

Sedimentary record of polycyclic aromatic hydrocarbons in a sediment core from a maar lake, Northeast China: evidence in historical atmospheric deposition

Yu-Feng Guan,^{ab} Jian-Lin Sun,^c Hong-Gang Ni^c and Jian-Yang Guo^{*a}

Received 12th June 2012, Accepted 14th June 2012

DOI: 10.1039/c2em30461a

A maar lake is an excellent ecosystem to study the atmospheric deposition of pollutants, as its contaminants are primarily by atmospheric deposition. In this study, a sediment core from Sihailongwan Maar Lake, Northeast China, was collected and the historical atmospherically deposited polycyclic aromatic hydrocarbons (PAHs) were analyzed. The concentrations of TPAHs (the sum of the US EPA proposed 16 priority PAHs, excluding naphthalene and pyrene) ranged from 473.9 to 2289 ng g⁻¹ with a slow increasing stage in the deeper sediments and a sharp increasing stage in the upper sediments. The input rate of TPAHs, especially that of PAH₉ (the sum of fluoranthene, benzo(*a*)anthracene, chrysene, benzo(*b*)fluoranthene, benzo(*k*)fluoranthene, benzo(*a*)pyrene, indeno(1,2,3-*cd*)pyrene, dibenzo(*ah*)anthracene, and benzo(*ghi*)perylene), correlated well to the Chinese historical socioeconomic data. This indicates that sediment PAHs were mainly derived from human activities and PAH₉ can be regarded as a better indicator of the local socioeconomic development. Source identification suggested that PAHs were originated primarily from mixed sources (*e.g.*, coal and biomass burning and petroleum combustion), except for perylene which was mostly of diagenetic origin. In addition, the down-core PAHs profile clearly illustrated that PAHs sources in Northeast China experienced a transformation from low- and moderate temperature to high-temperature combustion processes, especially after the late 1980s. Additionally, an ecological risk assessment using two redefined biological thresholds (TEQ_{ERL} and TEQ_{ERM}) indicated that most of the PAHs measured in the present sediment core would not cause an immediate toxic effect; only FLU and PHEN are a potential source of concern for biological impairment.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are of great environmental concern because of their potential toxic, mutagenic and

carcinogenic properties.¹ They can be transported over long distances through the atmosphere and affect various aquatic systems, even at remote sites.² Lacustrine sediment cores have been used for assessment of the historical inputs of PAHs in previous literature.³⁻⁷ However, PAHs in sediments are usually derived from many input sources, such as atmospheric deposition, riverine input, municipal runoff, accidental oil spills, *etc.*⁸ Furthermore, PAHs in sediments are also influenced by in-lake processes, such as remobilization from the catchment, losses through outfall and sediment redistribution.^{9,10} These processes are influenced by the

^aState Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang 550002, China. E-mail: guojianyang@mails.gyig.ac.cn

^bSchool of Chemistry and Environment, South China Normal University, Guangzhou 510006, China

^cShenzhen Graduate School, Peking University, Shenzhen 518055, China

Environmental impact

China has been undergoing rapid socioeconomic development within the last century, especially over recent decades. Intensive anthropogenic activities have resulted in large amounts of PAHs entering the ambient atmosphere. Sihailongwan Maar Lake (SHLW) is an excellent ecosystem which can be used to assess the historical atmospheric deposition of PAHs due to the specific conditions for preservation of environmental information. This study reports the historical atmospheric deposition of PAHs in a sediment core from SHLW. The possible source changes and potential ecological risks were also discussed. This is important to better understand the relationship between the anthropogenic activities and the historical pollution accumulation.

configuration of the lake basin which may change with time. In this context, finding a suitable environmental system to assess solely the historical atmospheric deposition of PAHs is crucial.

In Long Gang Volcanic Field, Jilin province, Northeast China, there are 8 maar- and crater lakes surrounded by a mixed conifer-hardwood forest region at elevations between 600 and 800 m above sea level.¹¹ The hydrological catchment areas of these lakes (which comprise only the inner crater slopes) are closed without a natural tributary or outlet. Due to their specific conditions for development and preservation of environmental information, a maar lake is one of the most important terrestrial archives of environmental information. These special hydrological properties made them receiving pollutants only from atmospheric deposition and to be a unique environment for assessing the atmospheric pollution.

Sihailongwan Maar Lake (SHLW, 42°17'N, 126°36'E) is a typical maar lake surrounded by virgin forest. It is an enclosed circular lake, with the maximum depth of *ca.* 50 m. The surface area of SHLW is 0.5 km² and the catchment area is only 0.7 km² (Fig. 1). SHLW is far from any pollution sources and human activities seldom occurred here. Under these conditions, sediments in SHLW accurately record the historical pollutants, which can allow us to reconstruct the pollutants' historical load in this area. In the present work, a sediment core from SHLW was collected and analyzed for PAHs using GC/MS measurement. The main objective of this work is to assess the historical atmospheric deposition of PAHs in Northeast China and to identify the possible emission source of sediment PAHs.

2. Materials and methods

2.1. Sampling

A sediment core (~30 cm length) was collected from SHLW, Northeast China, in September 2009. The sampling site is at the centre of the lake (Fig. 1). The sediment core was collected using a gravity corer and sectioned at 0.5 cm intervals *in situ*. The core sediments were seldom disturbed, as indicated by the clear overlying water, sediment interface and the preservation of fine sediment laminations, thus, with little influence on the chemistry results. After collection, the cores were wrapped in pre-cleaned aluminum foil, cooled with ice during transport to the laboratory where they were stored at -20 °C until further treatment.

