



Historical changes in polycyclic aromatic hydrocarbons (PAHs) input in Lake Baiyangdian related to regional socio-economic development

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ABSTRACT

The accumulation of polycyclic aromatic hydrocarbons (PAHs) over a period of almost 180 years was studied in a sediment core collected from Lake Baiyangdian in northern China. Total PAHs concentration varied from 97.2 to 2402 ng g⁻¹ dry weight. We found the highest total PAH concentration in 1940s and 1990s, and a decreasing trend from 1990 until present. The warfare and increasing economic activity had the largest impact on the PAH vertical distribution. The implemented measures for pollution control in catchment since 1990 might reduce point source input of PAH in some degree in recently. The historical record of PAHs is different from the developed countries and areas due to difference in socio-economic development condition. PAHs in the core are dominantly pyrogenic in source, i.e., they are mainly from the incomplete combustion of wood and coal. PAHs from terrigenous organic matter input decreased obviously from the 1950s due to rainfall reduction during this period.

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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous in the environment, and are great concerned because of their toxic and carcinogenic effects. Owing to their low solubility and hydrophobic nature, PAHs tend to be associated with fine particles, are introduced into lakes and seas by runoff and atmospheric fallout [1,2]. Thus, seas or lakes often act as a trap for PAHs and can provide insight about their fate in aquatic ecosystems [3–7]. Because of their potentially toxic, mutagenic, and carcinogenic properties, considerable efforts have been made to reduce PAH pollution in many countries [8,9]. Many studies have indicated that reconstruction of the PAH pollution history by investigating lacustrine core samples of sediments is helpful to understand pollution mechanisms and develop effective countermeasures [10–12]. This approach can also provide a useful way to elucidate the relationship between catchment economic development and pollution [13]. Even though PAHs are generated by both natural and anthropogenic process [14], most PAHs are associated with industrial and urban development [15,16]. Thus, PAHs in the lake sediments can be used as an effective proxy to trace the impact of socio-economic changes in catchment [17–19].

Lake Baiyangdian (38°43'N to 39°02'N, 115°45'E to 116°07'E) is the largest shallow freshwater lake in northern China (Fig. 1), which plays an important role in providing habitats for native plant

and animal species, for water supply, and for protection against floods. The lake consists of more than 100 small lakes that are linked together by thousands of ditches, and covers a mean total area of 362 km² within a catchment of 31,200 km². Most parts of the lake are not more than two meters in depth. The catchment has a total population of approximately 2.04 million. As a famous tourist resort in China, Lake Baiyangdian received more than 850,000 tourists every year. Diesel boats are the most important transportation means in BYD Lake. There is a large amount of aquatic emergent macrophytes (dominated by reeds) distributed in the lake's littoral zones. However, due to increasing industrial and living activities around the catchment in the past three decades, the lake's water resource faces a serious threat such as water levels dropped and water quality deterioration [20,21]. Therefore, know of pollution problems in the lake is necessary to protect and remedy the catchment environment. In this study, a lacustrine sediment core collected from Lake Baiyangdian was analyzed for PAHs. The catchment PAHs pollution history was reconstructed and how temporal changes in human activities and historical events affect the environment was further investigated.

2. Materials and methods

2.1. Sampling

Sampling was carried out on October in 2009 in Lake Baiyangdian (Fig. 1). A 78 cm-long sediment core was collected using a Beeker 04.23 core sampler (100 cm length × 57 mm i.d.; Eijkelpamp Co., Giesbeek, the Netherlands) at the Caiputai site located the

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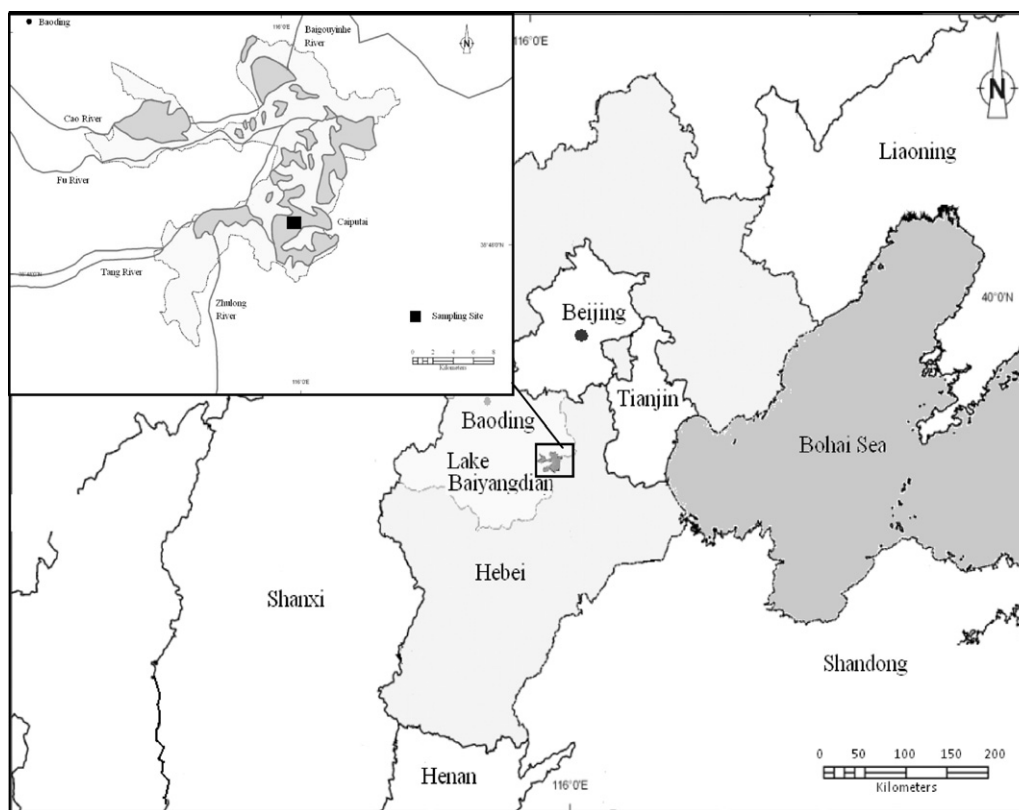


