

PAHs Contamination in Surface Sediments from Lake Hongfeng, China

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Abstract

Polycyclic aromatic hydrocarbons (PAHs) are potentially carcinogenic and mutagenic compounds that have raised considerable environmental concerns. In the present research, sixteen PAH compounds in ten sediment samples collected from Lake Hongfeng, one of the five drinking water sources for Guiyang City, were estimated based on gas chromatography-mass spectrometry (GC-MS) method. The results indicated that the total amount of PAHs ranged from 656.8 to 4860.9 $\mu\text{g}/\text{kg}$ with the mean concentration of 2520.7 $\mu\text{g}/\text{kg}$ in sediments from Lake Hongfeng, and naphthalene was the dominant PAH compound and its concentrations ranged from 108.9 to 4370.3 $\mu\text{g}/\text{kg}$ with the mean concentration of 1987.4 $\mu\text{g}/\text{kg}$. Both principal component analysis (PCA) and correlation study suggested that the distribution characteristics of PAH compounds in sediments from the lake were affected by three potential factors. One factor should be their physicochemical properties, such as their molecular weight and number of rings. The other two probably are associated with their origin (point and non-point pollution sources). In addition, the analysis of PAH composition demonstrated that the PAHs in the sediments were mainly from pyrolytic origins.

Introduction

Polycyclic aromatic hydrocarbons (PAHs) in the environment are attracting an increased attention since they are potentially carcinogenic and mutagenic compounds and widely distributed in the environment¹. Due to their special structures, they can not be decomposed by microorganisms easily, and thus they will persist in the environment for a long time. PAHs in the environment are primarily from incomplete burning of carbon-containing materials like oil, wood, garbage or coal. Many useful products such as mothballs, blacktop, and creosote wood preservatives also contain PAHs. They have also been found at low concentrations in some special-purpose skin creams and antidandruff shampoos that contain coal tars. PAHs can be introduced into the aquatic system through many ways such as atmospheric deposition, urban runoff, oil spill, domestic and industrial wastewater discharges².

Lake Hongfeng (E: 106°24' - 106°43', N: 26°31' - 26°34') is located about 32 km west of Guiyang City, the capital of Guizhou Province in southwestern China. The lake is the largest artificial lake on the Guizhou Plateau, and has a flood storage capacity of 600 million cubic meters and covers an area of 57.2 square kilometers. The lake consists of two parts: the North Lake and the South Lake (Figure 1), and the North Lake is a little smaller than the South Lake. The lake is one of the five drinking water sources for Guiyang City, and it is a multi-functional water body not only for drinking-water provision, but for flood control, shipping and fishery as

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well. The lake is situated on the Maotiao River, which flows into Wujiang River, a major tributary of Yangtze River. Therefore the pollution status of Lake Hongfeng has a close relationship not only with social development of Guiyang area and but also with ecology systems of Yangtze River. During the past two decades, a large amount of various pollutants were discharged into the lake with the development of the industrial and commercial activities in the watershed. The main pollutant sources of industrial effluents include coal-fired power plants, fertilizer plants, electroplating, printing, metal finishing and chemical industries located around nearby Qingzhen City and chemical industries located along the Yangchang River, which is the main headstream of the Lake Hongfeng. Studies focused on nitrogen, phosphorus, heavy metals and organic matter in sediments of Lake Hongfeng have been conducted by a number of researches³⁻⁶, and however, few studies have concerned pollution of PAHs in sediments of Lake Hongfeng have been carried out. The main objectives of this research were to investigate the sixteen PAH compounds, which are on the United States Environmental Protection Agency (US EPA) priority pollutant list, in the bottom sediments of Lake Hongfeng, and to study their distribution characteristics in the Lake and identify their possible pollution sources.