2.2. Extraction and instrumental analysis

The detailed sample extraction procedures have been reported elsewhere.⁵ Briefly, an aliquot (~3 g dry weight) of freeze-dried,

homogenized sample, spiked with a mixture of five deuterated PAHs (naphthalene-d₈, acenaphthene-d₁₀, phenanthrene-d₁₀, chrysene-d₁₂, and perylene-d₁₂) as surrogate standards, underwent Soxhlet extraction with a 200 mL mixture of hexane and acetone (1 : 1, v/v) for 48 h. About 1 g activated copper was added for desulphurization. The extracts were filtered, concentrated to ~1 mL, and solvent-exchanged to hexane. The cleanup and fractionation were performed on an alumina/silica gel chromatography column. The PAHs fraction was eluted with 70 mL dichloromethane/hexane (3 : 7, v/v) and finally concentrated to 500 µL under a gentle flow of nitrogen. The internal standards, 2-fluoro-1,1-biphenyl and terphenyl-d₁₄, were added prior to instrumental analysis.

Instrumental analysis was performed on an Agilent 7890 gas chromatograph system equipped with an Agilent 5975 mass selective detector operating in selective ion monitoring mode. A DB-5MS fused silica capillary column (30 m length × 0.25 mm i.d. × 0.25 µm film thickness) was used for chromatographic separation. Splitless injection of 1.0 µL of sample was conducted with an auto-sampler. The GC oven temperature was programmed from 80 to 200 °C at a rate of 10 °C min⁻¹, to 220 °C at a rate of 2 °C min⁻¹, and then to 290 °C at a rate of 5 °C min⁻¹ (held for 15 min). Ultrahigh purity helium was employed as the carrier gas at a constant flow rate of 1 mL min⁻¹. The injector and detector temperatures were 280 °C and 250 °C, respectively. Mass spectra were acquired in the electron ionization mode with an impact voltage of 70 eV. The compounds which were quantified included naphthalene (NAP), acenaphthylene (ACY), acenaphthene (ACE), fluorene (FLU), phenanthrene (PHEN), anthracene (ANT), fluoranthene (FLUO), pyrene (PYR), benzo(*a*)anthracene (BaA), chrysene (CHRY), benzo(*b*)fluoranthene (BbF), benzo(*k*)fluoranthene (BkF), benzo(*a*)pyrene (BaP), benzo(*e*)pyrene (BeP), indeno(1,2,3-*cd*)pyrene (INP), dibenzo(*ah*)anthracene (DBA), benzo(*ghi*)perylene (BghiP) and perylene (PERY).

2.3. Quality control and quality assurance

The recoveries of the surrogate standards in all samples were 52.3 ± 14.1% for naphthalene-d₈, 75.6 ± 15.9% for acenaphthene-d₁₀, 84.4 ± 7.8% for phenanthrene-d₁₀, 99.9 ± 3.5% for chrysene-d₁₂, and 89.8 ± 4.0% for perylene-d₁₂. For quality control, a procedural blank (solvent), a spiked blank (standards spiked into solvent), and a spiked matrix (standards spiked into matrix) were analyzed. The mean recoveries of target PAHs ranged from 75.8 ± 4.9% to 114.3 ± 8.2% in a spiked blank and from 60.8 ± 1.1% to 120.9 ± 9.1% in a spiked matrix. Instrument stability was calibrated daily with standard solution and the daily calibrations were <10% for all of the target analyses. Detection limits were 0.05–0.1 ng g⁻¹ dry weight for PAHs (defined as *S/N* > 10). In the present study, we did not examine the certified reference materials because the whole sample preparation procedure was the same as in ref. 12. All the results were expressed on a dry weight basis and not corrected for surrogate recoveries. Relatively high levels of NAP and PYR were found in blank samples. Therefore, they were excluded entirely from the discussion below.

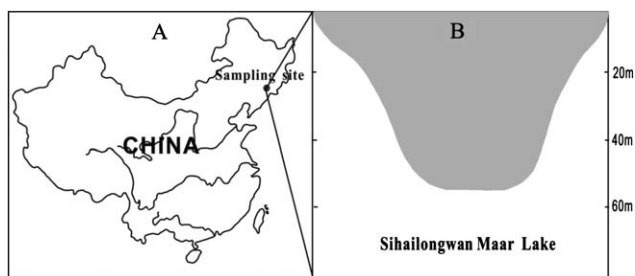


Fig. 1 Map of the sampling site (A: location of sampling site; B: cross-section of the SHLW Maar Lake).

3. Results and discussion

3.1. Temporal trends of PAHs

Using ^{210}Pb and ^{137}Cs , the sedimentation rate of SHLW has been investigated previously.¹³ A sedimentation rate of 0.11 cm a^{-1} achieved from the previous investigation was used in the present work.¹³ Based on the sedimentation rate of SHLW, only the upper portion of the core (0–10 cm) was analyzed, which covered a time-span of approximately 100 years. The vertical profile and the depositional fluxes of TPAHs (the sum of the US EPA proposed 16 priority PAHs, excluding for NAP and PYR) are shown in Fig. 2A. The TPAHs' concentrations and the depositional fluxes ranged from 473.9 to 2289 ng g^{-1} and 127.7 to 617.0 ng cm^{-2} per year, respectively. Overall, TPAHs' concentrations increased successively from the deeper segments analyzed to the surface with a slowly increasing rate in the deeper segments (1920s to the early 1980s) and a sharply increasing rate in the upper segments (the late 1980s to the present). From 1980 to the present, TPAHs increased 204%, from 753.8 ng g^{-1} to 2289 ng g^{-1} . The temporal trend of TPAHs' concentrations in SHLW was very similar to those recorded in the sediment cores from Qinghai Lake in Northwest China, Erhai Lake in Southwest China,^{5,14} and the sediment core from the Pearl River Estuary, South China,¹⁵ but different from those reported in developed countries, such as Europe,¹⁰ the United State,¹⁶ Canada,¹⁷ South Korea⁸ and Japan.¹⁸ In remote lakes across the Europe, the pyrolytic PAHs generally reached a climax in 1960–1980.¹⁰ Similar to that in Rhode Island, USA¹⁶ and Shield Lake, Canadian,¹⁷ the pyrolytic PAHs in Osaka, Japan¹⁸ also peaked in the 1950s. The period (1950s–1980s) in which PAHs started to decrease in developed countries is the very period that PAHs started to increase sharply in China.

