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History of Fuel Consumption Inferred from Polycyclic Aromatic Hydrocarbons in Sediments from the South Lianhuan Lake, Northeast China

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Abstract Polycyclic aromatic hydrocarbons (PAHs) are a group of persistent organic pollutants of global concern. The current study uses differences in PAH profiles in 1 cm core sediment samples from south Lianhuan Lake, Heilongjiang Province, China to evaluate historical changes in fuel sources. Individual core segments were dated using ^{137}Cs techniques and concentrations of 16 priority PAHs were measured. Principal components analysis with multivariate linear regression and PAH profiles of specific combustion sources were used to identify historical fuel use. During the early 1940s to the early 1970s, PAHs concentrations increases with the increased combustion of coal, and relatively high petroleum source could be linked to the establishment of the Daqing Oil Field. The source apportionment suggested that coal combustion replaced wood burning and became the dominant fuel since the 1940s and petroleum source increased. These results were coincidence with the rapid economic growth occurring in China.

Keywords Lianhuan Lake · Sediments · PAHs · PCA/MLR · Source

Polycyclic aromatic hydrocarbons (PAHs) are a group of persistent organic pollutants (POPs) widely distributed in the environment (Ravindra et al. 2008). Because some PAHs are toxic and potential carcinogens, the United States Environmental Protection Agency (USEPA) identified 16 PAHs as "priority pollutants" (Liu et al. 2009). Polycyclic aromatic hydrocarbons are mainly derived from incomplete combustion of organic matter (e.g., coal, wood, diesel, gasoline and petroleum, etc.) and the accidental spillage of crude or refined oil (Liu et al. 2005; Agarwal et al. 2006). Studies indicated that anthropogenic sources far outweigh the inputs from natural sources of PAHs (Martins et al. 2010). Hence, PAHs can be useful indicators of changes in fuel consumption and potential environmental contamination (Yan et al. 2009; Martins et al. 2010).

Previous research has focused mainly on current concentrations in the atmosphere, soil, and water, and the distribution, sources, fate, transport as related to ecological risk of PAHs (Qu et al. 2002; Karlsson and Viklander 2008; Sun et al. 2009). Study of core samples can provide historical evidence of anthropogenic input sources. Previous studies revealed that the variations of PAHs concentrations based on time records followed economic development; demonstrating that changes in energy usage were correlated with a booming economy, especially in China (Yan et al. 2009). However, these investigations apportioned PAHs sources qualitatively only and have been limited in identifying the contributions of sources from different time phases quantitatively. The current study evaluates historical changes in PAH profiles, to further investigate the changes of energy usage that can be inferred from PAHs, and to quantify the relative contributions of the sources in different periods using PCA/MLR method.

Materials and Methods

A 34 cm long sediment core was collected at the center of the south Lianhuan Lake, Heilongjiang Province, China (Fig. 1) during July 2007, using a stainless steel static

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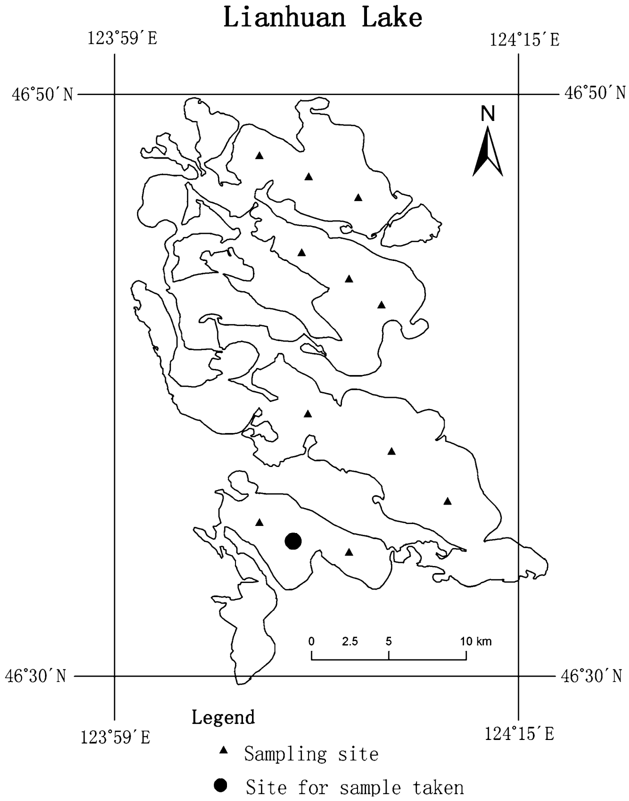

Fig. 1 Map of sampling sites and the site for sample taken in the Lianhuan Lake, northeast China

gravity piston corer. The core sample was immediately extruded into 1 cm long segments, placed in clean plastic bags, and stored at −18°C before analysis.