Materials and methods

The surface sediment samples used in the present study were sampled during Oct. 2008 in Lake Hongfeng with a stainless steel grab-sampler. Superficial sediment samples were taken at 10 locations: MT, JMY, TLHJC, BHHX, TX, HYDDQ, HYD, AL, LHW and HWHDC (Figure 1), which were selected based on the size, shape and water flowing direction of the lake, and the possible origin of pollutants was taken into account as well. The surface sediment samples were put in pre-clean glass bottles (1000 cm³ volume) and immediately transported to our laboratory, where the sediment samples were centrifuged and the supernatant were discarded, and then resulting sediments were stored for analysis.

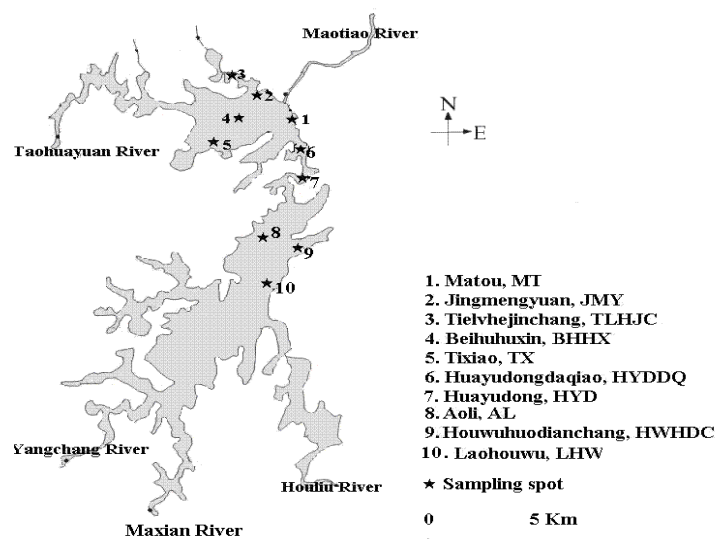


Figure 1. Distribution of sampling spots in Lake Hongfeng.

The following instruments were used in this research: (1) gas chromatography-mass spectrometry (GCMS-QP2010) was from Shimadzu Corporation, Japan; (2) water purification system (Nex Power 2000)

from Human Corporation, Korea; (3) rotary evaporator (N-1001) from Eyela Corporation, Japan; (4) immersion oscillator (SHZ-C) from Shanghai Medical Instruments Corporation, China. The PAHs standard mixture was purchased from AccuStandard Inc., USA. All reagents used in this study were made in China. The petroleum ether (analytical reagent) was purchased from Tianjing Zhiyuan Chemical Reagent Co., dichloromethane (analytical reagent) from Chengdu Kelong Chemical Reagent Limited Co., acetone from Sinopharm Chemical Reagent Co., Ltd, isooctane from Tianjing Damao Chemical Reagent Factory, and silica gel (zcx. II, 100-200) from Qingdao Haiyang Chemical Factory.