As for the selected individual PAHs, the temporal trends of 4–6 rings PAHs were very similar to each other, with a quite flat stage in the deeper sediments (approximately the 1920s to the middle 1950s), a slowly increasing stage from the segment

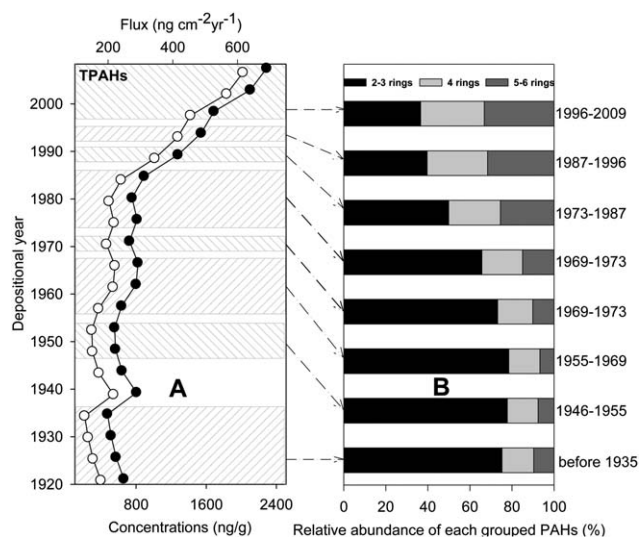


Fig. 2 Vertical profile of TPAHs (A) (solid circle: concentration; open circle: flux) and relative abundance of each grouped PAHs in different time span (B).

7.5–7.0 cm to 4.0–3.5 cm (the middle 1950s to the early 1980s) and a rapidly increasing stage in the upper sediments (the early 1980s to the present) (Fig. 3). These results were comparable to the sediment record of PAHs in Erhai Lake, Southwest China.¹⁴ The concentrations of 4–6 rings PAHs are quite constant below $\sim 7.5\text{ cm}$ depth (before the 1950s), which mirrors the background level. As they increased to the upper sediments, their concentrations were 2–3 times the background level during the early 1980s, and 7–25 times the background level in the surface sediment. PHEN was the most abundant high molecular weight PAH in the core and its temporal trend was similar to that of TPAHs, especially in the deeper sections, but differed from that of 4–6 rings PAHs. This would result in the down-core variation of relative abundances of each grouped PAHs (Fig. 2B). Prior to the 1970s, 2–3 ring PAHs (including ACY, ACE, FLU, PHEN and ANT) were dominant in the deeper sediments and accounted for $76.2 \pm 2.4\%$ of the TPAHs. After that, this group of PAHs gradually decreased until it only contributed an average of 36.5% of the TPAHs in recent years (1996–2009). Simultaneously, 4 ring PAHs (including FLUO, BaA and CHRY) and 5–6 ring PAHs (including BbF, BkF, BaP, INP, DBA and BghiP) increased from $15.9 \pm 0.9\%$ and $8.5 \pm 1.6\%$ (prior to the 1970s) to an average of 30.3% and 33.2% in recent years (1996–2009),

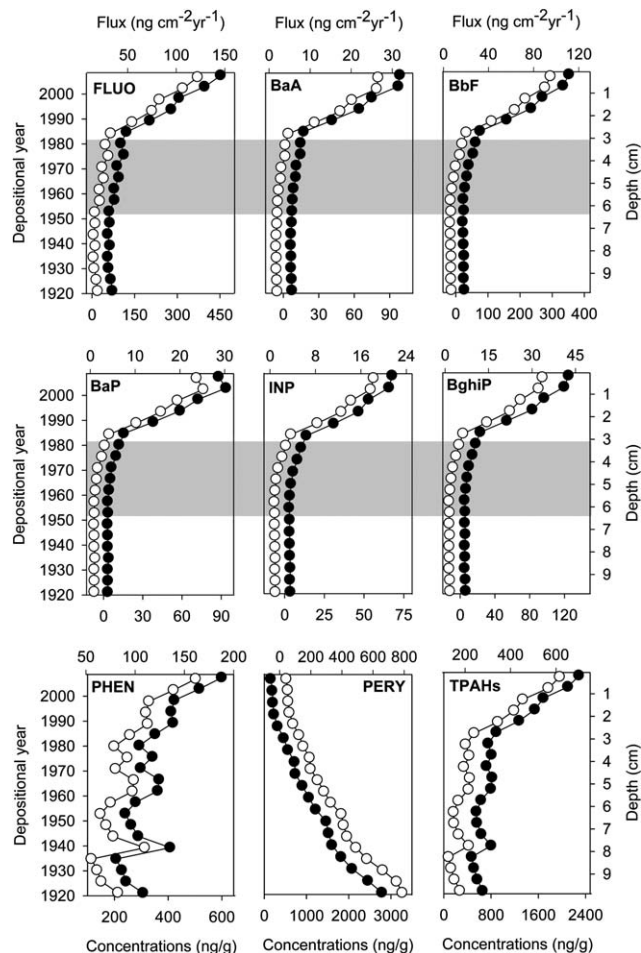


Fig. 3 Vertical profiles of selected PAHs and TPAHs (solid circle: concentration; open circle: flux).