Fig. 1. Map of the study area and location of the sampling site.

south of the lake and is without human interference, where the water depth is about 3.5 m. This core was sectioned at 2 cm intervals and each section about 17–65 g (dry weight, dw) was placed into aluminum foil cleaned with acetone, and then each section was freeze-dried, homogenized and stored in a cool and dark place until further treatment.

2.2. Extraction and analysis of PAHs

The same extraction and analysis of PAHs was performed based on previously reported methods [22,23]. About 2–5 g (dw) of each sample was extracted with 250 mL of dichloromethane-hexane (1:1, v/v) for 24 h using a Soxhlet apparatus. A known mixture of surrogates (naphthalene-d₈, acenaphthene-d₁₀, phenanthrene-d₁₀, chrysene-d₁₂) was added to each blank and sample before extract. The extract was passed through a 1:2 alumina:silica (v/v) gel glass column with 1 g anhydrous sodium sulfate overlaying the silica gel. The first fraction was discarded, containing aliphatic hydrocarbons, was eluted with 15 mL of hexane. The second fraction containing PAHs was collected by eluting 70 mL of hexane-dichloromethane (7:3, v/v). Then the collected fraction was concentrated to 0.5 mL under a gentle stream of purified N₂. After adding a known quantity of an internal standard (hexamethylbenzene), we analyzed the PAHs using gas chromatography and mass spectrometry (GC/MS).

To analyze the samples, we used a Varian 4000 mass spectrometer (Varian Inc., Palo Alto, CA) interfaced with a Varian CP-3800 gas chromatograph equipped with a Varian VF-5MS column (30 m × 0.25 mm i.d. × 0.25 μm film thickness), with helium as the carrier gas. The injection port, ion trap, manifold, and transfer-line temperatures were maintained at 290, 200, 45, and 280 °C, respectively. The column temperature was programmed to rise from 80 °C (held for 3 min) to 230 °C (held for 2 min) at a rate of 15 °C min⁻¹, followed by a ramp to

290 °C (held for 8 min) at a rate of 5 °C min⁻¹. We quantified the concentration of the following compounds: naphthalene (Naph), acenaphthene (Aceph), acenaphthylene (Ace), fluorene (Fl), phenanthrene (Phen), anthracene (Ant), fluoranthene (Flu), pyrene (Pyr), benzo[a]anthracene (BaA), chrysene (Chr), perylene (Per), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), dibenz[ah]anthracene (DBA), benzo[ghi]perylene (BgP), and indeno[1,2,3-cd]pyrene (InP). For each compound, we used analytical-grade standard solutions (AccuStandard Inc., New Haven, CT) to calibrate the measurements. All data were subject to strict quality control procedures [22]. The method detection limit (MDL) for PAHs ranged from 0.02 to 3.07 ng g⁻¹. The recoveries for the surrogate PAHs ranged from 61.0 to 88.0%. Spiked samples in each set of 15–20 samples had mean recoveries ranging from 64.0 to 103%. Each sample was analyzed in duplicate, and relative standard deviations were less than 15%.

2.3. Dating of the sediment core

The dating of the sediment core from Lake Baiyangdian was calculated by using ¹³⁷Cs and ²¹⁰Pb dating techniques [24]. In brief, the ²¹⁰Pb activity in sediment samples was determined by γ emissions at 46.5 keV, ²²⁶Ra activity was determined by γ-rays emitted at 352 keV, and ¹³⁷Cs activity was determined by emissions at 662 keV. ²¹⁰Pb_{ex} was obtained by subtracting ²²⁶Ra activity from total ²¹⁰Pb activity [25]. In this study, dates based on ²¹⁰Pb were calculated using a constant rate of supply dating model [26]. Profiles of ¹³⁷Cs activity in sediment cores were compared to scattering nuclides from nuclear testing, thermonuclear weapons testing in the middle 1960s, and accidents such as the one at the Chernobyl nuclear accident in 1986 [24]. Thus, we obtained relatively accurate dates from the ²¹⁰Pb