Extraction, clean-up and analysis procedures, which were mainly based on the international standard (ISO 18287:2006(E), Soil quality - Determination of polycyclic aromatic hydrocarbons (PAHs) - Gas chromatographic method with mass spectrometric detection (GC-MS))⁷. Ten gram (accurate to 0.0001 gram) of sediment sample was weighed and placed into a conical flask, and then 50 ml of acetone was added into the conical flask and subsequently the conical flask was closed. The extraction was carried out by shaking thoroughly for 1 hour on the shaking machine mentioned above. Then 50 ml of petroleum ether was added, the shaking was going on for another hour, the supernatant was decanted. Another 50 ml of petroleum ether was added and the flask was shaken again. After allowing setting, the supernatant was decanted. The extracts were combined, and then the acetone and other polar components were removed by shaking twice with 400 ml of water. The organic layer was dried over anhydrous sodium sulfate, and transferred to concentration apparatus. At the same time 100 μ l of isooctane was added as keeper. The resulting solution was concentrated on a water bath set at 30 °C to about 10 ml with the rotary evaporator under reduced pressure. Then the solution was cleaned with silica gel adsorption chromatography and concentrated under room temperature. Finally, the obtained solution was prepared to 2 ml with petroleum ether. 1 microlitre of each solution prepared above was injected in a splitless mode into the GC-MS equipped with a capillary column which was a 50 m Se-54 (0.25 mm i.d, 0.33 μ m film thickness). Helium was used as carrier gas at a constant flow rate of 1 ml/min. Before sample injection, the column temperature was programmed from an initial temperature of 60 °C (4 min hold) to 120 °C (4 min hold) at the rate of 20 °C/min, then to 270 °C (25 min hold) at the rate of 5 °C/min, and finally to 290 °C (25 min hold) at the rate of 10 °C/min. The injection temperature of gas chromatographic was 290 °C. The ion source temperature and interface temperature of mass spectrometric were both set at 250 °C, and the mass spectrometer was in selective ion monitoring (SIM) mode at an electron impact energy of 70 eV. Quantification was performed by the external standard method by using a 16 PAH compounds standard mixture. The 16 PAH compounds in the standard mixture solution were detected in the sequence of naphthalene (Nap), acenaphthylene (Acy), acenaphthene (Ace), fluorene (Fle), phenanthrene (Ph), anthracene (An), fluoranthene (Fla), pyrene (Py), benzo[a]-anthracene (BaA), chrysene (Chr), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), indeno[1,2,3-cd]pyrene (InD), dibenzo[a,h]anthracene (DahA), and benzo[g,h,i]perylene (BghiP).

Results and discussion

Table 1 lists the concentration levels of sixteen PAH compounds in the sediment samples collected from Lake Hongfeng. The concentration levels of the sixteen PAHs decreased in the order Nap > Ph > Fla > Py > BaP > Fle

Table 1. Concentration levels of PAH compounds in sediment samples from Lake Hongfeng ($\mu\text{g}/\text{kg}$, dry weight)

Sampling sites	Nap	Acy	Ace	Fle	Ph	An	Fla	Py	BaA	Chr	BbF	BkF	BaP	InD	DahA	BghiP	Σ PAHs
MT	2641.4	6.3	10.5	28.5	98.2	11.2	70.0	55.8	21.6	32.5	20.2	3.1	45.9	10.5	4.4	24.7	3084.8
JMY	2053.5	2.5	5.6	26.2	105.3	9.1	102.4	76.4	15.6	36.5	ND*	ND	11.4	ND	ND	ND	2444.4
TLHJC	108.9	36.4	42.5	39.9	61.4	38.6	73.5	83.1	17.8	19.7	4.3	15.0	56.9	28.8	13.7	16.4	656.8
BHHX	1876.3	2.8	5.1	16.3	52.2	8.5	44.4	40.1	18.5	20.0	31.1	32.1	89.7	40.2	13.9	46.9	2338.1
TX	985.3	99.1	108.5	114.8	155.5	98.7	153.4	147.3	86.7	98.9	51.7	19.6	33.1	ND	ND	ND	2152.5
HYDDQ	722.7	1.2	2.6	6.8	23.8	2.8	7.5	10.9	3.3	3.8	ND	ND	ND	ND	ND	ND	785.4
HYD	400.3	5.0	7.3	16.8	63.4	11.3	32.2	33.8	63.9	59.6	82.0	59.0	92.9	33.9	25.2	124.1	400.3
AL	3619.9	9.5	13.7	48.3	147.2	23.5	107.4	79.8	28.9	24.8	41.8	42.5	58.7	31.2	7.7	39.7	3619.9
HWHDC	3095.2	3.7	8.2	32.3	113.3	10.0	90.4	62.1	11.0	19.1	ND	ND	3.7	ND	ND	ND	3448.9
LHW	4370.3	0.9	17.2	65.7	175.1	12.6	70.8	53.8	14.2	48.4	3.6	ND	10.8	ND	ND	17.6	4860.9
Minimum	108.9	0.9	2.6	6.8	23.8	2.8	7.5	10.9	3.3	3.8	ND	ND	ND	ND	ND	ND	656.8
Maximum	4370.3	99.1	108.5	114.8	175.1	98.7	153.4	147.3	86.7	98.9	82.0	59.0	92.9	40.2	25.2	124.1	4860.9
Mean	1987.4	16.8	22.1	39.6	99.5	22.6	75.2	64.3	28.1	36.3	23.5	17.1	40.3	14.4	6.5	26.9	2520.7
Std. Deviation	1440.2	30.8	32.4	31.4	49.5	28.6	41.6	36.8	26.3	27.2	28.0	21.1	34.3	16.9	8.6	38.2	1436.0

*ND, not detected.