respectively. 2–3 ring PAHs mostly stemmed from low- and moderate-temperature combustion processes (biomass and domestic coal burning), while 5–6 ring PAHs mainly originated from high temperature combustion processes involving industrial coal combustion, vehicular emission and gas-fired cooking, *etc.*^{12,19,20} The abundant variation of 2–3 ring PAHs and 5–6 ring PAHs clearly suggest that PAHs sources in Northeast China experienced a transformation from low- and moderate temperature to high-temperature combustion processes. This is more notable after the 1980s.

3.2. Correlation of PAHs fluxes with historical socioeconomic data

PAHs in the environment may be generated from natural and anthropogenic processes and the latter contribution is usually more significant than inputs from other sources.¹⁰ Therefore, PAHs could be a good indicator of anthropogenic activities. Over the past several decades, China has experienced remarkable economic development accompanying a rapid increase in energy consumption. This is evident after the initiation of the “Reform and Open” policy in 1978 (Fig. 4). The concentration of PAHs are dependent not only on the source emissions, but also the sedimentary rate and sediment dilution in the environment.²¹ It is more meaningful to assess the PAHs input in terms of depositional flux. The relationship between socioeconomic indexes and the depositional fluxes of PAHs are shown in Fig. 4. There is good correlation between TPAHs and the Chinese GDP increasing or the coal consumption (Fig. 4A and C). If TPAHs are substituted by PAH₉ (FLUO, BaA, CHR, BbF, BkF, BaP, INP, DBA and BghiP), the correlation is more significant

(Fig. 4B and D). Therefore, we conclude that the PAHs in the sediment core are mainly derived from the anthropogenic sources and PAH₉ may be regarded as the better indicator of anthropogenic activities. The Chinese GDP slowly increased from 0.07×10^{12} RMB to 0.72×10^{12} RMB during the period 1952 to 1985, followed by a sharply increasing trend (0.72×10^{12} RMB to 26.6×10^{12} RMB in 2007). In the meantime, the atmospheric input rate of PAH₉ to SHLW slowly increased from 34.4 ng cm^{-2} per year during the early 1950s to 87.5 ng cm^{-2} per year in the early 1980s, and then quickly increased to 389.6 ng cm^{-2} per year to date, which correlates strongly to the GDP increase. This is also the case for the Chinese coal consumption during the same period.

3.3. Original source of PAHs

The original source of PAH in sediments can be classified as petrogenic (formed by diagenic processes at low temperature over geological time scale), pyrogenic (formed during the incomplete combustion processes), and diagenic (formed recently from plant precursors).¹⁷ The frequently adopted method for source identification uses diagnostic ratios (typically isomers). This method is based on the hypothesis that paired chemicals are diluted to a similar extent and that the ratios remain constant *en route* from sources to receptors.²² Although exceptions could occur in some cases,²³ the diagnostic ratios of PAH can still provide some useful information on the original source identification. For example, the ratio of ANT/ANT + PHEN allows a broad distinction to be made between petrogenic and pyrogenic sources.²⁴ The ratio of INP/INP + BghiP greater than 0.5 could imply a source of combustion of coal and biomass, and if the INP/INP + BghiP ratio is between 0.2 and 0.5, a liquid fossil fuel combustion source of origin is suggested.²² Both ratios of BaA/BaA + CHR and INP/INP + BghiP less than 0.2 would suggest a source of petrogenic origin.^{25,26} The depth profiles of ANT/ANT + PHEN, BaA/BaA + CHR and INP/INP + BghiP are shown in Fig. 5. Throughout the whole core, the ratios of ANT/ANT + PHEN and BaA/BaA + CHR ranged from 0.10 to 0.15 (mean: 0.13 ± 0.01) and from 0.32 to 0.41 (mean: 0.36 ± 0.02), respectively. This is clearly indicative of a pyrogenic source of PAHs, but does not discriminate as clearly among fuels. The INP/INP + BghiP values ranged from 0.34 to

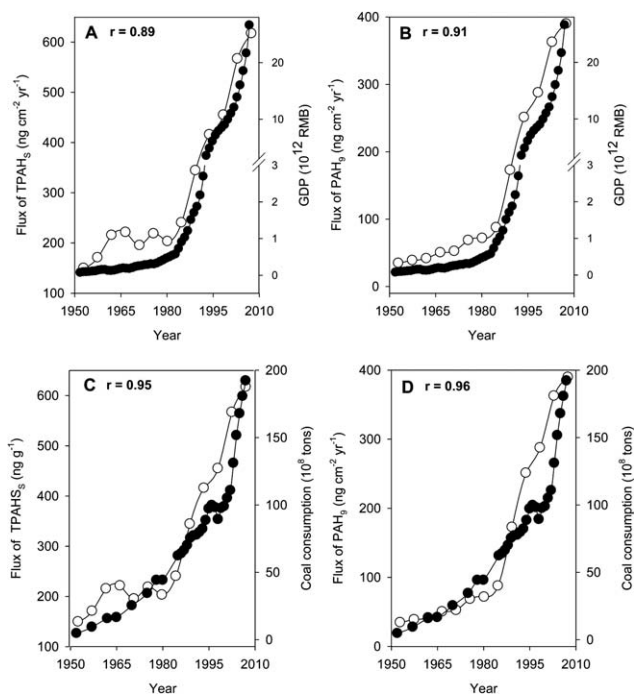


Fig. 4 Relationship between GDP/coal consumption (solid circle) and flux (open circle) of TPAHs/PAH₉ during 1950 to 2007. Pearson's correlation was conducted using SPSS 16.0 software and the correlation is significant at the 0.01 level, 2-tailed.