Individual core segments were dated using ^{137}Cs assay using a hyper-pure Ge detector and Ortec919 controller (made by EG&G Ortec) with a 16 K multichannel analysis system. Core dating was determined by the Nanjing Institute of Geography and Limnology, Chinese Academy of Sciences, Nanjing, China.

Sixteen priority PAHs were measured in 10 g of dried sample from each core segment following Methods 3545A, 3630 and 8275a of the United States Environmental Protection Agency (USEPA 1996). The analysis was done by the Heilongjiang Environmental Monitoring Centre, Harbin, China and included naphthalene (Nap), acenaphthylene (Acey), acenaphthene (Ace), fluorene (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene (Fluo), pyrene (Pyr), chrysene (Chr), benzo[a]anthrancene (BaA), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), indeno[1,2,3-cd]pyrene (IcdP), dibenzo[a,h]anthracene (DahA), and benzo[g,h,i]pyrene (BghiP). These priority PAHs were extracted from the samples using hexane/acetone (1:1, v/v) solution in an accelerated solvent system (ASE 300) at a pressure of 1500 psi and 100°C. Extracted samples were reduced to 1ml using nitrogen stream and PAH concentrations measured using GC/MS in the SIM mode.

Method blanks, reagent blanks, and triplicate spiked blanks were analyzed as quality control measures. The surrogate recoveries in all sediment samples were 45 %–66 % for naphthalene-d_8, 75 %–87 % for acenaphthene-d_{10}, 83 %–106 % for phenanthrene-d_{10}, 88 %–101 % for chrysene-d_{12}, and 89 %–104 % for perylene-d_{12}. The detection limits (DL) for PAHs was 1–12 ng/g dry weight. The results were corrected with surrogate recoveries. Statistical analysis of data was performed using SPSS 11.5 software.

Results and Discussion

The total concentrations of 16 PAHs in sediments ranged from 198 to 1,056 ng/g dry weight and the over all mean concentration was 446 ng/g (Table 1). The predominant PAH was Phe, followed by Nap and Flu, accounting for roughly 41.8 %, 18.4 % and 16.6 % of the total PAHs, respectively. In general, the 16 PAHs were dominated by low molecular weight (LMW, 2–3 ring PAHs) congeners, and 3-ring PAHs were the prevalent congeners in most samples, accounting for a mean of 64.7 %. Higher molecular weight PAHs (HMW, 4–6 ring) especially 5 and 6-ring PAHs were less prevalent, accounted for a mean of only 1.44 %. These results are consistent with our previous study of PAHs in core sediments in north Lianhuan Lake, where the concentrations of PAHs ranged from 297 to 1,328 ng/g with the LMW components predominated (Sun et al. 2011).

In the present study, the method of PCA was used to separate PAHs that have similar source profiles and modes of input and at the same time to quantify the source contributions to PAHs (Liu et al. 2009; Lv et al. 2010). The combustion of different materials may release different individual PAHs compound. Wood combustion is typically represented by Acey and Phe (Mai et al. 2003), and high contents of Fluo and Pyr typically represent biomass burning (Simoneit 2002). Marr et al. (1999) and Dobbins et al. (2006) reported that Nap, Flu and Ace are abundant in petrogenic source, and Harrison et al. (1996) indicated that Phe, Ant, Fluo, Pyr, Chr, BbF and BkF are representative of coal combustion. In traffic emissions, combustion of gasoline will mainly generate BghiP and DahA, and diesel will generate IcdP (Simcik et al. 1999). Although sources of PAHs are very complex, we can use PAH profiles to classify sources in different core sediments according to the findings of former researches.