Table 2. Correlations between PAH compounds in sediment samples from Lake Hongfeng

	Nap	Acy	Ace	Fle	Ph	An	Fla	Py	BaA	Chr	BbF	BkF	BaP	InD	DahA	BghiP
Nap	1															
Acy	-0.283	1														
Ace	-0.192	0.991**	1													
Fle	0.272	0.822**	0.881**	1												
Ph	0.753**	0.345	0.434	0.797**	1											
An	-0.186	0.992**	0.992**	0.875**	0.442	1										
Fla	0.396	0.656*	0.685*	0.833**	0.819**	0.717*	1									
Py	0.164	0.827**	0.847**	0.884**	0.706*	0.869**	0.956**	1								
BaA	-0.223	0.749**	0.735*	0.648*	0.359	0.767**	0.505	0.626*	1							
Chr	0.026	0.727*	0.759**	0.800**	0.602	0.758**	0.633*	0.708*	0.903**	1						
BbF	-0.202	0.321	0.288	0.228	0.109	0.350	0.130	0.211	0.828**	0.601	1					
BkF	-0.215	0.084	0.044	-0.017	-0.060	0.124	-0.039	0.029	0.564	0.267	0.891**	1				
BaP	-0.183	0.059	0.026	-0.066	-0.103	0.079	-0.040	0.057	0.427	0.187	0.738**	0.850**	1			
InD	-0.224	-0.151	-0.193	-0.299	-0.307	-0.131	-0.247	-0.168	0.119	-0.170	0.529	0.807**	0.906**	1		
DahA	-0.524	-0.172	-0.221	-0.422	-0.522	-0.184	-0.481	-0.360	0.206	-0.077	0.585	0.769**	0.761**	0.833**	1	
BghiP	-0.167	-0.229	-0.248	-0.262	-0.160	-0.206	-0.313	-0.271	0.390	0.181	0.794**	0.860**	0.799**	0.713*	.827**	1

* $p < 0.05$ (two tailed), ** $p < 0.01$ (two tailed).

> Chr > BaA > BghiP > BbF > An > Ace > Acy > BkF > InD > DahA (based on the mean values from all ten locations). The total amount of PAHs ranged from 656.8 $\mu\text{g}/\text{kg}$ to 4860.9 $\mu\text{g}/\text{kg}$, and decreased in the order of LHW > AL > HWHDC > MT > JMY > BHHX > TX > HYDDQ > TLHJC > HYD. Nap is the dominant one among the sixteen PAH compounds, and its concentrations in most samples were larger than 1500 $\mu\text{g}/\text{kg}$. The concentration of Nap ranged from 108.9 to 4370.3 $\mu\text{g}/\text{kg}$, and its mean concentration was up to 1987.4 $\mu\text{g}/\text{kg}$ that was about twenty times higher than those for the other PAH compounds under consideration in the present research. The highest concentration of Nap turned up at sampling site LHW, which is located in the South Lake (Figure 1). The LHW site is closer to the estuary where the Yangchang River flows into the lake. As mentioned above, the Yangchang River is a main headstream of Lake Hongfeng, and should be one of the main pollution sources for the lake. Furthermore, Nap gave rather high concentrations at sampling sites AL (3619.9 $\mu\text{g}/\text{kg}$) and HWHDC (3095.2 $\mu\text{g}/\text{kg}$). Near the sampling site HWHDC, there is a coal-fired power plant which has combusted a large amount of coal, therefore the power station should be regarded as one of the main origins for Nap at this site. Acy, Ace, Fle, Ph, An, Fla, Py, BaA and Chr were also important since they were detected in all sediment samples collected.

