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Exploring the relationship between polycyclic aromatic hydrocarbons and sedimentary organic carbon in three Chinese lakes

Fengchang Wu · Libin Xu · Yongge Sun · Haiqing Liao · Xiaoli Zhao · Jianyang Guo

Abstract

Purpose Previous studies have shown a positive correlation between concentrations of polycyclic aromatic hydrocarbons (PAHs) and total organic carbon (TOC) in lake sediments. However, with respect to the complex organic matter in recent sediments, it is still unclear which part of TOC plays a key role in controlling PAHs distributions in natural sediments. The aim of this study was to examine the relationships between PAHs and TOC components of different origins in lake sediments.

Materials and methods Sediment cores from three Chinese lakes with different trophic conditions—Lakes Bosten, Dianchi, and Poyang—were collected using a piston core sampler. The cores were sectioned into 1- or 2-cm intervals immediately after collection and transported on ice to the laboratory where they were stored at −20 °C. The subsamples were freeze-dried and ground with a mortar and pestle for analyses. PAHs were analyzed by GC–MS and TOC was determined with a PE elemental analyzer after the removal of carbonates. Rock-Eval 6 pyrolysis technique was used to deconvolute the TOC in the sediments into free and volatile hydrocarbons (S1), kerogen-derived hydrocarbons (S2), and residual carbon (RC); S2 was further separated into thermal less stable macromolecular organic matter (S2a) and high molecular weight kerogens (S2b).

Results and discussion Positive correlations between TOC and PAHs were observed in these lakes. Results show that the more labile, minor components of TOC (S1 and S2a) played a more important role in controlling PAH distributions than the major components of TOC (S2b and RC), probably due to the different accessibilities of the organic components. The algae-derived organic carbon had a greater influence on the distribution of low molecular weight PAHs than that of high molecular weight PAHs in sediments. This suggests that PAHs scavenging in the water column by algae is mainly targeted at low molecular weight PAHs, and that preferential scavenging of low molecular weight PAHs may be due to the different atmospheric phases of low and high molecular weight PAHs.

Conclusions Algal scavenging had an important influence on the PAH concentrations, especially the lower molecular weight PAH concentrations in the lake sediments. The results suggest that PAH concentrations and their molecular ratios in lake sediments may neither accurately represent the pollution history of PAHs, nor the origin PAHs source differentiation. This study has significant implications for understanding the roles of organic matter in affecting the distributions of PAHs and other similar organic pollutants in lake sediments.

Keywords Lake sediment · Organic component · Polycyclic aromatic hydrocarbon · Rock-Eval pyrolysis

F. Wu (✉) · L. Xu · H. Liao · X. Zhao
State Key Laboratory of Environmental
Criteria and Risk Assessment,
Chinese Research Academy of Environmental Sciences,
Beijing 100012, People's Republic of China
e-mail: wufengchang@vip.skleg.cn

Y. Sun
Institute of Environmental and Biogeochemistry,
Department of Earth Sciences, Zhejiang University,
Hangzhou 310027, People's Republic of China

J. Guo
State Key Laboratory of Environmental Geochemistry,
Institute of Geochemistry, Chinese Academy of Sciences,
Guiyang 550002, People's Republic of China

1 Introduction

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous in the environment. They are of great concern because they have toxic or carcinogenic properties (White 1986; Pahlmann and Pelkonen 1987). PAHs can be derived from different sources, but are mainly from anthropogenic sources in lakes and coastal waters (Wakeham et al. 1980a, b; Hoffman et al. 1984; Yang 2000). Previous studies have mainly focused on reconstructing the historical pollution of PAHs in lake sediments and determining sources of PAHs by examining the ratios of different PAHs, such as phenanthrene/anthracene, fluoranthene/pyrene, chrysene/benzo[a]anthracene, and the ratio of low molecular weight PAHs/high molecular weight PAHs (Colombo et al. 1989; Soclo et al. 2000; Yunker et al. 2002; Qiao et al. 2006). PAHs in lake sediments are mainly bound to natural organic matter, and the composition and origin of the natural organic matter would be expected to significantly affect the distributions of PAHs in sediments (Chefetz et al. 2000; Accardi-Dey and Gschwend 2002; Salloum et al. 2002). Investigations of PAHs sorption mechanisms of soil/sediment organic matter with different characteristics have been mainly carried out using experimental methods (Gustafsson et al. 1996; Huang and Weber 1997; Bucheli and Gustafsson 2000; Chefetz et al. 2000; Accardi-Dey and Gschwend 2002; Salloum et al. 2002; Song et al. 2002; Xiao et al. 2004; Cornelissen et al. 2006). For example, some studies (e.g., Gustafsson et al. 1996; Bucheli and Gustafsson 2000; Accardi-Dey and Gschwend 2002) showed that condensed aromatic carbon (e.g., black carbon or soot carbon) present in organic matter in sediments was heavily involved in the sorption of PAHs. But recent studies suggest that aliphatic hydrocarbons, such as amorphous polymethylene carbon, also play an important role in the sorption of pyrene (Chefetz et al. 2000) and phenanthrene (Salloum et al. 2002). Those studies usually focused on naphthalene, phenanthrene, and pyrene in experimental studies, and little is known for other PAHs. Studies of natural sediments (Fernandez et al. 1999, 2000; Yang 2000) also suggest that total organic carbon (TOC) was an important factor in controlling the distribution of PAHs. Significant positive correlations were observed between TOC and PAHs in sediments (Boehm and Farrington 1984; Yang 2000; Wang et al. 2001) and soils (Liu et al. 2007; Nam et al. 2008). Fernandez et al. (2000) examined historical records of deposition fluxes of PAHs in 10 remote high-altitude lakes in Europe and found that TOC-normalized PAHs showed a similar regional uniformity pattern as that observed in atmospheric inventories, providing further evidence that TOC controlled PAHs in lakes. Organic matter in the natural environment can have very variable compositions depending on its origin, and the relationships between PAHs and different organic components of different origins remain unclear. In addition, whether relationships between organic components and different PAHs vary also remains unclear.