According to the variation of PAH concentrations, three periods may be distinguished (Table 1; Fig. 2). Some individual PAHs such as BkF and BghiP were excluded

Table 1 Concentrations of 16 PAHs in the core sediments (ng/g)

PAH	Overall		Period I		Period II		Period III	
	Range	Mean	Range	Mean	Range	Mean	Range	Mean
Nap	15.0–191	82.2	15.0–98.6	54.0	58.7–191	115	93.8–149	130
Acey	n.d.–7.8	0.7	n.d.–7.8	0.8	n.d.–2.3	0.4	n.d.–6.9	1.0
Ace	2.4–17.4	8.6	2.4–14.5	6.3	4.1–17.4	10.7	9.9–15.3	13.2
Flu	27.7–129	74.2	27.7–129	59.6	48.4–129	94.2	78.6–115	95.6
Phe	88.9–353	186	88.9–353	152	151–339	238	165–312	234
Ant	4.4–35.1	12.9	4.4–33.6	10.3	7.3–35.1	17.4	9.8–20.3	15.9
Fluo	13.7–65.6	30.3	13.7–32.1	22.5	21.1–65.6	41.2	23.1–58.7	41.6
Pyr	7.5–386	37.3	7.5–386	39.8	15.0–84.7	36.9	18.2–46.0	30.7
Chr	1.1–17.5	5.1	1.1–7.7	3.8	2.8–8.7	6.2	3.7–17.5	7.5
BaA	n.d.–6.3	1.4	n.d.–1.6	0.8	0.7–2.8	1.9	0.9–6.3	2.6
BbF	0.7–18.7	4.0	0.7–5.5	2.7	2.4–7.0	4.4	2.9–18.7	7.6
BkF	n.d.–4.5	0.2	n.d.	n.d.	n.d.	n.d.	n.d.–4.5	1.0
BaP	n.d.–5.7	0.6	n.d.–1.1	0.4	n.d.–1.7	0.5	0.3–5.7	1.6
IcdP	n.d.–9.3	0.7	n.d.–0.6	0.1	n.d.–1.0	0.4	n.d.–9.3	2.4
DahA	0.9–2.1	1.0	0.9–1.2	1.0	0.9–1.3	1.0	0.9–2.1	1.3
BghiP	n.d.–8.4	0.3	n.d.	n.d.	n.d.	n.d.	n.d.–8.4	1.2
ΣPAHs	198–1056	446	198–1056	354	326–809	569	408–783	587

n.d. not detected

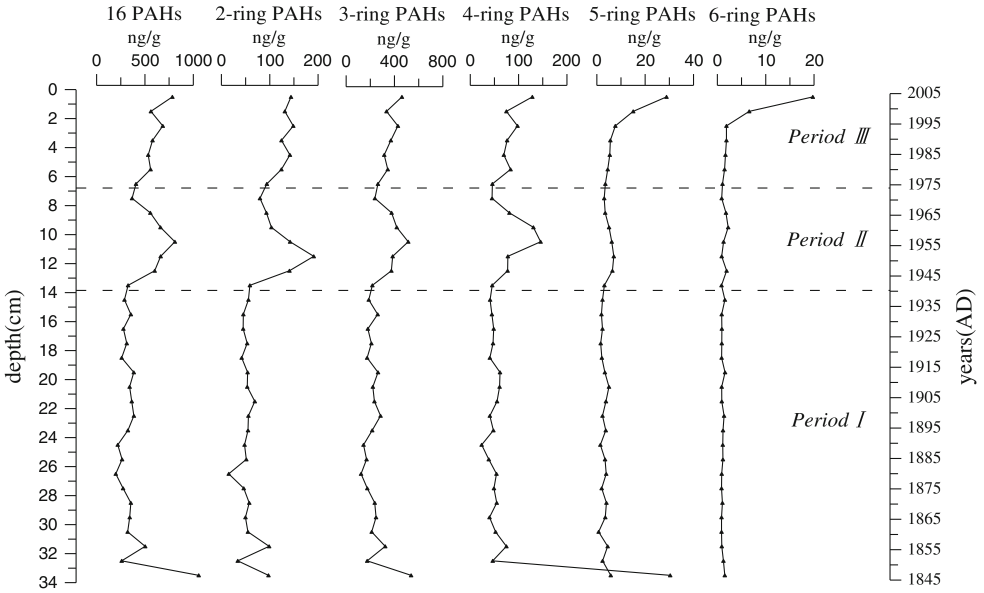

Fig. 2 Concentrations of 16 PAHs and character of each PAHs obtained in different depths and years

because they were not detected in most sediment samples in the period I and II. Furthermore, the sample in the lowest layer (33.5 cm) was also excluded due to the extreme outlier.