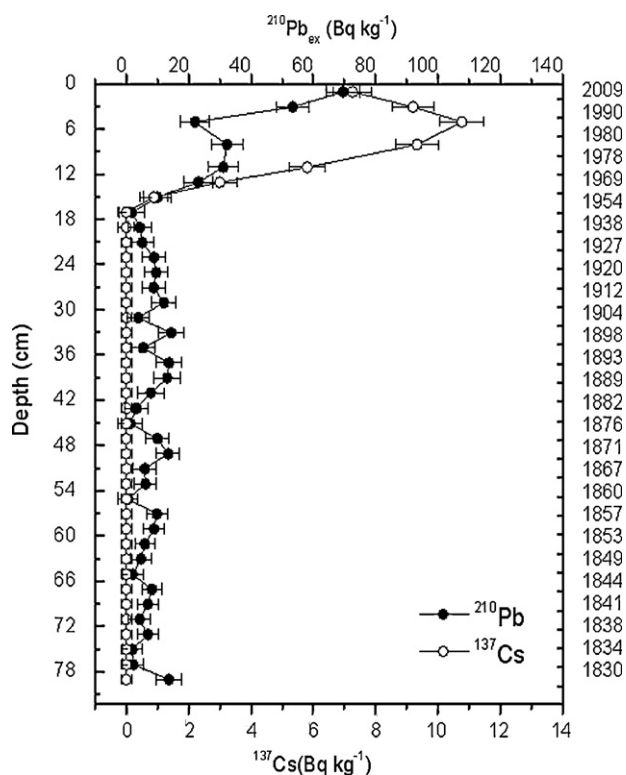


Fig. 2. ^{210}Pb and ^{137}Cs activity-depth profiles in core from Lake Baiyangdian.

dating, verified by the ^{137}Cs dating (Fig. 2). The sediment deposition rate ranged from 0.13 to 1.5 cm y^{-1} , with a mean value of 0.57 cm y^{-1} .

3. Results and discussion

3.1. Concentrations and temporal trends of PAHs

Table 1 summarizes the distribution of the PAHs in core sediment samples from Lake Baiyangdian. Although high-molecular-weight PAHs are more easily accumulated in sediments due to their hydrophobic character, some high-molecular-weight PAHs such as InP, DBA, and BgP, were not detected in all samples. It might indicate that PAHs sources from fuel combustion produced InP, DBA, and BgP is relative less in the study area. Table 1 presents the concentration of 14 PAHs against depth and year of deposition. The total PAH concentration in the sediments ranged from 97.2 to $2402\text{ ng g}^{-1}\text{ dw}$, and are higher than those reported in lakes in western China (29.1 to $475\text{ ng g}^{-1}\text{ dw}$) [27], and close to that in sediments from Lake Taihu in eastern China (88 – $1600\text{ ng g}^{-1}\text{ dw}$) [13]. Of the individual PAHs, Phen (11.1 – $769\text{ ng g}^{-1}\text{ dw}$), Ant (8.46 – $376\text{ ng g}^{-1}\text{ dw}$), Flu (7.16 – $599\text{ ng g}^{-1}\text{ dw}$), and Pyr (9.91 – $508\text{ ng g}^{-1}\text{ dw}$) were the dominant compounds in Lake Baiyangdian sediment, and the ratio of these individual PAHs content to total PAH content reached 29.7%, 21.0%, 15.2%, and 16.4% respectively. Dominance of low molecular weight PAHs (2–3 rings PAHs) suggests local sources of PAHs [5].

Our analysis of the ^{210}Pb and ^{137}Cs geochronologies suggests that the core from Lake Baiyangdian covered nearly 180 years (1830–2009) of sediment accumulation (Fig. 2). Fig. 3 shows the variation in the total PAH content for each sedimentary date during this period. The total PAH concentration exhibited two peaks: one between 1940 and 1950 and another between 1985 and 1995. Combustion of wood and fossil is a main source of PAHs. The area of north China is an important battlefield of World War II and the subsequent Chinese Civil War between 1940 and 1950. Some materials



Fig. 3. Vertical profile of the total PAH concentration in the sediment core from Lake Baiyangdian.

such as wooden construction of house and oil facilities of storage and transportation were struck by bombs during air attacks and gunfire. Moreover, there was no other significant event capable of causing the high level of PAHs due to lagged economic development and less industrial activities. Thus the period from 1940 to 1950 considered to have the greatest influence on PAH production is World War II and the subsequent Chinese Civil War. The second peak occurred between 1985 and 1995, fast industrialization and urbanization in this period in the catchment might cause much more PAH emission [28]. These results suggest that the periods of warfare and recent accelerated economic activities had strong impacts on the vertical distribution of PAHs [29,30].

The variation in the total PAH concentration over time is basically consistent with the historical economic and social development of this catchment for China. The total PAH profile reveals four different stages: prior to the 1930s, from 1937 to 1949, from the 1950s to the mid-1980s, and from the 1990s to the present (Fig. 2). During the first stage (1830–1930), the total PAH concentration ranged from 97.3 to $692\text{ ng g}^{-1}\text{ dw}$ and peaked in the 1850s and the 1920s. During this period, China experienced Two Opium Wars (1840–1842 and 1856–1860), the Westernization Movement (1860–1894), and the modern development of national industries (1900–1930) [31].

During the second stage (1937–1949), the total PAH concentration rose sharply from 182 ng g^{-1} in the 1930s to 1366 ng g^{-1} in the 1940s. This might show the effect of World War II (1937–1945) and the Chinese Civil War (1946–1949).

During the third stage (1950s to mid-1980s), the total PAH concentration gradually increased, and ranged from 530 to 1078 ng g^{-1} . This period in China begins with the establishment of the People's Republic of China (1949–1966), continues with the Cultural Revolution (1966–1976), and ends with the “reform and opening” period that began ca. 1978. Many of manufacturing plants either closed or greatly reduced production in the period of

Table 1
Concentrations (ng g⁻¹ dw) of individual PAHs and sediment characteristics in the sediment core from Lake Baiyangdian.