Rock-Eval pyrolysis is a simple and rapid method for determination of free and volatile hydrocarbons (S1), kerogen-derived hydrocarbons (S2), and residual carbon or dead carbon (RC), depending on pyrolysis temperature, peak position, and organic carbon origin. It has been widely used for petroleum exploration and has been applied in soil/sediment research in recent years (Lafargue et al. 1998; Disnar et al. 2003, 2008; Sanei et al. 2005; Stern et al. 2005; Sanei and Goodarzi 2006; Outridge et al. 2007; Carrie et al. 2009). In sediments, S1 originates from the pyrolysis of mainly lower molecular weight amorphous carbon, including free hydrocarbons; readily volatilized plant geolipids; and a component of humic acid-derived hydrocarbons (Sanei et al. 2005; Outridge et al. 2007). S2, which is strongly associated with aquatic plants, may be a good indicator of aquatic primary productivity (Outridge et al. 2007). RC includes the final thermostable fraction of organic carbon from algae, terrestrial cellulose, and black carbon (Outridge et al. 2007; Carrie et al. 2009), which are rich in condensed aromatic carbon. Carrie et al. (2009) analyzed S1, S2, and RC in surface sediments of the Mackenzie River Basin in Canada, and RC was shown to be the main form of organic carbon present in these sediments; algae-derived S1 and S2 organic carbon concentrations were found to be much higher in the lake-fed tributaries than in the main channel. Sanei and Goodarzi (2006) separated the organic carbon in recent sediments from eutrophic lakes in central Alberta, Canada into S1, S2, and RC, and found that S1 had a significant correlation with mercury (Hg) levels, indicating that S1 may control Hg distributions in the sediments. Outridge et al. (2007) used S2 in Canadian high Arctic lake sediments to represent aquatic primary productivity, and found that a large fraction of the increased Hg concentrations observed during the twentieth century could be explained by scavenging by aquatic primary productivity.

Organic matter of different origins may have different compositions, and the relationships of different organic components—S1, S2, and RC—with PAHs are unknown. In this work, sediment cores from Lakes Bosten, Dianchi, and Poyang in China, which have different trophic conditions, were studied to examine the relationships between TOC and PAHs. Based on Rock-Eval pyrolysis, sedimentary organic carbon was separated into S1, S2, and RC; S2 was further separated into thermal less stable macromolecular organic matter (S2a) and high molecular weight kerogens (S2b). The relationships between different organic components and various PAHs in the sediments were examined to better understand aquatic primary productivity, and how organic matter and eutrophic status affect PAH distributions in lake sediments.

2 Sampling and methods

Three lakes were selected for sampling: Lake Bosten (BS) in northwestern China, Lake Dianchi (DC) in southwestern China, and Lake Poyang (PY) in eastern China (Fig. 1). Detailed information about these lakes is given in Table 1. Three sediment cores were collected from the central and deepest area of each lake using a piston core sampler in July 2007 in BS, May 2006 in PY, and October 2006 in DC. The core sediments were undisturbed, as indicated by a clear water–sediment interface and the preservation of fine sediment laminations. In each lake, one core was used for TOC and PAHs analyses: 07BS4-2, 20 cm depth (BS); DC-1, 20 cm depth (DC); and PY-2, 19 cm depth (PY). The other cores were used for sediment dating (^{137}Cs and Pu isotopic analyses) and other chemical analyses published elsewhere (Liao 2007; Fang 2010; Wang 2010; Wu et al. 2010). The cores were sectioned into 1- or 2-cm intervals immediately after collection, wrapped and weighted in pre-cleaned (by heating at 450 °C) aluminum foil in the field, then transported on ice to the laboratory where they were stored at −20 °C until further treatment. The subsamples were dried using a vacuum freeze dryer (Techcorp FD-3-85-MP-79-36 mT) and then re-weighed to determine mass depths and porosity. Dried subsamples were ground with a mortar and pestle and passed through a 100-mesh sieve for further analyses.

PAHs in sediments were analyzed by GC–MS, and TOC was analyzed by a PE elemental analyzer after the removal of carbonates. Organic carbon in bulk sediments was operationally characterized using Rock-Eval 6 analysis (Vinci Technologies, Rueil-Malmaison, France) at the Guangzhou Institute of Geochemistry, Chinese Academy of Sciences.

Details of experimental methods are contained in the Electronic supplementary material.

The PAH compounds of interest and their acronyms are naphthalene (Nap), acenaphthylene (AcPy), acenaphthene (AcP), fluorene (Flu), phenanthrene (PA), anthracene (Ant), fluoranthene (Flt), pyrene (Pyr), benzo[a]anthracene (BaA), chrysene (Chr), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), indeno[1,2,3-cd]pyrene-InP, dibenzo[a,h]anthracene (DBA), and benzo[ghi]perylene (BghiP).

