



Historical trends of concentrations, source contributions and toxicities for PAHs in dated sediment cores from five lakes in western China



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HIGHLIGHTS

- Contribution of vehicular emission to PAHs in lake sediments is increasing with time.
- Contribution of coal combustion to PAHs in lake sediments is decreasing with time.
- Unmix–BaPE combined methods were used to assess the toxicity risk of PAH sources.
- Historical trends of source contributions for PAHs and toxicities were consistent.

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ABSTRACT

In this work, sixteen U.S. EPA priority PAH compounds in the dated sediment cores were detected from five lakes in western China. In most lakes, the concentrations of the total PAHs (Σ PAHs) increased from the deep layers to the surface sediments. Two source categories, i.e. vehicular emission and biomass & domestic coal combustion were identified by Unmix, a factor analysis receptor model to explore the source contributions of PAHs in the dated sediments. The source apportionment results showed that biomass & domestic coal combustion contributed larger proportion of PAHs in the five lakes. The toxicities of PAHs in the dated sediments, assessed by BaP equivalent (BaPE) values showed that the BaPE increased gradually from the deep layers to the surface sediments in most lakes. For the first effort, the contribution of each source to BaPE was apportioned by Unmix–BaPE method, and the result indicated that the vehicular emission posed the highest toxic risk. The percentage contribution of vehicular emission for PAHs and BaPE also increased from the deep layers to the surface sediments, while biomass & domestic coal combustion exhibited the opposite tendency.

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1. Introduction

Due to the toxicity and persistence, polycyclic aromatic hydrocarbons (PAHs) have been listed as persistent organic pollutants (POPs) and priority pollutants (Christensen and Arora, 2007; Chung et al., 2007; Hu et al., 2007; Tsang et al., 2011; Zhang et al., 2004). PAHs can exert adverse effects on the environment and human health even far away from their origin (Petra et al., 2010). Lots of studies reported that PAHs were widespread and often accumulated in various environmental systems (Liu et al., 2007). In the aquatic system, PAHs tend to be adsorbed tightly to sediments (Li et al., 2009; Mouton et al., 2009). The deposition of the contaminants varied at different time, leading to the difference of PAHs

at different depths, which was closely related to the differences in energy structure and economic development (Guo et al., 2007; Guo et al., 2010). To investigate the vertical distribution of PAHs in sediment cores is a good way to explore the historical trends of PAHs in sediment.

The temporal trends of PAHs in sediment cores have been studied extensively around the world (Barakat et al., 2011; Guo et al., 2010; Jung et al., 2008; Li et al., 2001; Zhang et al., 2013), and many of them showed that the temporal trends corresponded to the vertical distributions in sediment cores. Most of these works were focused on the historical trends of the Σ PAHs concentration, however, few was conducted on the historical trends of the source contributions to Σ PAHs in the dated sediments, not to mention the toxicity risks of the PAH sources. In addition, the knowledge of historical trend of PAH sources in developing countries is relatively limited.

Receptor models, such as principal component analysis (PCA) and Unmix, can be used to identify the possible PAH sources in the sediment (Li et al., 2012; Shi et al., 2012; Zhang et al., 2012; Feng et al., 2007; Li

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et al., 2012; Malik et al., 2011). The models can also be employed to assess the toxicity risks of PAH sources in sediments by combining the PAH source contribution with BaP equivalent (BaPE) (Zhang et al., 2012).

In the present study, sediment cores from five lakes in western China were collected. In the previous study, the Σ PAH concentrations in dated sediments have been explored and the ages corresponding to each depth have been determined (Guo et al., 2010). This study is a continuation of the previous work to further investigate the possible PAH sources and their historical trends. The purpose of this study is (1) to quantitatively apportion source contributions of the Σ PAHs in dated sediments and to further study the historical trends of source contributions, and (2) to quantitatively apportion the toxicities of the PAH sources in sediments and to explore their historical trends. This study will provide valuable information and methods for the investigation on historical trends for persistent organic pollutants in sediment cores.

2. Materials and methods

2.1. Sediment sampling

The sediment samples were collected from five lakes, including Qinghai Lake (QH), Bosten Lake (BS) and Sugan Lake (SG) in northwest China, Erhai Lake (EH) and Chenghai Lake (CH) in southwest China (Fig. 1, Table S1 in the supplementary materials). These lakes were selected because they are remote and deep lakes in western China, far from any large pollution sources and lacking of major water inputs from the catchment. The sampling sites were in the center of these lakes with few sediment redistribution and few anthropogenic processes. Therefore, the pollution sources are mainly atmospheric origin. The sediment cores were collected from the deepest point in each lake using a gravity corer and sectioned at 1 or 2 cm intervals. Upon collection, cores were wrapped in pre-cleaned aluminum foil, and transported on ice to the laboratory, where they were stored at $-20\text{ }^{\circ}\text{C}$ until further treatment. In this study, the following 16 compounds were determined: naphthalene (Nap), acenaphthylene (Acy), acenaphthene (Ace), fluorine (Flu), anthracene (Ant), phenanthrene (Phe), fluoranthene (FLua), pyrene (Pyr), benzo[a]anthracene (BaA), chrysene (Chr), benzo[a]pyrene

(BaP), benzo[b]fluoranthene (BbF), ben-zo[k]fluoranthene (BkF), indeno [1,2,3-c,d]pyrene (IcdP), dibenzo[a,h]anthracene (DahA) and benzo(ghi) perylene (BghiP).