Depth (cm)	Year	Naph	Aceph	Ace	Fl	Phen	Ant	Flu	Pyr	BaA	Chr	Per	BkF	BbF	BaP	Total PAHs	TOC %
0–2	2009	15.8	4.32	13.9	34.6	140	137	55.6	88.9	3.52	3.41	3.14	2.73	1.18	1.28	505	2.92
2–4	2000	18.2	4.65	12.8	55.0	245	234	108	135	6.13	5.06	3.07	3.94	2.68	1.66	835	2.62
4–6	1990	54.4	15.6	34.6	113	769	116	599	508	92.5	80.4	7.47	4.08	5.77	3.02	2402	1.89
6–8	1980	66.0	9.19	28.8	93.4	292	308	104	155	5.99	3.41	4.56	4.11	1.71	1.69	1078	2.32
8–10	1975	16.0	3.51	11.3	44.1	183	178	68.2	77.2	7.71	5.32	3.70	1.73	2.06	0.84	603	1.46
10–12	1969	9.93	4.02	13.8	52.6	213	209	70.9	79.3	6.40	5.12	2.18	2.20	1.76	0.67	671	1.19
12–14	1960	23.0	5.10	12.3	56.3	200	26.0	84.2	85.4	11.0	10.8	7.60	3.73	2.31	2.43	530	1.02
14–16	1949	21.7	4.19	13.0	79.3	385	376	208	167	38.3	33.3	18.8	10.6	8.01	2.86	1366	0.88
16–18	1938	8.70	2.62	6.09	13.0	48.9	51.4	16.9	25.7	2.33	2.24	1.13	0.54	1.17	0.90	182	1.11
18–20	1930	5.94	2.05	4.96	18.1	117	115	60.3	69.0	8.76	7.89	3.53	3.14	1.37	0.94	418	0.52
20–22	1924	6.64	2.34	6.40	18.5	80.5	8.46	21.6	39.3	1.88	2.01	1.49	0.90	1.06	0.68	192	0.43
22–24	1920	6.85	2.93	4.12	46.9	256	40.4	144	129	23.1	20.1	8.05	5.10	3.50	1.95	692	0.41
24–26	1914	3.05	0.71	2.15	7.43	41.4	44.1	24.9	34.0	1.60	2.46	1.99	1.58	0.84	1.01	167	0.39
26–28	1910	7.17	1.67	5.51	21.9	12.1	12.0	45.5	54.4	3.03	5.85	3.87	3.08	0.70	0.63	177	0.38
28–30	1904	6.80	1.58	4.64	14.8	81.1	80.3	40.2	42.2	5.81	5.05	3.12	2.76	2.23	0.62	291	0.32
30–32	1900	5.44	1.08	3.63	12.7	95.4	94.0	47.1	55.3	4.93	4.89	2.91	2.47	1.41	0.30	332	0.48
32–34	1896	3.84	1.24	3.11	11.5	11.1	10.0	43.2	54.2	5.40	3.57	1.94	1.72	1.22	0.85	153	0.55
34–36	1893	10.16	2.00	7.77	24.9	150	148	68.4	68.2	6.88	5.04	6.54	5.44	2.54	1.29	507	0.61
36–38	1890	6.42	1.63	5.66	10.3	24.6	26.9	7.16	9.91	1.12	1.30	0.91	0.68	0.39	0.32	97.3	0.64
38–40	1887	8.13	1.43	3.21	10.4	42.0	45.8	13.8	15.4	1.14	0.92	0.70	0.45	0.30	0.38	144	0.77
40–42	1882	4.46	0.95	3.63	8.75	43.0	43.6	20.3	26.2	2.17	1.57	1.02	0.95	0.65	0.55	158	0.89
42–44	1877	4.91	0.96	3.36	7.76	30.5	29.1	20.4	21.5	1.45	2.04	1.35	1.19	0.68	0.99	126	1.14
44–46	1874	8.38	1.67	6.29	17.6	85.7	93.7	41.5	46.2	2.96	2.59	3.55	3.16	1.18	2.11	317	1.01
46–48	1871	8.30	1.40	4.53	11.5	73.4	80.1	46.3	48.5	3.21	3.31	2.16	1.36	1.50	0.95	287	1.21
48–50	1868	5.37	1.48	5.88	13.4	81.2	84.4	43.1	49.7	3.69	4.98	3.95	2.78	2.23	1.97	304	1.14
50–52	1865	6.05	2.55	11.4	28.1	171	167	75.9	76.1	4.96	4.31	6.51	3.19	3.00	2.78	563	1.07
52–54	1860	5.17	2.13	2.36	39.8	170	169	55.2	53.9	4.86	4.55	2.33	3.39	1.97	1.07	516	0.98
54–56	1858	5.61	2.33	6.12	12.2	60.7	60.1	28.4	44.6	4.39	2.27	1.80	1.01	1.31	0.72	232	1.02
56–58	1855	4.78	2.69	3.21	8.60	122	117	65.5	55.2	2.12	4.25	8.95	4.12	4.93	0.68	404	1.06
58–60	1853	8.25	3.57	8.24	37.9	196	192	96.9	94.5	14.0	12.	14.1	7.28	3.49	1.18	689	0.82
60–62	1850	12.7	2.95	10.2	21.1	67.7	66.4	27.0	43.5	2.31	2.26	5.89	4.14	1.44	1.73	269	0.92
62–64	1847	48.5	8.37	20.5	112	51.7	46.9	42.6	50.9	2.26	1.94	1.47	1.98	0.78	0.74	391	0.88
64–66	1844	3.38	1.07	3.82	24.9	128	19.8	62.6	56.6	2.97	2.58	3.09	2.30	1.26	0.67	313	1.02
66–68	1842	16.9	2.52	8.71	25.5	132	14.7	57.3	61.1	6.00	5.37	3.08	2.52	1.07	0.87	337	0.91
68–70	1840	18.9	5.18	11.8	32.4	94.5	93.3	22.2	34.1	2.29	2.23	1.43	0.69	0.37	0.46	320	0.74
70–72	1838	16.5	2.80	12.4	23.2	97.8	98.4	35.2	49.4	1.61	2.16	2.33	1.21	1.75	0.25	345	0.62
72–74	1835	8.79	1.40	4.94	23.8	154	152	95.2	85.5	11.9	10.9	7.05	5.60	2.84	1.95	566	0.81
74–76	1832	13.6	2.71	11.5	46.2	209	29.4	88.3	106	7.80	6.26	7.31	5.22	2.31	1.84	537	1.24
76–78	1830	4.16	2.00	4.62	12.9	69.9	8.73	30.2	105	1.87	1.81	2.56	2.39	1.11	0.61	248	1.62