3 Results and discussion

3.1 PAHs and TOC in sediments of Lakes Bosten, Dianchi, and Poyang

The PAHs and TOC distributions in the sediment cores of Lakes Bosten, Dianchi, and Poyang are shown in Fig. 2. In the sediment core of Lake Bosten, mean PAHs concentration was 821.2 ± 236.5 ng g^{-1}, with the maximum of 1,394.1 ng g^{-1} near the bottom and a minimum of 334.9 ng g^{-1} at 6 cm depth (see Fig. 2). The core could be divided into two sections (see Fig. 2): (1) below 6 cm depth, where the PAHs concentration decreased continuously; and (2) above this depth, where the PAHs concentration increased continuously. In Lake Dianchi, mean PAHs concentration was $2,249.2\pm1,497.6$ ng g^{-1}. From 13 cm to 6 cm depth, the PAHs concentration had a significant increasing trend; below this section concentrations were relatively low, while above this section concentrations were high (see Fig. 2). In Lake Poyang, mean PAHs concentration was 459.3 ± 205.3 ng g^{-1} and had an overall decreasing trend with

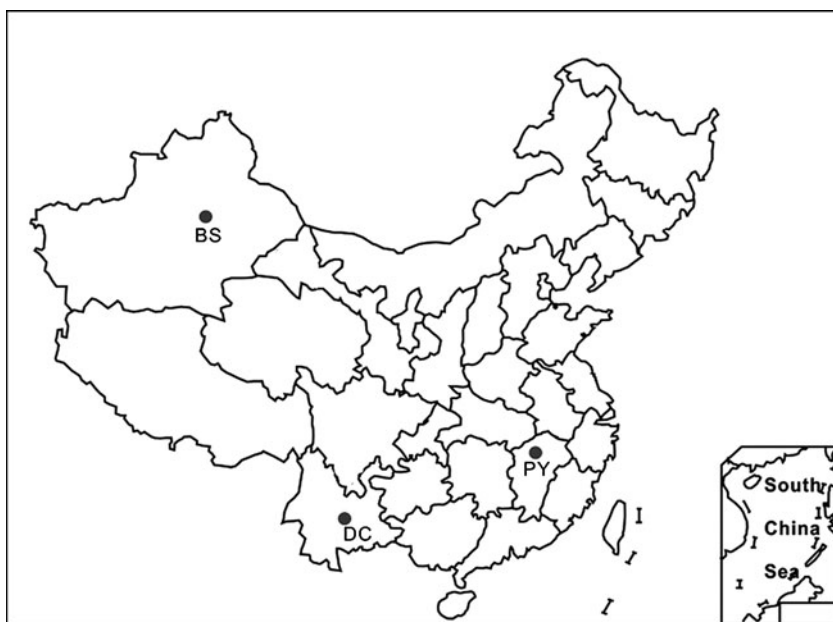Fig. 1 Map of the sampling sites. *BS* Lake Bosten, *DC* Lake Dianchi, *PY* Lake Poyang

Table 1 Characteristics of the three selected Chinese lakes

Lakes	Sampling sites	Sampling date	Lake area (km^2)	Maximum depth (m)	Catchment area (km^2)	Location	Lake trophic condition
Bosten	41°59′N, 87°11′E	Jul 2007	972	16.5	27,000	Northwestern China	Medium trophic[a]
Dianchi	24°50′N, 102°43′E	May 2006	306.3	10.4	2,920	Southwestern China	Eutrophic[a]
Poyang	29°12′N, 116°16′E	Oct 2006	3,914	29.2	162,215	Southeastern China	Oligotrophic[b]

[a] Obtained from Wang (2010)

[b] Obtained from Hu et al. (2010)

several fluctuations (see Fig. 2). Lake Dianchi had the highest PAHs concentrations while Lake Poyang had the lowest.

Among the complex processes which controlled the distribution of PAHs in sediments, organic matter may be one of the most important factors (Fernandez et al. 1999, 2000; Yang 2000). The relationships between TOC and PAHs in the three different trophic level lakes were examined. TOC values ranged from 2.16 % to 3.96 %, with a mean of 2.77 % for Lake Bosten; from 0.73 % to 5.30 %, with a mean of 2.66 % for Lake Dianchi; and from 0.09 % to 0.73 %, with a mean of 0.41 % for Lake Poyang. TOC was the lowest in Lake Poyang and the highest in Lake Dianchi (see Fig. 2), which is in agreement with the trophic levels of those three lakes, i.e., eutrophic in Lake Dianchi, medium trophic in Lake Bosten, and oligotrophic in Lake Poyang. Significant correlations between TOC and PAHs were observed in all three lakes: for Lake Bosten, $r=0.592$, $p=0.020$; for Lake Dianchi, $r=0.978$, $p<0.001$; and for Lake Poyang, $r=0.776$, $p<0.001$. This provides further proof that organic matter played an important role in controlling PAHs in different trophic lakes. The structural differences of PAHs may have an important influence on their relationship with organic carbon. PAHs were separated to low molecular weight (LMW) PAHs (up to 3 rings) and high

molecular weight (HMW) PAHs (four, five, and six rings) to further examine their relationships with TOC. The correlations between TOC and LMW PAHs were 0.726 ($p=0.002$, $N=15$), 0.960 ($p<0.001$, $N=20$), and 0.809 ($p<0.001$, $N=19$) in Lakes Bosten, Dianchi, and Poyang, respectively. In the three lakes, TOC was significantly correlated with LMW PAHs, indicating that TOC played an important role in controlling the LMW PAHs in sediment. A significant correlation between TOC and HMW PAHs was only observed in Lake Dianchi ($r=0.985$, $p<0.001$). The different correlations between LMW and HMW PAHs with TOC suggest that the organic matter played a more important role in controlling the LMW PAHs than HMW PAHs in sediments. Relatively few studies have reported this finding.