2.2. PAH analysis

The samples were extracted by soxhlet extraction technique (Mai et al., 2002; Xu et al., 2007). Sediment samples were freeze-dried and ground in a mortar to pass through a sieve with 0.5 mm openings, and homogenized. A mixture of deuterated PAHs (naphthalene- d_8 , acenaphthene- d_{10} , phenanthrene- d_{10} , chrysene- d_{12} , and perylene- d_{12}) as recovery surrogates was added to a certain amount of sediment (5–10 g dry weight), which was Soxhlet extracted with a mixture of hexane and acetone (200 mL, 1/1, v/v) for 48 h. Approximately 2 g of activated copper was added for desulfurization. The extracts were filtered, concentrated, and solvent-exchanged to hexane. The cleanup and fractionation were conducted by passing through an alumina/silica gel chromatograph column. The column was eluted with 15 mL of hexane and 75 mL of dichloromethane/hexane (v/v, 3/7). The second fraction was concentrated under a gentle flow of nitrogen to 200 μL . The internal standards, fluorobiphenyl and terphenyl- d_{14} , were added prior to instrumental analysis.

Analyses of PAHs were performed on an Agilent 6890 gas chromatograph system equipped with an Agilent 5975C mass selective detector operating in selective ion monitoring mode using a DB-5 capillary column (60 m length, 0.25 mm i.d., 0.25 μm film thickness). Splitless injection of 1.0 mL of sample was conducted with an auto-sampler. The GC oven temperatures were programmed from 90 to 180 $^{\circ}\text{C}$ at a rate of 10 $^{\circ}\text{C}/\text{min}$, to 220 $^{\circ}\text{C}$ at a rate of 2 $^{\circ}\text{C}/\text{min}$, and then to 290 $^{\circ}\text{C}$ at a rate of 8 $^{\circ}\text{C}/\text{min}$ (hold for 30 min).

All analytical procedures were monitored with strict quality assurance and control measures. Laboratory quality control procedures include analyses of method blanks (solvent), spiked blanks (standards spiked into solvent), matrix spikes/matrix spike duplicates, and sample duplicates. Instrument stability and response were checked using NIST standard solutions. The instruments were calibrated daily with calibration standards and the relative percent differences between the seven-point calibration and the daily calibrations were <20% for all target

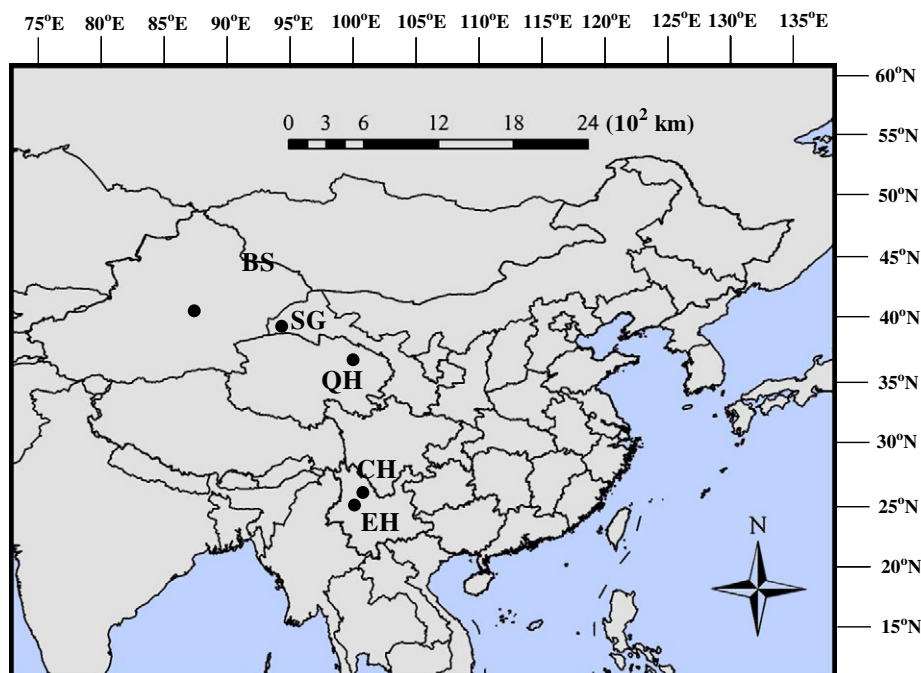


Fig. 1. Map of the sampling sites. BS: Bosten Lake; SG: Sugan Lake; QH: Qinghai Lake; CH: Chenghai Lake; EH: Erhai Lake.