From Table 2, it is evident to find that there were some close relationships between levels of the PAH compounds, and the highest Pearson correlation coefficient was up to 0.992 ($p > 0.01$) that existed between Acy and An, and between Ace and An. As marked in Table 2, the table may be divided into three sections according to their Pearson correlation coefficients, and this probably means that their distribution characteristics were affected by three factors. In order to present an in-depth analysis of distribution characteristics and pollution sources of PAHs in sediments from Lake Hongfeng, principle component analysis (PCA), a multivariate statistical analysis, was carried out. The main reason why PCA was selected was that it offers the possibility to interpret multivariate data in terms of processes. The results of the statistical analysis were shown in Figure 2 (only loading scores greater than 0.5 were considered). Three principal components were extracted, and this result was in accordance with the correlation analysis. It can be inferred that the three potential factors may be as follows: one factor that should be the physicochemical property, such as their molecular weight and number of rings, and the other two factors that probably are associated with their origin (point and non-point pollution sources).

The analysis of PAH composition can be used as an indicator to assess the possible source and illustrate the fate and transport of PAHs in environment. Jiang et al reported that Ph and An are two structural isomers, and Ph is a thermodynamically more stable compound than An, and Fla and Py have the same condition as Ph and An⁸. The values of Fla/Py and Ph/An ratios are related to pyrolytic origins if the value of Fla/Py is greater than 1 and that of Ph/An less than 10 at the same time, while the value of Fla/Py less than 1 and that of Ph/An greater than 10 at the same time should be attributed to a petrogenic source (the ratios were calculated using the average concentrations of individual PAH in samples collected from different stations). In the present research, the value of Fla/Py was 1.17 that was greater than 1, and the value of Ph/An was 1.77 that was less than 10. Therefore, it probably means that the PAHs in sediments of Hongfeng Lake were mainly from pyrolytic origins. It is believed that major pollution of PAHs caused by some point sources, such as coal-fired power plant, fertilizer plant, and

the atmospheric deposition could also be major pollution source duo to combustion of a large amount of coal in local area.

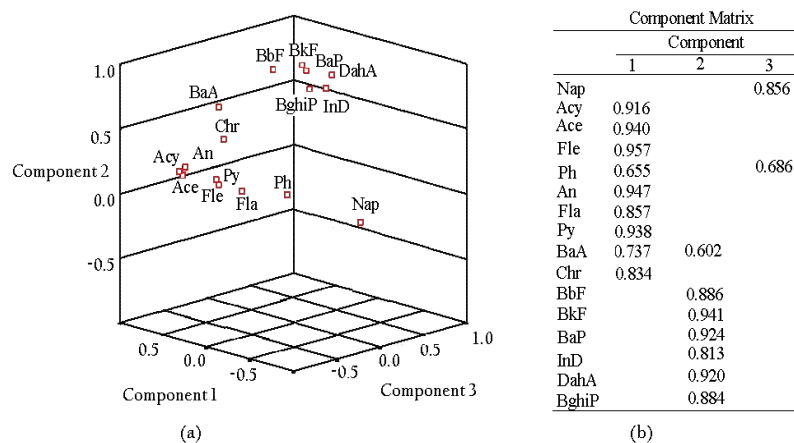


Figure 2. PCA of PAHs in sediments from Lake Hongfeng (a) component plot, (b) component matrix

In conclusion, Nap was the dominant of the sixteen PAH compounds, and the distribution characteristics of PAHs in sediments from Lake Hongfeng were mainly affected with three factors. It is believed that the pyrolytic origins should be main pollution sources for PAHs occurred in sediments of the lake: emissions from nearby power and fertilizer plants, and atmospheric deposition of PAHs from a number of other sources in local area which use large amounts of coal as raw materials or fuels.

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