In order to further examine the relationships between different PAHs and organic matter, Lake Bosten (with medium trophic level and low anthropogenic influence) was selected to examine the different organic components in the lake sediments. Lake Bosten is located in the Yanqi Basin of Xinjiang Province in northwest China, where the economic development is relatively low, and its urbanization and industry development are not as rapid as Eastern China. Furthermore, there are no big cities around Lake Bosten; the nearest is Kuerle city, which is 67 km downstream from

Fig. 2 PAHs and TOC profiles in sediments of Lake Bosten (*BS*), Dianchi (*DC*), and Poyang (*PY*)
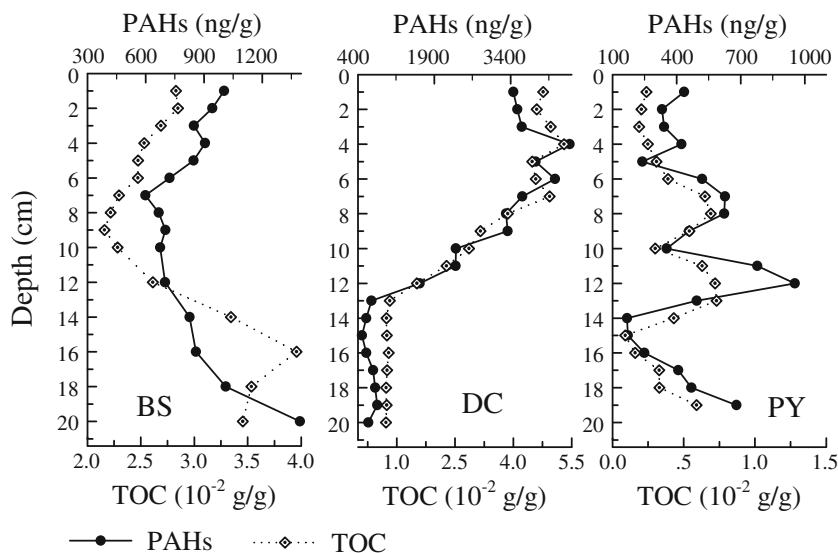
the lake. Therefore, urbanization and industry have low impacts on the lake, and the main origin of PAHs is atmospheric deposition, which makes it more suitable to investigate the relationships between organic matter and PAHs.

3.2 Rock-Eval pyrolysis of sediments

Using the Rock-Eval 6 technique, organic carbon in the sediments of Lake Bosten was separated into several components. Traditional Rock-Eval pyrolysis separated organic carbon into several groups, including S1, S2, S3CO (CO produced during pyrolysis), S3CO$_2$ (CO$_2$ produced during pyrolysis), and RC; generally the S1, S2, and RC groups are the most relevant to soil/sediment research (Sanei et al. 2005; Sanei and Goodarzi 2006; Outridge et al. 2007; Carrie et al. 2009). However, more sensitive parameters need to be drawn from Rock-Eval pyrolysis in order to provide more robust and accurate information (Disnar et al. 2003; 2008), especially in lake sediments.

Figure 3b and c shows the typical pyrolysis curves of sediments in Lake Bosten. In the general analysis of mineral

Fig. 3 Formation of hydrocarbon peaks (*S1* and *S2*) during pyrolysis stage of algae and sediments of Lake Bosten

samples, there was one main peak corresponding to kerogen pyrolysis during high temperature pyrolysis (300–650 °C), and all other peaks were negligible (Lafargue et al. 1998). But in Lake Bosten, there were two obvious peaks in the S2 group, one with a maximum at about 360 °C, which was defined as S2a, and the other at about 470 °C, defined as S2b. S2b, which was the typical kerogen-derived hydrocarbon, was more abundant than S2a, although S2a was not negligible. The range of TpkS2a (the oven temperature at the maximum of the S2a peak) was 360–365 °C, which was much lower than TpkS2b (the oven temperature at the maximum of the S2b peak) with a range from 466 to 477 °C (Fig. 4). Figure 3a shows the pyrolysis curve of cyanobacteria from Lake Bosten (one of the main types of algae in Lake Bosten; Lai 2009). Only one main peak was observed in high temperature pyrolysis, whose position is similar to S2a of the sediments, suggesting that S2a may originate from algae.

The S2b peak observed in the sediment was not present in the algae (see Fig. 3), indicating that algae may not be the main origin of S2b in Lake Bosten. The S2b in Rock-Eval pyrolysis was probably mainly derived from HMW kerogens, while the S2a consisted mainly of thermal less stable macromolecular organic matter, such as aliphatic-rich humic acid and kerogen precursor (Peters 1986). The pyrolysis results suggest that S2a was mainly derived from algae and that S2a may be a better indicator of algal productivity in lakes.