Period I (33.5–14.5 cm) was from the 1840s to the late 1930s according to ^{137}Cs dating. The concentrations of PAHs were relatively low and stable. There were four factors that accounted for 82.64 % of the variability in this period (Table 2). Factor 1, which explained 28.96 % of total variance, is heavily weighted in Ace and Flu, along with moderate loadings for Nap, Acey and Pyr. This factor mainly represented wood combustion source, together with the source of petroleum emission. Factor 2, contributing 22.56 % of the variance, is highly weighted by BbF, Chr and BaA with moderate loadings of BaP and Fluo. The highest factor loadings of BaA, BbF and Chr are indicative of coal combustion. Factor 3 is responsible for 17.64 % of the variance, which is predominately composed of Ant, Phe and Fluo. Relatively high loadings of Phe and Fluo were also consistent with the sources of plant coking and biomass burning. Factor 4, which explained 13.49 % of the variance, is mainly dominated by DahA and IcdP. High loadings of 6-ring compounds appeared to be related to sources of traffic emissions.

Period II (13.5–7.5 cm, from the early 1940s to the early 1970s) the concentrations of PAHs increased significantly from 13.5 cm to between 9.5 and 11.5 cm where the greatest values were detected, and then PAHs decreased abruptly to 7.5 cm. The concentrations of most LMW PAHs were greater than the mean concentrations of the whole sediment core. The results of PCA also resulted in four factors which accounting for 96.84 % of the variance. Factor 1 is responsible for 38.37 % of the variances, which is heavily weighted by Nap, Ace, Flu, Chr, BaA and BbF. This group of PAHs is consistent with the characteristic of coal combustion and petroleum emission source. Factor 2, contributing 21.33 % of the variance, is predominately composed of Pyr, Ant and Phe, which represented sources of wood and biomass burning. Factor 3 is responsible for 20.83 % of the variance, and is highly loaded with DahA, IcdP and Fluo, representing traffic emissions. Factor 4, contributing 16.31 % of the variance, is predominately weighted in Acey and BaP. This factor included just two PAHs, one a LMW and one a HMW PAH, and the specific source is difficult to identified from the two compounds, we speculated that there maybe an unknown source.

Period III (6.5 cm to the surface) was dated from the 1970s to present. The concentrations of 16 PAHs increased gradually, especially the HMW PAHs that increased markedly from 2.5 cm to the surface. The mean concentrations of the HMW PAHs in the core segments in this period were greater than the mean concentrations in the whole sediment core. Three factors accounting for 95.77 % were identified. The first factor was responsible for 47.80 % of the total variance, and is heavily weighted by 4–6 rings PAHs, including Chr, BaA, BbF, BkF, BaP, IcdP, DahA and BghiP. This group of PAHs is consistent with the emission characteristic of coal combustion and it is also similar to that of traffic emissions. Factor 2, accounting for 39.06 % of the variance, is predominately loaded with 2–4 rings PAHs, such as Ant, Ace, Fluo, Phe, Flu, Nap and Pyr. This factor is associated with sources of wood and biomass burning and petroleum emission source. Factor 3, contributing 8.92 % of the variance, is only highly weighted by Acey. It is believed that this factor is consistent with factor 4 in the second time phase, although BaP did not exist, because one component can not explain the specific source.

In general, the PAH sources around the Lianhuan Lake area primarily result from wood burning, coal combustion, vehicular emission and petroleum spillage. For further evaluation of human activity-related energy usage, MLR was performed to determine the percentage contributions of the major sources in different periods. The multiple