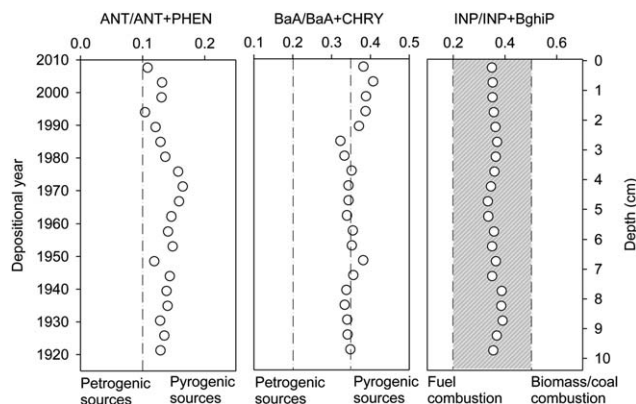


Fig. 5 Vertical profiles of the diagnostic ratios.

0.39 (mean: 0.36 ± 0.02), indicating mixed sources of coal and biomass burning and petroleum combustion.

Apart from the 16 priority PAHs proposed by the US EPA, significantly high levels of PERY ($157.4\text{--}2928 \text{ ng g}^{-1}$) were also recorded in the sediment core. The varying concentration of PERY was totally different to the other PAHs discussed above (Fig. 3). As with other individual PAH congeners, PERY in sediment also has various origins, such as the combustion of biomass and fossil fuels, and *in situ* diagenesis of organic matter in anoxic sediments.^{27,28} The latter source could be predominant in older core sections,²⁹ while the pyrogenic origin of PERY accounts for a small portion of its parent PAHs. The ratio of PERY to the sum of 5 ring PAHs (PERY/ Σ 5R-PAHs) has been used for differentiating the various PERY sources.²⁸ If the ratio of is less than 0.1, a pyrolytic source of PERY is suggested. Otherwise, a diagenetic source is proposed. In the present work, the values of PERY/ Σ 5R-PAHs were between 0.23 and 46.7 (Fig. 6), which are much higher than 0.1, clearly indicating a predominant diagenetic source, *i.e.*, diagenesis of organic matter.

3.4. Ecological risk assessment of PAHs

Two sets of guidelines, based on the effects of range-low (ERL) and range-median (ERM) criteria, have been developed and widely used for sediment toxicity screening to assess potential biological effects.^{2,30–33} Generally, the ERL and ERM criteria delineate three concentration ranges for a particular chemical. Concentrations below the ERL value represent a minimal-effects range within which effects would be rarely observed. Concentrations equal to or above the ERL but below the ERM represent a possible-effects range within which effects would occasionally occur. Finally, the concentrations equivalent to or above the ERM value represent a probable-effects range within which effects would frequently occur. Considering the toxic equivalency quotients (TEQs) of toxic compounds is more suitable than their concentrations to assess the corresponding acute toxicities. Therefore, we define two guidelines, TEQ_{ERL} and TEQ_{ERM} , to achieve this objective using the following eqn (1) and (2):

$$TEQ_{ERL} = ERL_i \times TEF_i \quad (1)$$

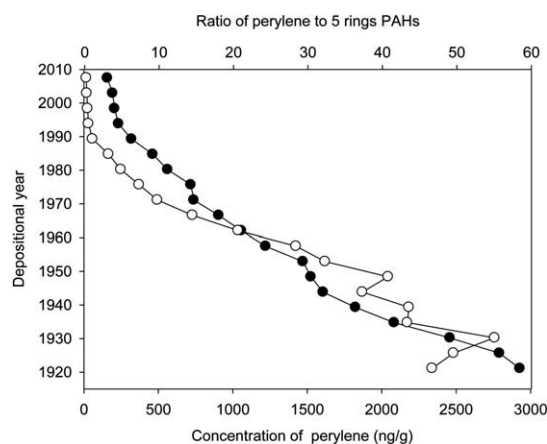


Fig. 6 Vertical profiles of PERY concentration (solid circle) and ratio of perylene/5 rings PAH (open circle).

$$TEQ_{ERM} = ERM_i \times TEF_i \quad (2)$$

where ERL_i and ERM_i were the ERM and ERL values of individual PAHs, and TEF_i was the corresponding toxic equivalent factors (TEFs) of an individual PAH relative to BaP. The defined TEQ_{ERL} and TEQ_{ERM} are shown in Table 1. Then, using the reported TEFs,^{34,35} we estimated the TEQs of PAHs in the current sediment core using the following eqn (3):

$$TEQs = \Sigma C_i \times TEF_i \quad (3)$$

where C_i is the concentration of individual PAH congener, and TEF_i was the toxic equivalent factors of individual PAH relative to BaP. The estimated TEQs concentrations of individual PAHs are listed in Table 2. In summary, the concentrations of TEQs ranged from $0.002 \text{ ng-TEQ g}^{-1}$ for ACE (6.5–7.0 cm) to $93.74 \text{ ng-TEQ g}^{-1}$ for BaP (0.5–1.0 cm). The TEQs of PAHs was lower in the deeper segments and increased from the bottom to the surface. Generally, the highest TEQs of sediment PAHs occurred in the top two layers (0–0.5 cm or 0.5–1.0 cm). Nevertheless, for PERY, the opposite was true, the highest TEQs were found in the deepest segment (9.5–10.0 cm).