S1 and S2a had similar concentrations and trends: higher levels were observed at deeper depths, with a slight increase observed from 20 to 14 cm, then a sharp decrease with very low levels observed at 10 cm, and finally a small increase from this depth to the surface (see Fig. 4). The S2b content was three to four times higher than S1 and S2a, and had a slightly different trend in the core, with a slow increase in levels from 20 to 10 cm, then a sudden decrease, followed by a slow increase to the surface. RC had a consistently high content in the sediments and showed a relatively stable trend throughout the core. S2b and RC accounted for most of the organic carbon in the sediments: 19.9–29.3 % and 43.6–76.7 % of TOC, respectively. S1 and S2a only accounted for 5.0–10.0 % and 5.9–12.4 % of the TOC, respectively. These results are similar to those reported by Song et al. (2002), who found that kerogen and black carbon were the major constituents of organic carbon in soils of the Guangzhou area.

3.3 Relationships between organic components and various PAHs in Lake Bosten

The single PAH profiles (Fig. S1) of Lake Bosten and their details are shown in the Electronic supplementary material. Different organic components were compared with various PAHs in Lake Bosten to investigate the interrelationships

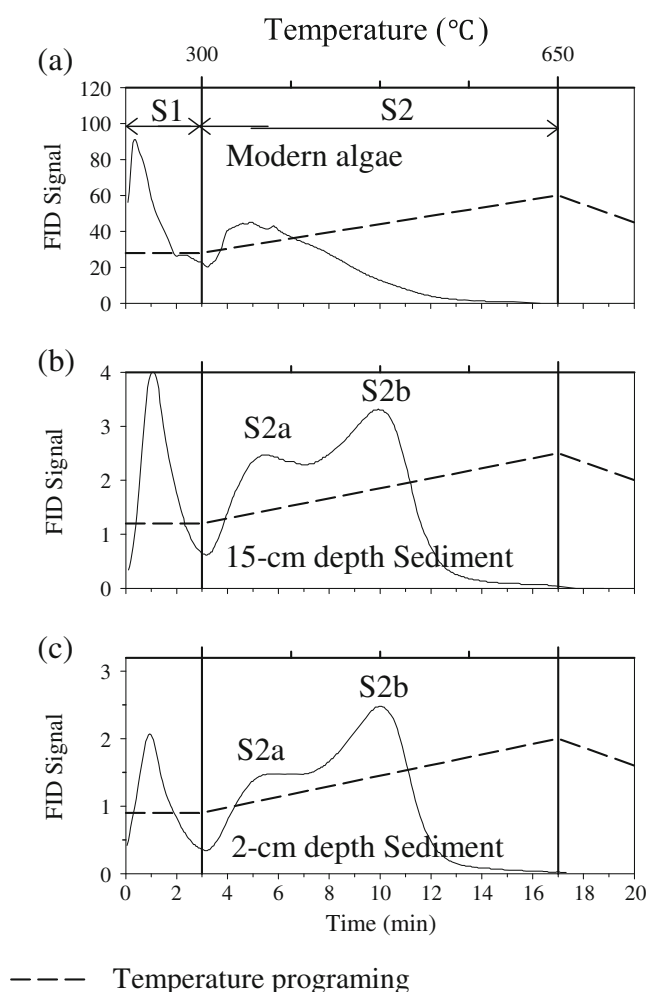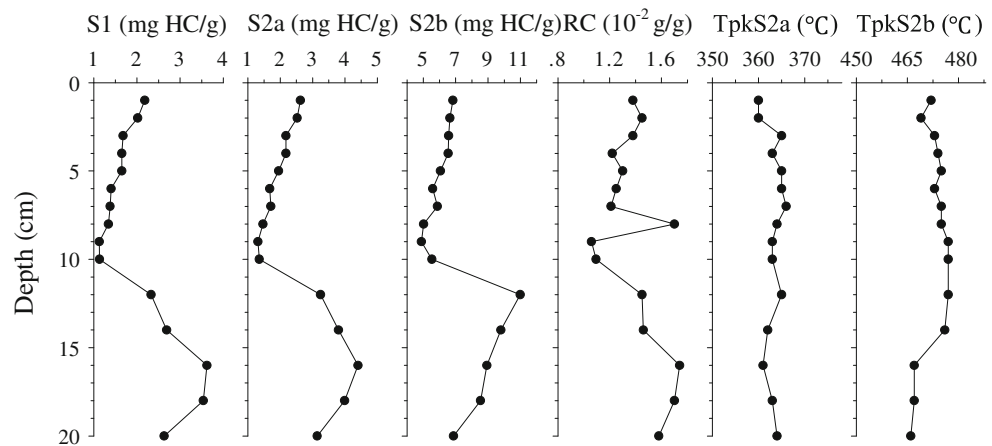**Fig. 4** Organic carbon profiles in the sediments of Lake Bosten

between them (Table 2). TOC had significant positive correlations with 3-ring PAHs (AcPy, AcP, Flu, Ant, and PA), and their correlation coefficients were 0.717, 0.764, 0.768, 0.644 ($p<0.01$), and 0.630 ($p<0.05$), respectively. TOC had no significant correlations with other PAHs. Among the 3-ring PAHs, AcPy, AcP, and Flu had significant positive correlations with RC ($r=0.552$, 0.601, 0.593, respectively; $p<0.05$). The sorption mechanism between organic matter and PAHs observed in experimental studies (e.g., Gustafsson et al. 1996; Bucheli and Gustafsson 2000; Accardi-Dey and