Table 2 Rotated component matrix of 16 PAHs in the three periods

	Period I (82.64 %)				Period II (96.84 %)				Period III (95.77 %)		
	PC1	PC2	PC3	PC4	PC1	PC2	PC3	PC4	PC1	PC2	PC3
Nap	**0.78**	0.13	0.37	0.06	**0.99**	0.10	−0.04	0.07	0.20	**0.84**	0.43
Acey	**0.73**	0.40	−0.16	0.27	0.13	−0.07	0.02	**0.99**	−0.17	−0.07	**0.97**
Ace	**0.97**	−0.04	0.06	−0.05	**0.93**	0.17	−0.18	−0.20	0.16	**0.92**	0.34
Flu	**0.92**	0.02	0.33	0.07	**0.88**	0.39	0.04	−0.08	0.38	**0.86**	−0.26
Phe	0.55	0.18	**0.78**	0.04	0.40	**0.77**	0.49	−0.03	0.42	**0.88**	−0.21
Ant	0.10	0.06	**0.93**	−0.01	0.38	**0.90**	0.14	−0.04	0.12	**0.96**	−0.16
Fluo	−0.12	**0.60**	**0.68**	0.01	0.38	0.47	**0.79**	−0.09	0.39	**0.92**	−0.08
Pyr	**0.64**	0.13	−0.14	−0.39	0.20	**0.92**	0.24	−0.19	0.39	**0.79**	−0.08
Chr	0.48	**0.83**	0.04	0.12	**0.84**	0.21	0.46	0.09	**0.91**	0.40	-0.04
BaA	−0.05	**0.83**	0.32	0.07	**0.79**	0.25	0.50	−0.01	**0.90**	0.42	−0.08
BbF	0.36	**0.89**	0.08	0.04	**0.93**	0.29	0.15	−0.08	**0.91**	0.41	−0.02
BkF	–	–	–	–	–	–	–	–	**0.98**	0.17	−0.05
BaP	−0.21	**0.61**	−0.10	−0.53	−0.15	−0.18	−0.16	**0.94**	**0.95**	0.26	−0.10
IcdP	0.02	0.02	0.20	**0.82**	0.03	0.26	**0.75**	0.53	**0.96**	0.28	−0.03
DahA	−0.06	0.14	−0.30	**0.83**	−0.10	0.13	**0.94**	−0.27	**0.97**	0.05	−0.12
BghiP	–	–	–	–	–	–	–	–	**0.86**	0.35	−0.06
Variance (%)	28.96	22.56	17.64	13.49	38.37	21.33	20.83	16.31	47.80	39.06	8.92

Factor loadings higher than 0.60 were highlighted in boldface

Rotation method: Varimax with Kaiser normalization

Table 3 Source contributions based on PCA/MLR in the three time phases

	Multiple regression model	R^2	Source contribution (%)			
			Factor 1	Factor 2	Factor 3	Factor 4
Period I	Y=0.770F1 + 0.213F2 + 0.596F3 + 0.003F4	0.992	48.7 (W+P)	13.5 (C)	37.7 (W)	0.2 (V)
Period II	Y=0.701F1 + 0.637F2 + 0.315F3 − 0.035F4	0.991	42.4 (C+P)	38.5 (W)	19.1 (V)	(U)
Period III	Y=0.500F1 + 0.864F2 − 0.052F3	0.999	36.7 (C+V)	63.3 (W+P)	(U)	

W wood source, *C* coal source, *V* vehicular source, *P* petroleum source, *U* unknown source

regression models, R^2 values and contributions of different sources are presented in Table 3. Factor 4 of period II and the factor 3 of period III were ignored in the analysis of sources contributions, as the regression coefficients of these factors were negative, and a negative source contribution is impossible. Furthermore, as previously discussed these two factors were identified as an unknown source; further research is needed to investigate their source and potential toxicity in the Lianhuan Lake.

The source of wood and biomass burning was mainly derived from domestic activities, especially in agricultural areas. In China, wood burning was considered as a major energy used before China's reform and opening-up, which can be explained by the fact that this kind of PAHs source dominated in period I in both the first factor and the third factor (with the contributions of 48.7 % and 37.7 %, respectively). In period II, the contribution of wood source decreased to 38.5 %, suggesting that burning of wood and plant biomass as energy source declined, suggesting that there may have been a change in energy usage.

The PCA factor of coal combustion elevated from the second factor in period I to the first factor in period II and III and petroleum and vehicular sources were identified in the first factors of period II and III, hence, it is difficult to investigate the source of coal combustion quantitatively. Results indicate that coal combustion has replaced wood burning and became a dominant source of PAHs since the 1940s. It is known that, with economic development, emissions from coal combustion result not only from domestic activities but also from industrial activities.

The traffic-related activity is another pyrogenic source of PAHs, which also reflects societal development. The contributions of vehicular source of PAHs increased largely from period I (0.19 %) to period II (19.1 %), and elevated to the first factor in period III, which is attributed to the increased use of motor vehicles during these periods.

As previously reported (Sun et al. 2011), the petroleum source of PAHs in the Lianhuan Lake area are thought to result from the lake being adjacent to the Daqing Oilfield and the spilled oil from drilling and transportation processes may result in the accumulated of petroleum in the sediments of the lake. In the current study, the environmental impact of the oilfield was further investigated. The factor of petroleum source downgraded from the first factor in the period I and II to the second factor in the period III. The establishment and exploitation of the oil field might explain why the relative high contribution was detected in period II. Then the contribution decreased in the period III, demonstrating the reduction of oil leakage.

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