Subsequently, we compared the estimated TEQ concentrations of individual PAHs in this sediment core to the TEQ_{ERL} and TEQ_{ERM} values defined above. The results are shown in Table 3. As expected, the majority of TEQs estimated were lower than the TEQ_{ERL} , including ACE, ACY, FLUO, ANT, BkF, BaP, CHRY, BaA, DBA, and BghiP, which indicated that most of the PAHs in the current sediment core rarely posed biological impairment. Nevertheless, the TEQs of FLU in the whole sediment core were higher than the TEQ_{ERL} but lower than TEQ_{ERM} , suggesting that FLU in this sediment core might occasionally pose biological impairment. Except for sediment core depths of 8.0–8.5 cm and 8.5–9.0 cm which were lower than TEQ_{ERL} , the TEQs of PHEN in other segments were higher than the TEQ_{ERL} but lower than TEQ_{ERM} . Additionally, the calculated TEQs of BbF were all lower than TEQ_{ERL} in layers below 1.0 cm, while the TEQs were higher than the TEQ_{ERL} but lower

Table 1 The redefined TEQ guidelines of individual PAHs in sediment (TEQ_{ERL} and TEQ_{ERM})^a

Compound	Concentration guideline (ng g^{-1})		TEQ guideline (ng-TEQ g^{-1})	
	ERL	ERM	TEQ_{ERL}	TEQ_{ERM}
ACE	16	500	0.016	0.5
ACY	44	640	0.044	0.64
FLU	19	540	0.019	0.54
FLUO	600	5100	0.6	5.1
PHEN	240	1500	0.24	1.5
ANT	85.3	1100	0.853	11
CHRY	384	2800	3.84	28
BkF	280	1620	28	162
BbF	320	1880	32	188
BaP	430	1600	430	1600
BaA	261	1600	26.1	160
DBA	63.4	260	63.4	260
BghiP	430	1600	4.3	16
Σ PAH	4022	44 792	590	2438

^a ERL: effect range-low; ERM: effect range-median.

Table 2 The estimated TEQs of PAHs in different depth of the sediment core (ng-TEQ g⁻¹)

Compounds		ACE	ACY	FLU	PERY	FLUO	PHEN	ANT	BghiP	CHRY	INP	BkF	BbF	BaP	BaA	DBA	∑PAHs
TEF		0.001	0.001	0.001	0.001	0.001	0.001	0.01	0.01	0.01	0.10	0.10	0.10	1.00	0.10	1.00	
Sediment core (depth, 0–10 cm)	0–0.5	0.005	0.027	0.143	0.157	0.453	0.599	0.690	1.248	1.587	6.767	8.899	35.24	88.06	9.871	13.47	167.2
	0.5–1.0	0.005	0.025	0.138	0.193	0.396	0.516	0.730	1.197	1.410	6.575	8.492	33.41	93.74	9.734	12.20	168.8
	1.0–1.5	0.005	0.019	0.114	0.206	0.307	0.424	0.595	0.967	1.172	5.294	6.750	26.97	72.31	7.492	8.820	131.4
	1.5–2.0	0.005	0.020	0.129	0.233	0.279	0.412	0.455	0.831	1.011	4.653	5.505	23.48	58.59	6.435	8.661	110.7
	2.0–2.5	0.004	0.022	0.139	0.320	0.203	0.419	0.542	0.538	0.698	3.094	3.851	15.86	38.12	4.129	5.867	73.80
	2.5–3.0	0.003	0.024	0.139	0.463	0.121	0.352	0.488	0.232	0.364	1.373	1.881	7.560	15.63	1.744	2.650	33.01
	3.0–3.5	0.004	0.026	0.123	0.562	0.102	0.293	0.432	0.180	0.295	1.039	1.511	6.175	11.97	1.483	2.337	26.54
	3.5–4.0	0.004	0.026	0.126	0.719	0.112	0.342	0.587	0.142	0.270	0.806	1.119	5.427	9.695	1.473	2.178	23.03
	4.0–4.5	0.004	0.035	0.139	0.738	0.089	0.298	0.537	0.101	0.212	0.540	0.924	4.044	6.221	1.117	1.860	16.86
	4.5–5.0	0.005	0.033	0.167	0.906	0.095	0.367	0.635	0.081	0.203	0.410	0.625	3.504	5.401	1.068	1.767	15.27
	5.0–5.5	0.006	0.038	0.183	1.058	0.078	0.361	0.574	0.067	0.170	0.341	0.507	2.870	3.328	0.879	1.793	13.25
	5.5–6.0	0.004	0.035	0.129	1.221	0.079	0.279	0.426	0.052	0.146	0.290	0.470	2.339	3.338	0.806	1.707	11.32
	6.0–6.5	0.003	0.026	0.119	1.471	0.061	0.241	0.388	0.060	0.139	0.326	0.550	2.546	3.584	0.761	1.632	11.91
	6.5–7.0	0.002	0.028	0.117	1.525	0.063	0.262	0.334	0.054	0.117	0.314	0.374	2.170	3.111	0.724	1.787	10.98
	7.0–7.5	0.003	0.028	0.155	1.607	0.055	0.289	0.451	0.061	0.120	0.331	0.494	2.370	3.428	0.666	1.465	11.52
	7.5–8.0	0.003	0.028	0.179	1.824	0.063	0.408	0.611	0.054	0.124	0.342	0.466	2.453	3.352	0.638	1.608	12.15
	8.0–8.5	0.003	0.025	0.086	2.084	0.055	0.207	0.313	0.057	0.136	0.362	0.549	2.628	4.053	0.683	2.044	13.28
	8.5–9.0	0.003	0.027	0.102	2.458	0.058	0.228	0.315	0.052	0.127	0.339	0.557	2.537	3.311	0.659	1.914	12.69
	9.0–9.5	0.003	0.033	0.108	2.791	0.066	0.244	0.355	0.062	0.138	0.364	1.787	2.510	3.477	0.718	2.033	14.69
	9.5–10.0	0.004	0.025	0.125	2.928	0.072	0.307	0.425	0.064	0.138	0.353	2.105	2.672	3.307	0.740	1.972	15.24

than TEQ_{ERM} at the top two layers. Consequently, our findings indicated that most of the PAHs in this sediment core would not cause immediate toxic effect.