Table 2 Correlation coefficients between different organic carbon components and individual PAHs in the sediments of Lake Bosten ($N=15$)

	S1	S2a	S2b	RC	TOC
Nap	0.244	0.329	0.437	0.223	0.173
AcPy	0.700**	0.758**	0.665**	0.552*	0.717**
AcP	0.717**	0.712**	0.477	0.601*	0.764**
Flu	0.742**	0.744**	0.536*	0.593*	0.768**
PA	0.579*	0.533*	0.259	0.479	0.630*
Ant	0.586*	0.536*	0.250	0.480	0.644**
Flt	0.203	0.157	−0.087	0.111	0.269
Pyr	0.197	0.155	−0.081	0.102	0.264
BaA	−0.136	−0.131	−0.183	−0.182	−0.122
Chr	−0.157	−0.170	−0.246	−0.210	−0.150
BbF	−0.475	−0.477	−0.472	−0.339	−0.452
BkF	−0.416	−0.417	−0.414	−0.291	−0.387
BaP	−0.289	−0.274	−0.239	−0.234	−0.261
DBA	0.240	0.195	−0.002	0.255	0.310
InP	−0.313	−0.301	−0.289	−0.229	−0.278
BghiP	−0.306	−0.281	−0.209	−0.317	−0.282
LMW PAHs	0.645**	0.597*	0.257	0.523*	0.726*
HMW PAHs	−0.063	−0.105	−0.305	−0.109	0.033
TPAHs	0.537*	0.499	0.232	0.430	0.591*

See text for the acronyms of the PAHs

*Significant at $p<0.05$, **significant at $p<0.01$

Gschwend 2002) shows that aromatic carbon structure (e.g. black carbon) played a dominant role. The rich aromatic structures in RC may, therefore, account for the significant correlation between AcPy, AcP and Flu and RC in the sediments. However, recent experimental studies have reported that the aliphatic carbon in organic matter may also play an important role (Chefetz et al. 2000; Salloum et al. 2002; Xiao et al. 2004). For example, Salloum et al. (2002) demonstrated a positive correlation between K_{oc} (organic carbon normalized sorption coefficient) for PA and paraffinic carbon content. The positive correlation between PA and aliphatic carbon content may also exist with other PAHs. Humic acid, kerogen, and its precursors were all rich in aliphatic carbon, resulting in high PAH K_{oc}, and this potentially explains the observed significant correlations between S2b and AcPy and Flu ($r=0.665$, 0.536, respectively, $p<0.05$), and between S2a and AcPy, AcP, Flu, PA, and Ant ($r=0.758$, 0.712, 0.744, 0.533, 0.536, respectively; $p<0.01$ for AcPy, AcP, and Flu, $p<0.05$ for PA and Ant). Significant correlations between S1 and AcPy, AcP, Flu, PA, and Ant ($r=0.700$, 0.717, 0.742, 0.579, 0.586, respectively; $p<0.01$ for AcPy, AcP, and Flu, $p<0.05$ for PA and Ant) were also observed, which may be explained by the large fraction of amorphous free hydrocarbon in S1.

The relationships between specific organic carbon components and different 3-ring PAHs were as follows: RC had significant correlations with three 3-ring PAHs, AcPy, AcP, and Flu ($p<0.05$); S2b had correlations with two, AcPy ($p<0.01$) and Flu ($p<0.05$); and S1 and S2a had correlations with five, AcPy, AcP, Flu, PA, and Ant ($p<0.01$ for AcPy, AcP, and Flu, $p<0.05$ for PA and Ant; see Table 2). This suggests that S1 and S2a played a more significant role than S2b and RC in controlling the distribution of PAHs in sediments. Comparison of the correlation coefficients between each 3-ring PAH and different organic carbon components shows that the correlation coefficients between PAH and S1 and S2a were significantly higher than those between PAH and S2b and RC. For example, no significant correlations between PA and S2b and RC were observed. But there were

significant correlations between PA and S1 and S2a. The correlation coefficients between Flu and S2b and RC are 0.536 ($p<0.05$) and 0.593 ($p<0.05$), respectively, which were lower than those between Flu and S1 and S2a, whose correlation coefficients were 0.742 ($p<0.01$) and 0.744 ($p<0.01$). This also suggests that the algal derived S1 and S2a, whose molecular weights were relatively small, were more significantly associated with the 3-ring PAHs (see Table 2). All these observations suggest that S1 and S2a played more important roles than S2b and RC in associating or controlling PAHs in the lake sediments.

These differences in the correlations of each organic carbon component may be related to differences in accessibility of organic carbon to PAHs. Xiao et al. (2004) found that isolated kerogen and black carbon fractions exhibited much higher sorption capacities when they were associated with soil/sediment matrixes, suggesting that a large fraction of the particulate kerogen and black carbon was not accessible to PAHs. The thermal instability and partial dissolution of humic acid in both diluted acid and alkali resulted in humic acid accumulating on the particle surface, making it more easily accessible to hydrophobic organic contaminants; while S1, composed of free hydrocarbon, was the major organic matter which covered sedimentary particle surfaces (Sanei et al. 2005; Sanei and Goodarzi 2006; Carrie et al. 2009). Therefore, S1 and S2a were more accessible than S2b and RC, which consisted largely of kerogen and black carbon, respectively. Therefore, the accessibility of different organic carbon components to PAHs may be the major reason why S1 and S2a played more important roles than S2b and RC in controlling the distributions of PAHs in sediments.