InP, DBA and BgP were under the limit of detection for PAHs.

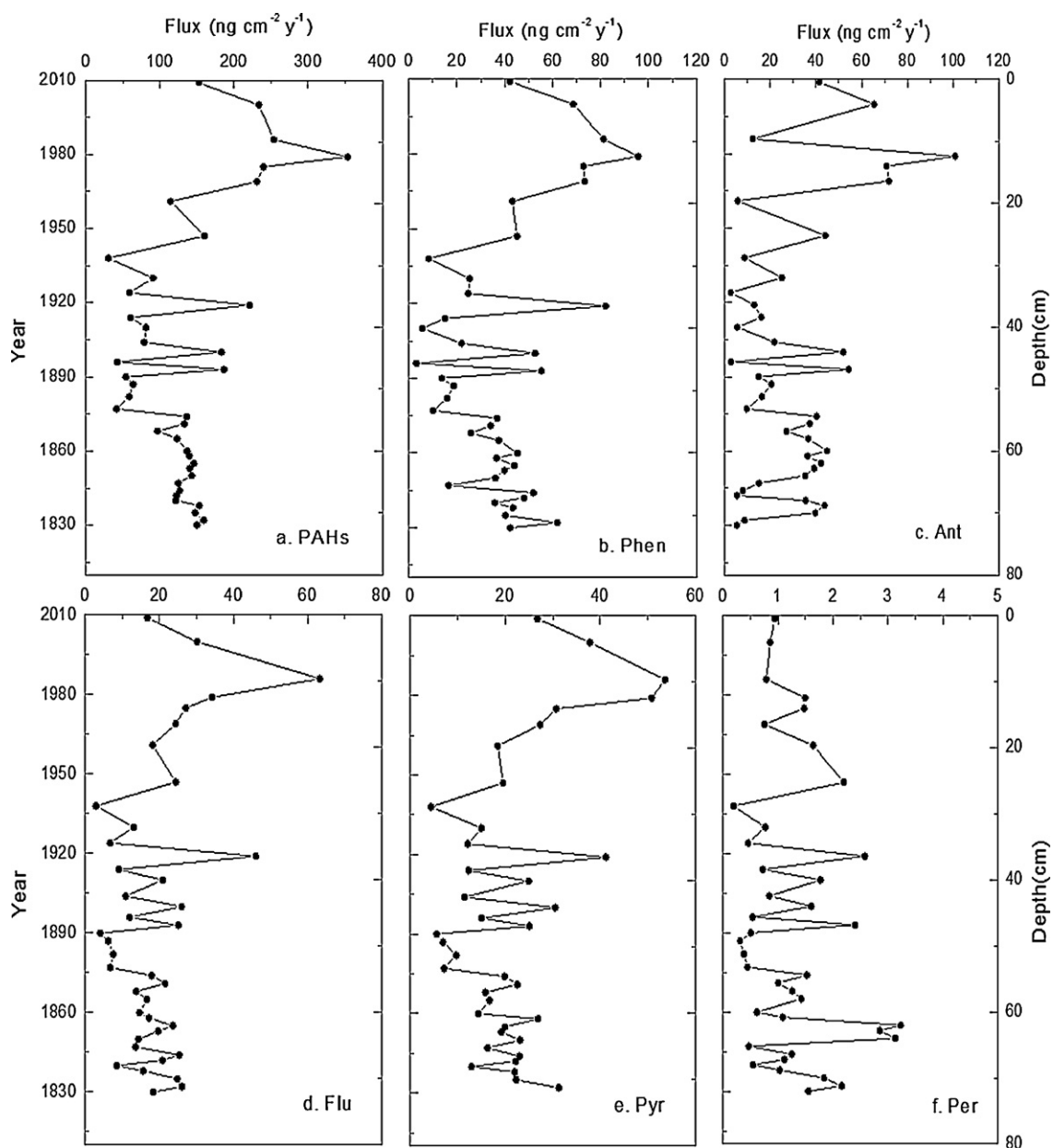


Fig. 4. Depositional flux profiles of total PAH and selected (stable and abundant) individual PAHs. PAHs, total PAH content; Phen, phenanthrene; Ant, anthracene; Flu, fluoranthene; Pyr, pyrene; Per, perylene.