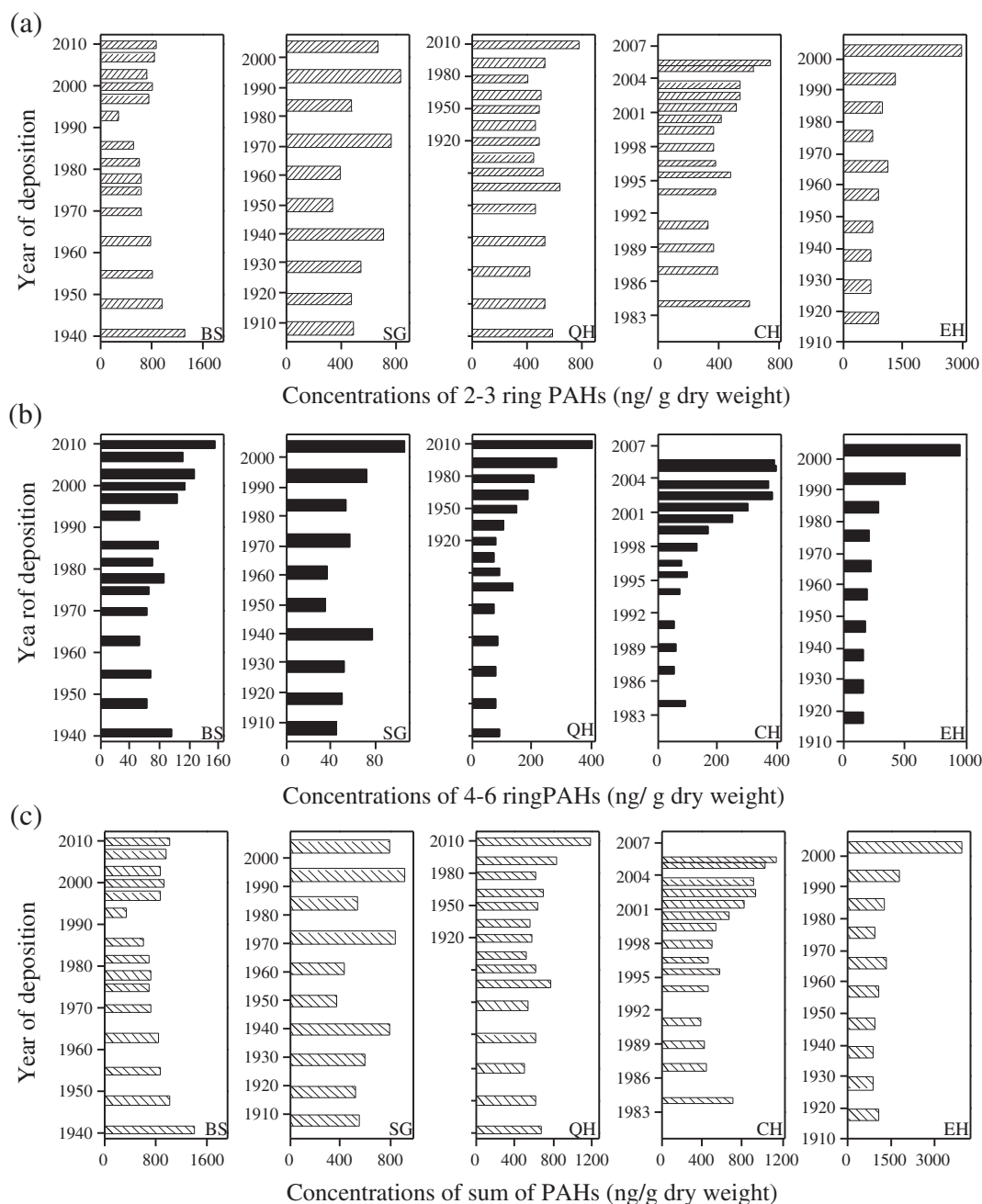


Fig. 2. Historical trends of the Σ PAH concentrations (ng g^{-1} dw). (a) For 2–3 ring PAHs; (b) For 4–6 ring PAHs; (c) For sum of PAHs.

analyses. The mean recoveries of sixteen target PAHs ranged from $75.8 \pm 4.9\%$ to $114.3 \pm 8.2\%$ in triplicate spiked blanks and from $60.8 \pm 1.1\%$ to $120.9 \pm 9.1\%$ in triplicate spiked matrices. Only trace levels of targets were detected in blanks and were subtracted from those in sediment samples. The surrogate recoveries in all samples were $64.1 \pm 8.6\%$ for naphthalene- d_8 , $82.6 \pm 9.6\%$ for acenaphthene- d_{10} , $84.1 \pm 11.6\%$ for phenanthrene- d_{10} , $84.4 \pm 11.8\%$ for chrysene- d_{12} , and $75.8 \pm 13.5\%$ for perylene- d_{12} . All results were expressed on a dry weight basis and corrected for surrogate recoveries.