The structural differences of PAHs had a significant impact on their relationship with organic carbon. In Lake Bosten, LMW PAHs showed a significant positive correlation with TOC, while HMW PAHs did not. Significant positive correlations were also observed between LMW PAHs and S1 and S2a, but not between HMW PAHs and S1 and S2a (see Table 2). The differences suggest that the algae-derived organic carbon had a more significant influence on the distribution of LMW PAHs than that of HMW PAHs in sediments.

Because of the position of Lake Bosten and its contributing environment, the PAHs of Lake Bosten were mainly derived from the atmosphere. LMW PAHs were more volatile than HMW PAHs; therefore, they were mainly in the gaseous phase of the atmosphere, while HMW were associated with atmospheric particles. This differentiated atmospheric distribution had a high impact on the transport and deposition mechanisms of those compounds. Wet deposition and air–water exchange were the main deposition processes for LMW PAHs, and particle deposition (dry and wet) was the main process for the HMW. Once in the aquatic system,

water solubility differences determined their distribution between dissolved and particulate phases. LMW PAHs were mainly associated with the dissolved phase, while HMW PAHs were mainly associated with the suspended particulate matter. Taking those differences into account, it is expected that the increase of productivity had a significant impact on the LMW PAHs inputs in the lake, and it was almost negligible for HMW PAHs.

Higher productivity resulted in a higher input of gas phase compounds to the aquatic systems by strongly affecting their air–water exchange (Dachs et al. 1999, 2002). Once in the aquatic system, the distribution of PAHs between dissolved and particulate phases was also affected by primary productivity, which resulted in an increase in suspended particles. Again, the increase of suspended particles had more impact on LMW PAHs (which can exchange between both phases) than on HMW PAHs, which had already associated with particles in the lakes. Therefore, the increase of primary production, and the suspended particulate matter, resulted in the increase in LMW PAHs in the lakes, which ultimately resulted in the increase in the sediments of the lakes. Therefore, LMW PAHs were significantly affected by S1 and S2a, which were mainly derived from algae, while HMW PAHs were not.

In all, the role of TOC in controlling PAHs in sediments may largely depend on the algal-derived organic carbon in lakes. Previous studies on C/N ratio and $\delta^{13}C$ in Lakes Bosten, Dianchi, and Poyang showed that the TOC in these lakes were mainly derived from lacustrine algae (Fang 2010), further supporting the significant correlations between TOC and PAHs in these lakes. When the aquatic primary productivity increased, it would firstly lead to higher inputs of LMW PAHs into water, and secondly the increased organic particulates would contribute more LMW PAHs to sediments. Thus, the LMW PAHs were preferentially scavenged by aquatic primary productivity. This would explain why TOC had significant correlations with LMW PAHs, but not with HMW PAHs in Lake Bosten and Poyang. In Lake Dianchi, both LMW and HMW PAHs had significant correlations with TOC, and this may be due to its eutrophic condition or relatively more anthropogenic input into the lake. The preferential scavenging to LMW PAHs may also result in the subtle change in molecular ratios in sediments, such as LMW/HMW PAHs. This indicates that the molecular ratios in the sediments may not accurately represent the original PAH sources for atmosphere sources. Further investigation should be undertaken to determinate to what extent the ratios can be changed in the lake sediments, particularly in eutrophic lakes.

3.4 Aquatic primary productivity scavenging of PAHs in Lake Bosten

Aquatic primary productivity had a large influence on contaminant distribution in sediments (Stern et al. 2005;

Outridge et al. 2007), and a large part of the increases in Hg concentrations during the twentieth century were explained by scavenging by aquatic primary productivity in Canadian high Arctic lakes (Outridge et al. 2007). Interestingly, our observation shows that this may be also the case for PAHs in Lake Bosten. The extent of anthropogenic input of PAHs in Lake Bosten has been of great concern since 1989 (corresponding to the 5 cm depth) (Liao 2007; Wu et al. 2010), which was the beginning of the "Tarim petroleum exploration battle" in Xinjiang Province. The larger petroleum exploitations in Northwest China mainly began after 1989, and whether the increase of PAHs in the surface of Lake Bosten (Electronic supplementary material, Fig. S1) was caused by human activities or organic components needs further assessment. Our discussion above indicates that S2a may be a better indicator to represent the aquatic primary productivity. As described by Outridge et al. (2007) and Stern et al. (2009), the predicted PAHs, AcPy, AcP, Flu, PA, and Ant concentrations after 1989 were calculated, based on S2a concentrations, from the pre-1989 S2a–PAHs, S2a–AcPy, S2a–AcP, S2a–Flu, S2a–PA, and S2a–Ant relationships (Fig. 5). If anthropogenic inputs were responsible for increases in PAH(s), predicted values should lie significantly below measured values, and if increases in aquatic primary productivity were the main factor, predicted values should lie close to the measured values. The results show that the measured values of AcPy, AcP, Flu, PA, and Ant after 1989 occurred within or near the confidence intervals of predictions (see Fig. 5), suggesting that aquatic primary productivity was the main driver of recent increases in these PAHs, and anthropogenic inputs had little influence. The measured values of PAHs for the surface sediments were slightly higher than predicted, indicating an increase in anthropogenic input of high ring PAHs. Other measured values of PAHs in Lake Bosten since 1989 were all in the range of confidence intervals of predictions, suggesting that increases in PAHs in Lake Bosten over the last 20 years had also been influenced little by anthropogenic inputs. Thus, it seems that PAHs concentrations or fluxes in sediments may not represent the real pollution history of PAHs, but may be also influenced by lake trophic condition, and the origin and composition of organic matter in lakes.