Cultural Revolution political movement. During these periods, China's economy went through rapid development, stagnate, and the recovery. The variation in the total PAH concentration basically coincided with economic development trends during this period [31]. After 1978, the consumption of energy increased drastically, resulting in a change in the energy structure from a single fuel (primarily coal) to multiple fuels (coal, oil and natural gas) [27,31].

During the most recent stage, from the mid-1990s to 2009, the total PAH content has steadily decreased, from 2402 to 505 ng g^{-1} . This may have resulted from pollution control of overall volume as a result of legal measures and the introduction of new technology. Although, economic development during this period remained rapid, the management of Lake Baiyangdian catchment took measures to mitigate the adverse effects on the environment. For example, measures to reduce pollution loading of point source discharge such as new built sewage treatment plant named Yingding

and Lugang (total treatment capacity reach 160,000 m^3/d), improve industrial wastewater treatment rate and cyclic utilization rate, and as well as closed and integrated some heavy contaminated factories including paper mills, chemical plants and printing and dyeing mills were implemented since 1990 [32]. Thus, total PAH concentrations have decreased from 1990 to the present. Moreover, the change of energy consumption structure from coal to a combination of oil and coal might also have led to the declining PAH concentrations [27,28,31].

The temporal trends in the Lake Baiyangdian sediment core differ from those in developed countries such as the United States and developed regions such as Europe [33,34] due to differences in the level of economic development and in the energy consumption structure. For example, a decline in PAH concentrations from the 1960s to the 1980s in developed countries was attributed to the switch from coal to oil and natural gas as energy sources, but the different trend was observed in China because the transition of

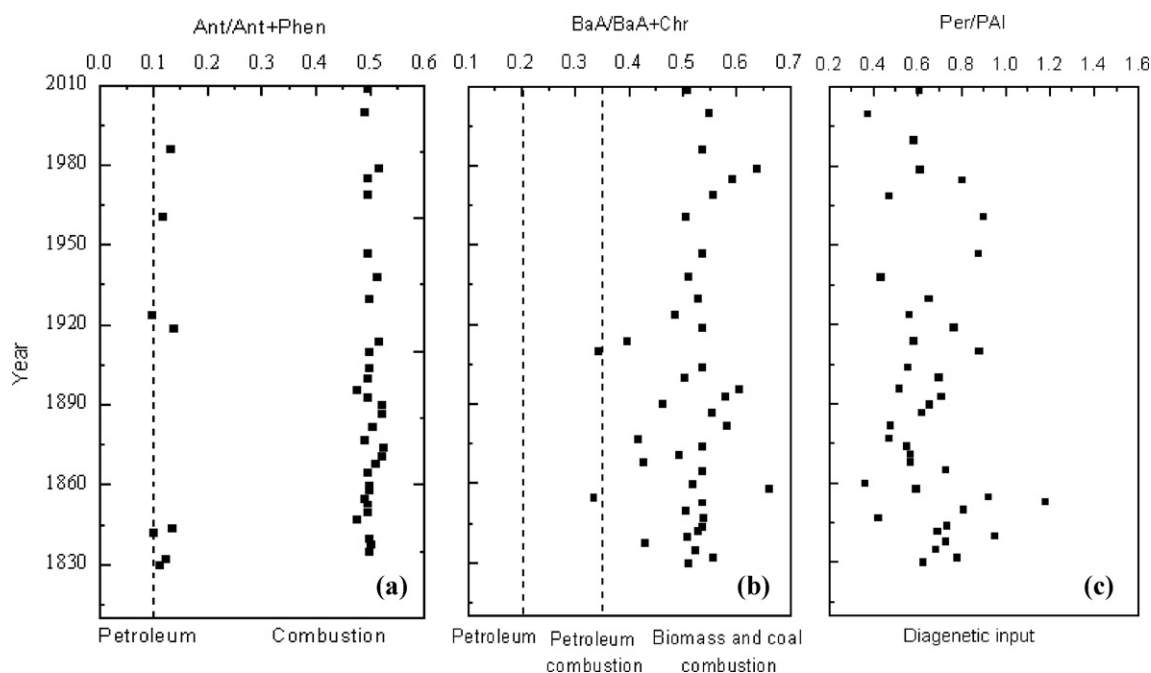


Fig. 5. Identification of PAHs sources in the sediment core. (a) Ant/Ant + Phen; (b) BaA/BaA + Chr; (c) Per/PAI.

the energy consumption structure in China lagged 10 to 30 years behind that in developed countries.