2.3. Dating of sediment cores

Additionally, the dating of the sediment cores was clearly described in the previous works (Guo et al., 2010).

2.4. Receptor models

Unmix is a new factor analysis receptor model for source apportionment in the atmospheric environment and recommended by US EPA (Zhang et al., 2012). This model does not need the prior knowledge of the source profiles, which can be described according to the equation as following:

$$x_{ik} = \sum_{j=1}^p g_{ip} f_{pk} + e_{ik} \quad (1)$$

where x_{ik} is the concentration of i^{th} species for the k^{th} sample; f_{pk} is the contribution of the p^{th} source to the k^{th} sample; g_{ip} is the i^{th} species

Table 1
Rotated factor loadings obtained by PCA model.

	Factor 1	Factor 2
Ace	0.42	0.86
Flu	0.39	0.86
Phe	0.23	0.97
Ant	0.04	0.95
Flua	0.31	0.87
Pyr	0.52	0.79
BaA	0.89	0.42
Chr	0.93	0.19
BbF	0.96	0.24
BkF	0.95	0.25
BaP	0.94	0.27
IcdP	0.94	0.29
BghiP	0.95	0.29
DahA	0.90	0.41
Eigenvalue	7.71	5.44
Variance %	55	39

The bolds show the source markers.

concentration from the p^{th} source; and e_{ik} is the error (Hopke, 2003). Factors extracted from the ambient concentrations can be linked to potential source categories.

Unmix model is based on the self-modeling curve resolution (SMCR) technique (Hopke, 2003). The algorithm of Unmix is to find edges in sets of points in N-dimensional space (Henry, 1997), and the edges of the projected data could represent the samples used to identify the sources (Larsen and Baker, 2003). In this work, EPA Unmix 6.0 model was applied on the dataset of PAHs in sediment cores. The detailed method of Unmix model can be found in the references (Henry, 1997; US EPA, 2007; Zhang et al., 2012).

In several source apportionment works, the researchers introduced the combined dataset from different sites into factor analysis receptor model and gained satisfactory results (Mooibroek et al., 2011; Cheng et al., 2012). Similar to the studies above, it is assumed that the variation between the profile of the same source category among five lakes is relatively small (Mooibroek et al., 2011). In this work, we have apportioned possible sources to PAHs in sediment cores using EPA Unmix 6.0 on the pooled dataset from the five lakes to identify and quantify the potential source contributions and their historical trends.

3. Results and discussion

3.1. Historical trends of Σ PAH concentrations in sediment cores

In the present study, sixteen U.S. EPA priority PAH compounds were detected in all dated sediment samples from the five lakes in western China. Concentrations of individual PAH and Σ PAHs in dated sediments from different locations were presented in Table S2. Σ PAH concentrations (sum of 16 EPA priority PAHs) were in the range of 334.92–3902.97 ng/g

Table 2
Source profiles obtained from Unmix model (ng g^{-1} dw).

	Factor 1	Factor 2
Ace	1.91	4.31
Flu	34.70	92.10
Phe	65.30	267.00
Ant	6.37	46.10
Flua	17.30	55.80
Pyr	18.30	31.30
BaA	5.00	2.61
Chr	7.86	2.17
BbF	19.10	1.79
BkF	7.11	1.48
BaP	6.91	0.87
IcdP	4.55	0
BghiP	20.30	0.50
DahA	21.60	3.33

Table 3
Estimated average percentage contribution (%) of two sources to Σ PAHs for five lakes, by Unmix.

Lakes	Sources	
	Vehicular emission	Biomass & domestic coal combustion sources
SG	9	93
QH	36	55
EH	30	61
CH	53	45
BS	9	89

dry weight, with the mean value of 804.62 ng/g dry weight. The results showed that in different lakes the concentrations of Σ PAHs in dated sediments decreased in the order of $\text{EH} > \text{BS} > \text{CH} > \text{QH} > \text{SG}$. The highest Σ PAHs occurred in EH and the lowest in SG, which may be attributed to the population densities. SG is located in the northwest China and there is little inhabitants living in the catchment.