4. Conclusion

Due to its specific conditions for development and preservation of environmental information, SHLW is an optimal environment for assessing the atmospheric PAHs loading in Northeast China. The TPAH concentrations successively increased from the deeper segments which were analyzed to the surface with a slowly increasing rate during the 1920s to the early 1980s and a sharply increasing rate during the late 1980s to date. There exists a good

correlation between the input rate of TPAHs (especially of PAH₀) and the Chinese historical socioeconomic data, which suggests that PAHs are mainly anthropogenically derived and PAH₀ is the better indicator of anthropogenic activities. Source identification suggests that both endogenous and exogenous PAHs were recorded in sediment core from SHLW. The endogenous origin PAH (PERY) was mostly from diagenesis of organic matter, while the exogenous origin PAHs were primarily from pyrogenic source, and in detail, a mixture of coal and biomass burning and petroleum combustion. Additionally, the down-core PAHs' profile clearly revealed that PAHs sources experienced a transformation from low- and moderate temperature to high-temperature combustion processes. This is more

Table 3 The ecological risk assessment results of individual PAHs in different depth of the sediment core^a

Compound		ACE	ACY	FLU	FLUO	PHEN	ANT	CHRY	BkF	BbF	BaP	BaA	DBA	BghiP	∑PAH
Sediment core (depth, 0–10 cm)	0–0.5	< ^a	<	~ ^b	<	~	<	<	<	~	<	<	<	<	<
	0.5–1.0	<	<	~	<	~	<	<	<	~	<	<	<	<	<
	1.0–1.5	<	<	~	<	~	<	<	<	<	<	<	<	<	<
	1.5–2.0	<	<	~	<	~	<	<	<	<	<	<	<	<	<
	2.0–2.5	<	<	~	<	~	<	<	<	<	<	<	<	<	<
	2.5–3.0	<	<	~	<	~	<	<	<	<	<	<	<	<	<
	3.0–3.5	<	<	~	<	~	<	<	<	<	<	<	<	<	<
	3.5–4.0	<	<	~	<	~	<	<	<	<	<	<	<	<	<
	4.0–4.5	<	<	~	<	~	<	<	<	<	<	<	<	<	<
	4.5–5.0	<	<	~	<	~	<	<	<	<	<	<	<	<	<
	5.0–5.5	<	<	~	<	~	<	<	<	<	<	<	<	<	<
	5.5–6.0	<	<	~	<	~	<	<	<	<	<	<	<	<	<
	6.0–6.5	<	<	~	<	~	<	<	<	<	<	<	<	<	<
	6.5–7.0	<	<	~	<	~	<	<	<	<	<	<	<	<	<
	7.0–7.5	<	<	~	<	~	<	<	<	<	<	<	<	<	<
	7.5–8.0	<	<	~	<	~	<	<	<	<	<	<	<	<	<
	8.0–8.5	<	<	~	<	~	<	<	<	<	<	<	<	<	<
	8.5–9.0	<	<	~	<	~	<	<	<	<	<	<	<	<	<
	9.0–9.5	<	<	~	<	~	<	<	<	<	<	<	<	<	<
	9.5–10.0	<	<	~	<	~	<	<	<	<	<	<	<	<	<

^a Denotes the estimated TEQ < TEQ_{ERL}. ^b Denotes TEQ_{ERL} ≤ the estimated TEQ < TEQ_{ERM}.

notable after the 1980s. Finally, ecological risk assessments of PAHs for this sediment core indicate that most of the PAHs measured in the present study would not cause immediate toxic effect, except for FLU and PHEN which might occasionally cause biological impairment.

Acknowledgements

The authors are grateful for the financial support from the National Natural Science Foundation of China (40973087) and China's national basic research program: "Water environmental quality evolution and water quality criteria in lakes" (2008CB418200).