3.2. PAH fluxes

The PAHs fluxes can be used to assess the input and sources of PAHs [3,27]. In the study, the flux of total PAH and some individual PAHs such as Phen, Ant, Flu, Pyr, and Per were calculated to understand the historical changes in the input and sources of PAHs (Fig. 4). The deposition flux (F) was calculated using the following equation [27]:

$$F = C_i \rho_i \gamma_i \quad (1)$$

where C_i (ng g^{-1}), ρ_i (g cm^{-3}), and γ_i (cm y^{-1}) refer to the concentration, the dry sediment density (dry weight/wet volume ratio) [24], and the sedimentation rate, respectively, for layer i . The depositional flux profiles for the selected individual PAHs except perylene (Per) were similar to the concentration trend for total PAH (Fig. 4).

Phen and Ant are produced mainly by low-temperature combustion processes such as biomass burning and domestic coal burning [35,36]. Flu and Pyr are tracers of coal and petroleum burning [31,37]. The flux of total PAH roughly followed the trends for Phen and Ant contents, which fluctuated greatly before ca. 1920, then increased more or less steadily until ca. 1980, and then decreased steadily until the present. Phen and Ant combined accounted for an average of 51% of the total PAH content (Table 1), so the correlation is to be expected. This can also be explained by the energy usage pattern, which was mainly from coal sources before 1980 [31]. The 10-year time lag for this decrease compared with the decrease in Phen and Ant suggests that there was a change in the regional energy consumption structure from coal to a combination of oil and coal. The fluctuating contents of these four compounds and of total PAH from 1830s to the 1920s can likely be attributed to social and economic turbulence during this period, combined with the effects of natural processes. With the rapid economic development, industrialization, and urbanization that have occurred in China, increasing anthropogenic impacts might have caused the flux to increase gradually from the late 1920s to the 1980s and the

1990s. The flux decreases after the 1980s and the 1990s could be attributed to pollution reduction measures in catchment [32].

Per content in sediment is believed to result from combustion processes [38] and diagenesis of organic matter in anoxic sediments [39]. The variation in the Per flux in the sediment core differed from that of total PAH and pyrogenic PAHs discussed above. The flux of Per varied widely, only in the top 25 cm of the core did the flux show obvious signs of a decreasing trend. In view of increasing anthropogenic activities, it might indicate that the natural inputs as a result of diagenesis of organic matter decreased from the 1950s to the present. A decrease in rainfall in this period can decrease inputs of terrestrial organic matter from woody plants and the soil [40–42].

3.3. PAH sources

3.3.1. Anthropogenic sources

Anthropogenic PAHs can be mainly divided into petrogenic and pyrogenic sources based on spills and incomplete combustion of fossil fuels, respectively [43]. The ratios of PAHs with similar molecular weights can be used to determine their origins [44]. In the present study, we calculated the ratios of Ant to Ant + Phen and of BaA to BaA + Chr and used the results to identify the PAH sources (Fig. 5a and b). A BaA/BaA + Chr ratio between 0.2 and 0.35 is attributed to the combustion of liquid fossil fuels (gasoline for vehicles, crude oil), whereas a ratio <0.2 corresponds to petrogenic sources and a ratio >0.35 corresponds to combustion of coal, grass or wood [10,43]. Similarly, an Ant/Ant + Phen ratio >0.1 represents combustion processes, whereas a ratio <0.1 represents petroleum contamination [45,46]. Fig. 5a and b suggests that the dominant source of PAHs in the samples during this period was incomplete combustion inputs, mainly from wood and coal combustion. Other research also indicated that coal combustion was the main sources of PAHs the catchment such as Tianjian [47,48].

3.3.2. Natural sources

Although Per is produced from diagenesis of organic matter [39] and combustion processes [38], Per is often used to diagnose natural process such as diagenesis of organic matter [49,50]. Plants,