The historical trends of 2–3 ring PAHs, 4–6 ring PAHs and Σ PAH concentrations in sediment cores were presented in Fig. 2(a), (b), (c). In general, the Σ PAH concentrations in most lakes increased from the deep layers to the surface sediments. This trend reflected the processes of industrialization and economic development in China. It is notable, however, that BS lake showed a reverse trend. Σ PAH levels decreased from the deep layer to the surface, which was similar to the phenomena reported by Jung et al. (2008) and Mikac et al. (2011). The reason for this trend in BS required further investigation.

Compared with the Σ PAH concentrations in sediments from other regions in the world, the concentrations of PAHs in the five lakes were higher than in the mariculture sediments of Hong Kong (Wang et al., 2010), the Taihu lake sediment in China (Zhang et al., 2012) and the deep Gulf of Mexico sediments (Wade et al., 2008), but lower than those in Lanzhou Reach of Yellow River in China (Shi et al., 2012), the Velke Kozmalovce in Slovakia (Hiller et al., 2011) and Lake Clarke in USA (Ko et al., 2007).

3.2. Source apportionment

Using EPA Unmix 6.0 software for source apportionment, the user should decide the number of the extracted factors. In this work, a traditional PCA method was employed to help Unmix determine the extracted factor number.

PCA is a statistical technique which can be applied to a set of variables to reduce their dimensionality (Shi et al., 2011). In PCA model, factors with eigenvalue greater than 1.0 were extracted. The extracted factors can be associated to possible sources and the factor loadings can help to identify the source categories. The detailed description of approach and application of PCA model were presented in the previous studies (Shi et al., 2009, 2011; Zhang et al., 2012).

In this work, a 65×14 dataset was introduced into PCA model. Sixty-five was the number of sediments and fourteen was the number of individual PAH compounds. Considering the uncertainty due to possible evaporative losses during chemical analysis or the missing data, individuals such as Nap and Acy were excluded from the PCA model. The performance of PCA on pooled PAHs dataset was exhibited in Table 1. Two factors were extracted by PCA, accounting for 94% of the total variance.

Factor 1 (55% of the total variance) got high loading for PAH species including BaP, DahA, IcdP and BghiP, which were used as the markers for vehicular emission source (Sofowote et al., 2008; Zhang et al., 2012). Factor 1 thus can be identified as the vehicular emission source. They may come from the motor boats on the lakes and the traffic activities near the lakes. Factor 2 (39% of the total variance) showed high loading for Flu, Phe and Ant, etc. Flu and Phe were rich in the coal combustion emission, and Phe and Ant can be used as the markers for biomass burning source (Harrison et al., 1996). Additionally, 2–3