References

- H.-S. Wang, Z. Cheng, P. Liang, D.-D. Shao, Y. Kang, S.-C. Wu, C. K. C. Wong and M. H. Wong, *Ecotoxicol. Environ. Saf.*, 2010, **73**, 900–906.
- R. Quiroz, J. O. Grimalt and P. Fernández, *Ecotoxicol. Environ. Saf.*, 2010, **73**, 559–564.
- P. Fernández, R. M. Vilanova, C. Martínez, P. Appleby and J. O. Grimalt, *Environ. Sci. Technol.*, 2000, **34**, 1906–1913.
- J. O. Grimalt, B. L. van Drooge, A. Ribes, R. M. Vilanova, P. Fernandez and P. Appleby, *Chemosphere*, 2004, **54**, 1549–1561.
- J. Guo, F. Wu, X. Luo, Z. Liang, H. Liao, R. Zhang, W. Li, X. Zhao, S. Chen and B. Mai, *Environ. Pollut.*, 2010, **158**, 2175–2180.
- K. Kannan, B. Johnson-Restrepo, S. S. Yohn, J. P. Giesy and D. T. Long, *Environ. Sci. Technol.*, 2005, **39**, 4700–4706.
- M. F. Simcik, S. J. Eisenreich, K. A. Golden, S.-P. Liu, E. Lippiatou, D. L. Swackhamer and D. T. Long, *Environ. Sci. Technol.*, 1996, **30**, 3039–3046.
- U. H. Yim, S. H. Hong, W. J. Shim, J. R. Oh and M. Chang, *Mar. Pollut. Bull.*, 2005, **50**, 319–326.
- E. Sverko, G. T. Tomy, E. J. Reiner, Y.-F. Li, B. E. McCarry, J. A. Arnot, R. J. Law and R. A. Hites, *Environ. Sci. Technol.*, 2012, **46**, 3141–3148.
- P. Fernández, R. M. Vilanova, C. Martínez, P. Appleby and J. O. Grimalt, *Environ. Sci. Technol.*, 2000, **34**, 1906–1913.
- J. Mingram, J. R. M. Allen, C. Brüchmann, J. Liu, X. Luo, J. F. W. Negendank, N. Nowaczyk and G. Schettler, *Quat. Int.*, 2004, **123–125**, 135–147.
- B. X. Mai, S. H. Qi, E. Y. Zeng, Q. S. Yang, G. Zhang, J. M. Fu, G. Y. Sheng, P. A. Peng and Z. S. Wang, *Environ. Sci. Technol.*, 2003, **37**, 4855–4863.
- G. Chu, Z. Gu, B. Xu, Q. Liu, Q. Sun, J. Han and J. Liu, *Quaternary Int.*, 2005, **25**, 202–207, (in Chinese).
- J. Guo, L. Zhang, H. Liao, Z. Tang, X. Zhao and F. Wu, *J. Environ. Sci.*, 2011, **23**, 1308–1315.
- G. Q. Liu, G. Zhang, X. D. Li, J. Li, X. Z. Peng and S. H. Qi, *Mar. Pollut. Bull.*, 2005, **51**, 912–921.
- A. L. C. Lima, T. I. Eglinton and C. M. Reddy, *Environ. Sci. Technol.*, 2003, **37**, 53–61.
- C. Gallon, A. Tessier, C. Gobeil and L. Beaudin, *Geochim. Cosmochim. Acta*, 2005, **69**, 3199–3210.
- M. Ishitake, H. Moriwaki, K. Katahira, O. Yamamoto, K. Tsuruho, H. Yamazaki and S. Yoshikawa, *Environ. Geol.*, 2007, **52**, 123–129.
- R. M. Harrison, D. J. T. Smith and L. Luhana, *Environ. Sci. Technol.*, 1996, **30**, 825–832.
- N. R. Khalili, P. A. Scheff and T. M. Holsen, *Atmos. Environ.*, 1995, **29**, 533–542.
- P. Fernández, R. M. Vilanova and J. O. Grimalt, *Environ. Sci. Technol.*, 1999, **33**, 3716–3722.
- A. Katsoyiannis, E. Terzi and Q.-Y. Cai, *Chemosphere*, 2007, **69**, 1337–1339.
- X. L. Zhang, S. Tao, W. X. Liu, Y. Yang, Q. Zuo and S. Z. Liu, *Environ. Sci. Technol.*, 2005, **39**, 9109–9114.
- M. B. Yunker, R. W. Macdonald, R. Vingarzan, R. H. Mitchell, D. Goyette and S. Sylvestre, *Org. Geochem.*, 2002, **33**, 489–515.
- Z. Guo, T. Lin, G. Zhang, Z. Yang and M. Fang, *Environ. Sci. Technol.*, 2006, **40**, 5304–5311.
- R. C. Brändli, T. D. Bucheli, T. Kupper, J. Mayer, F. X. Stadelmann and J. Tarradellas, *Environ. Pollut.*, 2007, **148**, 520–528.
- M. I. Venkatesan, *Mar. Chem.*, 1988, **25**, 1–27.
- P. Baumard, H. Budzinski, Q. Mchin, P. Garrigues, T. Burgeot and J. Bellocq, *Estuarine, Coastal Shelf Sci.*, 1998, **47**, 77–90.
- P. M. Gschwend, P. H. Chen and R. A. Hites, *Geochim. Cosmochim. Acta*, 1983, **47**, 2115–2119.
- E. Long, D. Macdonald, S. Smith and F. Calder, *Environ. Manage.*, 1995, **19**, 81–97.
- D. D. Macdonald, R. S. Carr, F. D. Calder, E. R. Long and C. G. Ingersoll, *Ecotoxicology*, 1996, **5**, 253–278.
- A. Liu, Y. Lang, L. Xue and J. Liu, *Environ. Monit. Assess.*, 2009, **159**, 429–436.
- E. R. Long, L. J. Field and D. D. MacDonald, *Environ. Toxicol. Chem.*, 1998, **17**, 714–727.
- P.-J. Tsai, T.-S. Shih, H.-L. Chen, W.-J. Lee, C.-H. Lai and S.-H. Liou, *Atmos. Environ.*, 2004, **38**, 333–343.
- M. Van den Berg, L. S. Birnbaum, M. Denison, M. De Vito, W. Farland, M. Feeley, H. Fiedler, H. Hakansson, A. Hanberg, L. Haws, M. Rose, S. Safe, D. Schrenk, C. Tohyama, A. Tritscher, J. Tuomisto, M. Tysklind, N. Walker and R. E. Peterson, *Toxicol. Sci.*, 2006, **93**, 223–241.