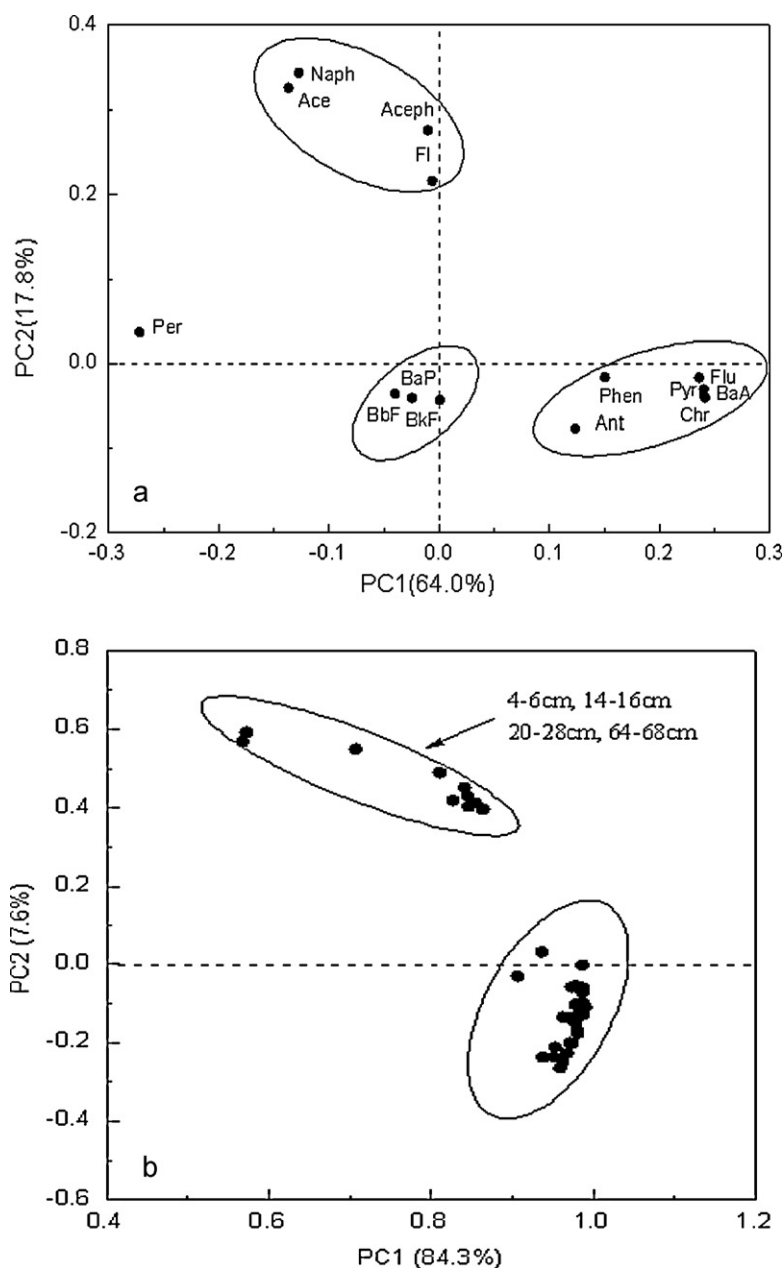


Fig. 6. Principal-components analysis (PCA) results for PAHs in the sediment core from Lake Baiyangdian: (a) Individual PAHs; (b) the change in total PAH content with depth.

fungi, and insects are considered to be the main terrestrial sources of Per precursors, and rain runoff could carry organic matter containing Per precursors into rivers or lakes [51]. The ration of Per to pentacyclic-aromatic isomers (PAI) can be used to suggest the PAHs source [37,45], where the ratio >0.1 indicate diagenetic inputs and that <0.1 a pyrogenic origin. The vertical distribution of Per/PAI is presented in Fig. 5c. The ratio ranged from 0.37 to 1.18 suggesting a probable diagenetic input [37]. The Per/PAI ratio fluctuated widely over time and showed a declining trend from 1950 to the present, which might be attributable to the decline of terrestrial organic matter input because of rainfall reduction in this period [40–42,51].

3.3.3. Principal-components analysis for PAH sources

Principal-components analysis (PCA) was used to further analyze historical changes in the PAH sources (Fig. 6) [24,31]. PCA of the normalized individual PAHs with organic carbon in the core

samples resulted in the first two components (64.0 and 17.8%, respectively) accounting for 81.8% of the total variance (Fig. 6a). PCA results in Fig. 6a showed that PAHs sources of the core samples could be generally divided into four groups: (1) moderate molecular weight PAHs (three and four rings PAHs; Phen, Flu, Pyr, BaA, and Chr) located in the high positive loading part of principal component 1 ($PC1$) were attributable to low-temperature pyrogenic sources [35–37]; (2) low molecular weight PAHs (two and three rings PAHs; Naph, Aceph, Fl and Ace) located in the high positive loading part of principal component 2 ($PC2$) were attributable to petrogenic sources [21,31]; (3) high molecular weight PAHs (five rings PAHs; BbF, BkF, and BaP) located in the negative part of $PC1$ and $PC2$ were attributed to high-temperature combustion sources [31,44]; (4) The position of Per clearly differed from those of the other PAHs, suggesting a different source (i.e., diagenetic input).

Fig. 6b shows the PCA results for the change in PAH content with depth based on parameter including individual PAHs, total PAH

content, TOC, and the Per/PAI, Ant/Ant + Phen, and BaA/BaA + Chr ratios. PCA in the core samples resulted in the first two components (84.3 and 7.60%, respectively) accounting for 91.9% of the total variance (Fig. 6b). Based on samples scores, all samples were located in the positive part of PC1, which might be attributed to the same input pathway of PAHs. However, some important anthropogenic activities might impact PAHs input and distribution. The core sediment samples were divided into two groups based on the PC2: (1) the group with a higher PC2 score (>0.4) included layers deposited during periods of war (World War II, 14–16 cm, 1937–1949; the Opium war, 64–68 cm, 1840–1847; and the Xinhai Revolution, 20–28 cm, 1910–1919) [31] as well as the period of fast economic development (4–6 cm, the 1990s) [28]; (2) the other group with a higher PC2 score (<0.1) comprised the other layers.

4. Conclusions

Reconstructing the history of PAHs pollution from a sedimentary record was an important in the study to understand the socio-economic development impact on the catchment of Lake Baiyangdian. The results indicated that human activities, including warfare (World War II and the subsequent Chinese Civil War in the 1940s) and increased industrial and urbanized activities (the “reform and opening” phase of from 1980s to the present) had a great contribution to PAHs input. The fluxes of PAHs generally increased from 1830 to 1990 due to the increase in human activities and rapid economic development, but have gradually decreased since the 1990s due to the implementation of pollution reduction measures in the region. The sources of PAHs had largely transferred from pyrogenic origin and were dominated by wood and coal combustion. Rainfall reduction affected the input of terrestrial organic matter into the lake from the 1950s, thereby affecting the relative contributions of terrestrial and algal PAHs inputs. The results of PCA confirmed further the analyses of PAHs sources.

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