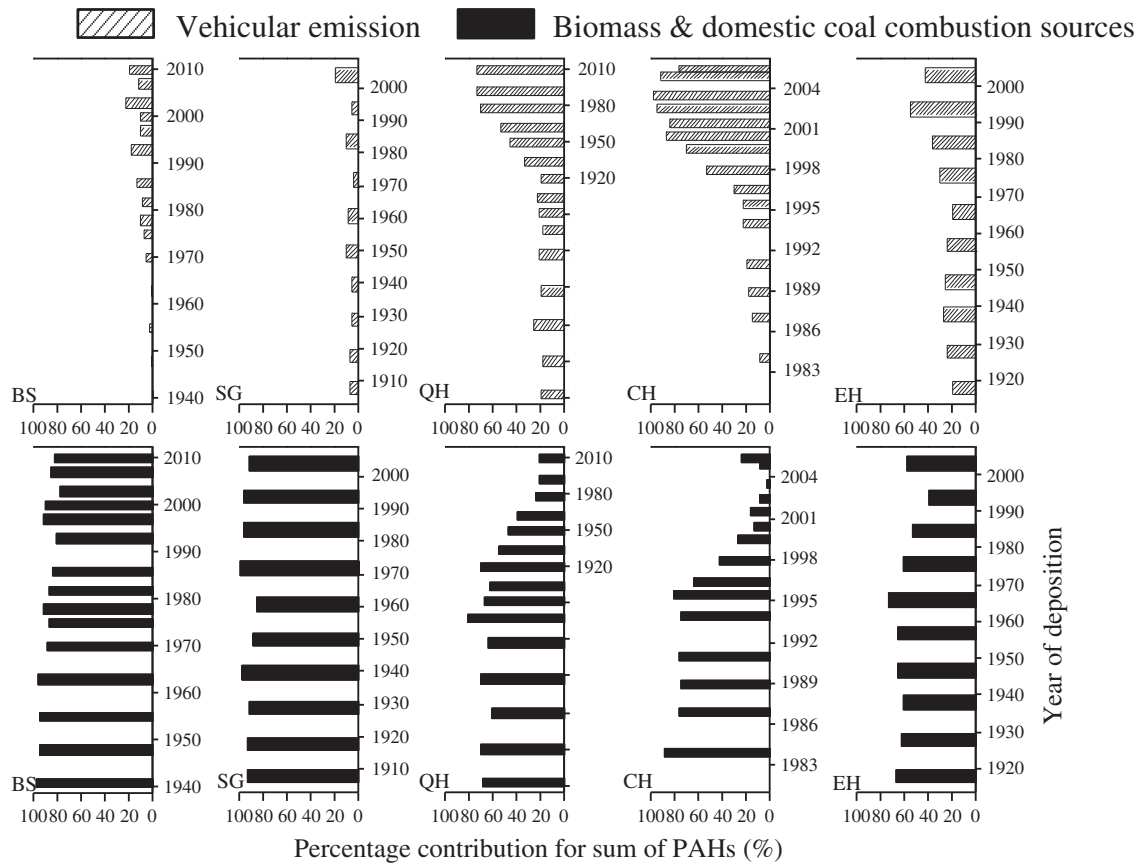


Fig. 3. Historical trends of percentage source contributions (%) to ΣPAHs against the year for five Lakes.

ring PAHs are mainly from low- or moderate-temperature combustion process such as biomass burning and domestic coal burning (Harrison et al., 1996; Guo et al., 2010; Miguel et al., 1998; Venkataraman et al., 1994). Therefore this factor was identified as the biomass & domestic coal combustion source. They may enter the lake sediments through particular matter deposition (Shi et al., 2012).

Similarly, a 65×14 dataset was introduced into Unmix model and the extracted source profiles ($\text{ng g}^{-1} \text{dw}$) were shown in Table 2. Compared with Factor 2, Factor 1 got relative higher concentrations for BaP, DahA, IcdP and BghiP, which can be considered as the vehicular emission source. The second factor with high level of Flu, Phe and Ant can be identified as the biomass & domestic coal combustion source. It indicated that Unmix and PCA yielded identical results.

The contribution to ΣPAHs for 65 sediment samples was estimated by Unmix. The fit between the measured and estimated ΣPAHs concentrations in 65 sediment samples by the Unmix was depicted in Fig. S1. (in Supplementary Material). According to the fitting plots it can be seen that the regressions were 1:0.98 with r value for 1.00, indicating that predicted ΣPAH concentrations were close to the measured concentrations. It also suggested the satisfying application of the Unmix model to the sediment dataset.

Table 3 lists the average percentage contributions (%) of two identified sources for five sediment cores from the five lakes. Biomass & domestic coal combustion source contributed larger proportion to ΣPAHs in the five lakes, accounting for 93% in SG Lake, 55% in QH Lake, 61% in EH Lake, 45% in CH Lake and 89% in BS Lake, respectively.

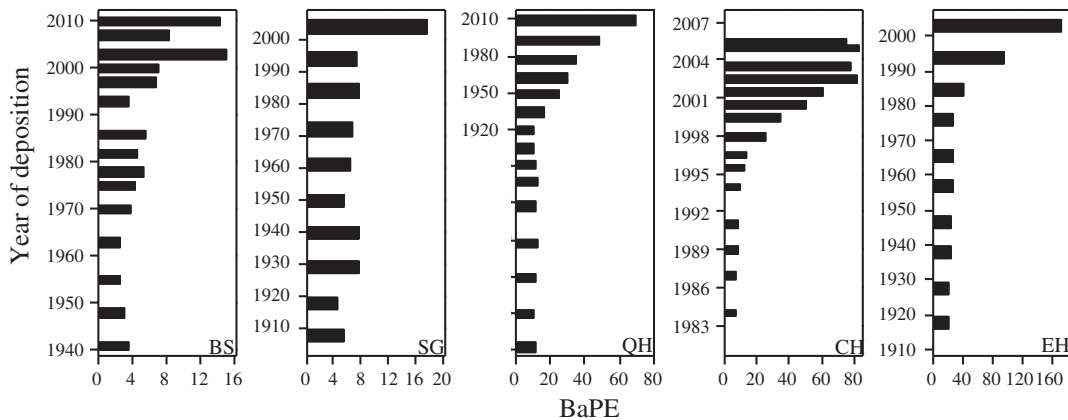


Fig. 4. Historical trends of the BaPE values ($\text{ng g}^{-1} \text{dw}$) against the year of deposition for five Lakes.

Table 4
Estimated average percentage contribution (%) of two sources to BaPE, for five lakes.

Lakes	Sources	
	Vehicular emission	Biomass & domestic coal combustion sources
SG	55	45
QH	87	13
EH	87	13
CH	88	12
BS	52	48

The vehicular emission contributed 9% in SG Lake, 36% in QH Lake, 30% in EH Lake, 53% in CH Lake and 9% in BS Lake. The quantitative source apportionment by Unmix was consistent with the qualitative findings by diagnostic ratio method in previous work (Guo et al., 2010).

