs (Machado et al., 2014). In addition, the substitution of coal combustion with cleaner-burning natural gas also led to a decrease in PAH emissions (Xu et al., 2005). Overall, the PAH contamination in Lake Chaohu was historically affected by socioeconomic development and anthropogenic activities, which explains the different pollution levels of PAHs between the western and eastern lake regions.

3. Conclusions

Fifteen priority PAHs were analyzed in four sediment cores from Lake Chaohu to reconstruct the historical record of PAH pollution over the last 100 years. The results showed that the PAHs had different distributions between the western and eastern lake regions. According to the PAH concentrations and depositional flux records, PAH contamination experienced three stages in the western region and two stages in the eastern lake region. Human activities, including warfare and increased
industrialization and urbanization during the 1950s–1990s, had a significant impact on the emission of PAHs, causing a sharp increase. With the implementation of PAH control measures, an obvious decline in PAH levels occurred in the urban western lake region. The PAHs were largely pyrogenic, stemming especially from the combustion of coal and wood, even in the present. The accumulation of PAHs was found to positively correlate with both sedimentary conditions and socioeconomic developments in the Lake Chaohu region. The construction of the dam resulted in significant changes in hydrological conditions, which accelerated the accumulation of PAHs in the sediments.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found in online version at http://dx.doi.org/10.1016/j.jes.2015.05.007.

REFERENCES