Fig. 5 Prediction of sediment PAH(s) concentrations after 1989 AD based on linear regressions, derived from PAH(s)–S2a relationships in the pre-1989 period in Lake Bosten. Pre-1989 data are in *solid circles*, and data after this are in *hollow circles*; *dashed lines* represent the 95 % confidence intervals for the predicted PAH(s) concentrations
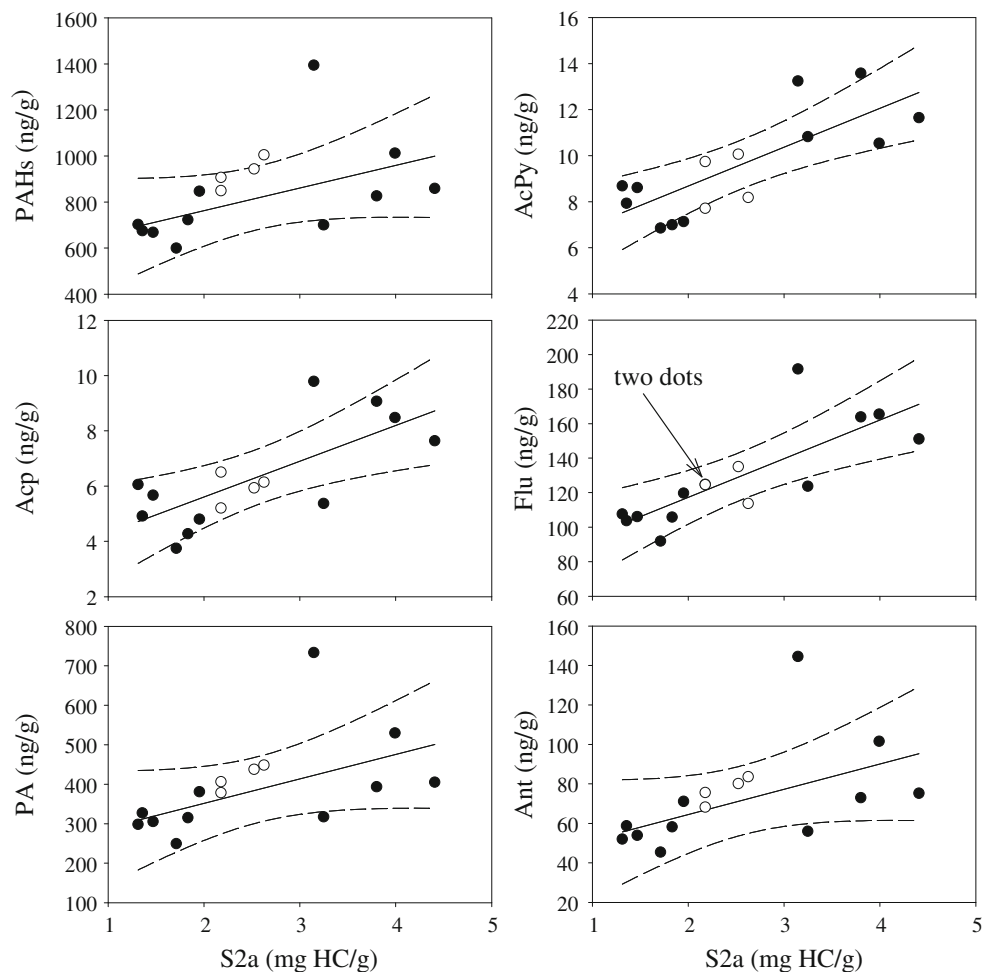
4 Conclusions

Three sediment cores from Lake Bosten, Dianchi, and Poyang, China, were investigated. In these different trophic status lakes, significant correlations were observed between TOC and PAHs, suggesting that TOC played an important role in controlling the distributions of PAHs in sediments. Rock-Eval pyrolysis technique was used to deconvolute TOC into S1, S2a, S2b, and RC components in Lake Bosten. The pyrolysis results suggest that S2a was mainly derived from algae and that S2a may be a better indicator of algal productivity in lakes. Results from Lake Bosten show that the more labile, minor components of TOC (S1 and S2a) played a more important role in controlling the distribution of PAHs because they were easily accessible to pollutants. The algae-derived organic carbon had a more significant influence on the distribution of LMW PAHs than that of HMW PAHs in sediments, suggesting that PAHs scavenging in the water column by algae is preferentially targeted at LMW PAHs. The results also suggest that PAH concentrations in lake sediments could not accurately represent the pollution history of PAHs. The preferential scavenging to LMW PAHs may also result in subtle changes in molecular ratios in sediments, such as LMW/HMW PAHs, and thus affecting the original source differentiation of the PAHs. This study has significant implications for understanding the roles of organic matter in controlling the distributions, bioavailability, and toxicity of PAHs and other similar persistent organic pollutants (POPs) in lakes.

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