The vertical profiles for percentage (%) of grouped PAHs (2–3 rings, 4 rings and 5–6 rings) in the sediment cores from the five lakes have been investigated by Guo et al. (2010). In this work, the correlations between biomass & domestic coal combustion (percentage contribution %) and 2–3 ring PAHs (percentage %), as well as the vehicular emission (percentage contribution %) and 4–6 ring PAHs (percentage %) were analyzed. Fig. S2 showed the plots of correlations. Pearson's correlation coefficients (r) were 0.99 for both plots, indicating that the source contributions have positive correlation with the levels of the dominated PAH species in sources.

3.3. Historical trends of source contributions

The historical trends of percentage source contributions (%) against the year of deposition for the five lakes were described in Fig. 3. For most lakes, the percentage contributions (%) of vehicular emission increased from the deep layers to the surface top sediments, while biomass & domestic coal combustion exhibited the opposite tendency. The different tendencies for the two sources agreed with the real

situation that the vehicle quantity in China has been increasing fast in recent years. Accordingly, the contributions of vehicular emission should be relatively larger in the surface sediments.

3.4. Risk assessment

The BaP equivalent (BaPE) is a useful index to assess the potential toxicity of PAHs in sediments, which can be calculated according to the following equation (Liu et al., 2009; Zhang et al., 2012):

$$[\text{BaPE}]_i = [\text{BaA}]_i \times 0.06 + [\text{BbF}]_i \times 0.07 + [\text{BkF}]_i \times 0.07 + [\text{BaP}]_i + [\text{DahA}]_i \times 0.60 + [\text{IcdP}]_i \times 0.08 \quad (2)$$

where $[\text{BaPE}]_i$ is the calculated BaPE concentration ($\text{ng g}^{-1} \text{dw}$) in the i^{th} sediment sample, $[\text{BaA}]_i$ is the concentration ($\text{ng g}^{-1} \text{dw}$) of BaA in the i^{th} sediment sample.

The calculated BaPE values were illustrated in Fig. 4. It can be seen that in the five lakes the BaPE values gradually increased from the deep layers to the surface sediments. The BaPE values varied from 2.5 to 88.3 ng/g dw , with the mean value of 14.6 ng/g dw . High BaPE values were found at EH Lake. The historical trends of the BaPE values and the concentrations of ΣPAHs in the five lakes were consistent, indicating that higher ΣPAH concentrations were corresponded to greater toxicities.

The contribution (%) of each source to BaPE was also calculated, using Unmix–BaPE combined method. This method can be described as follows:

$$[\text{BaPE}]_{ij} = [\text{BaA}]_{ij} \times 0.06 + [\text{BbF}]_{ij} \times 0.07 + [\text{BkF}]_{ij} \times 0.07 + [\text{BaP}]_{ij} + [\text{DahA}]_{ij} \times 0.60 + [\text{IcdP}]_{ij} \times 0.08 \quad (3)$$

where $[\text{BaPE}]_{ij}$ is the calculated contribution ($\text{ng g}^{-1} \text{dw}$) of the j^{th} source to BaPE in the i^{th} sediment sample, $[\text{BaA}]_{ij}$ is the estimated contribution ($\text{ng g}^{-1} \text{dw}$) of the j^{th} source for BaA in the i^{th} sediment sample.

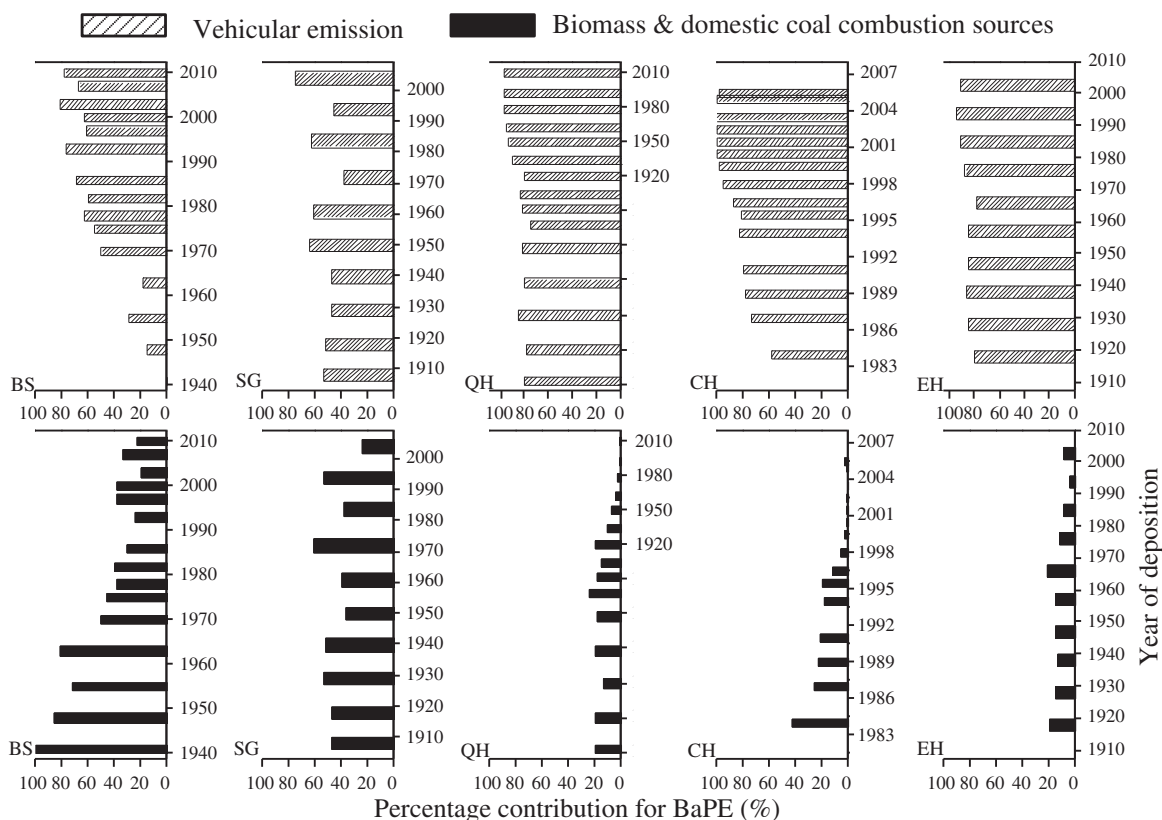


Fig. 5. Historical trends of percentage source contributions (%) to BaPE against the year of deposition for five Lakes.

$$[\text{BaA}]_{ij} = f(\text{BaA})_j \times g_{ij}/100 \quad (4)$$

where $f(\text{BaA})_j$ is the fraction (%) of BaA to ΣPAHs in the j^{th} source profile; g_{ij} is the estimated contribution ($\text{ng g}^{-1} \text{dw}$) of the j^{th} source to the i^{th} sediment sample, by Unmix model.

The percentage contribution (%) of the j^{th} source to BaPE in the i^{th} sediment sample can be calculated accordingly:

$$[\text{BaPE}\%]_{ij} = [\text{BaPE}]_{ij}/[\text{BaPE}]_i \quad (5)$$

Table 4 listed the average percentage contributions (%) of source to BaPE for the five lakes. It showed that vehicular emission was the significant contributor to BaPE, accounting for 55% in SG, 87% in QH, 87% in EH, 88% in CH and 52% in BS, respectively. The contribution from biomass & domestic coal combustion was relatively low: 45% in SG, 13% in QH, 13% in EH, 12% in CH and 48% in BS, respectively.

Comparing the values in Tables 3 and 4, we found that vehicular emission offered low contribution (%) to ΣPAHs but high contribution (%) to BaPE, and biomass & domestic coal combustion presented the opposite situation. There are two key factors involved in the estimation of source contribution to BaPE: the estimated source contribution to ΣPAHs and the fraction (%) of toxic compounds (including BaA, BbF, BkF, BaP, DahA and IcdP) in the source profile. As shown in Table 2, the toxic compounds were quite more prominent in the vehicular emission profile, resulting in its high contribution to BaPE.

Additionally, the historical trends of source contribution (%) to BaPE were also investigated (Fig. 5). The vehicular emission presented an obvious increasing tendency from deep to top sediments, for each Lake, while biomass & domestic coal combustion source exhibited the opposite tendency. This is because vehicular emission source got heavy contributions (%) in the surface sediment while biomass & domestic coal combustion source contributed larger proportions (%) in the deep sediments, as shown in Fig. 3.

4. Conclusions

In this study, the historical trends of concentrations, source contributions and toxicity of PAHs in dated sediments from the five lakes in western China were investigated. The results showed that the concentration of ΣPAHs in dated sediments gradually increased from the deep layer to the surface sediments. The possible source categories and their contributions for PAHs in sediment cores were identified by PCA and Unmix models. The vehicular emission and biomass & domestic coal combustion were the main source categories, and contributions estimated by the two receptor models showed that biomass & domestic coal combustion contributed larger proportion. Risk assessment of each source category was performed by Unmix–BaPE combined method. The trends of toxic risk for the sources were relative similar to that of source contributions that the values increased from the deep layers to the top sediments for most lakes. The vehicular emission posed the highest toxic risk, although it contributed less to ΣPAHs . The historical trends of contribution for BaPE were consistent with the historical trends of the contribution for PAHs. The method employed in this study can provide useful information for the analysis of sources and risks of PAHs and other related contaminants in the sediments and other environmental matrices.

Conflict of interest

There is no conflict of interest.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.scitotenv.2013.10.022>.

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