

Environmental Behavior of PAHs in Dianchi Lake Distributions, Sources and Risk Assessment of Polycyclic Aromatic Hydrocarbons in Surface Sediments from Dianchi Lake, China

Zhao, S.M.^{1,3}, Wang, B.², Wang, D.W.¹, Li, X.M.³, Huang, B.¹, Hu, P.³, Zhang, L.W.³ and Pan, X.J.^{1*}

¹ Faculty of Environmental Science and Engineering, Kunming University of Science and Technology, Kunming, Yunnan, 650500, P. R. China

² School of Environment and Resource, Southwest University of Science and Technology, Mianyang, Sichuan, 621010, P. R. China

³ Kunming Environmental Monitoring Center, Kunming Environmental Protection Bureau, Kunming, Yunnan, 650228, P. R. China

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ABSTRACT: Polycyclic aromatic hydrocarbons (PAHs) in the priority controlling list of US EPA were systematically evaluated in surface sediments in Dianchi Lake and its estuaries. Total PAH concentrations (Σ PAHs) varied from 210 to 11,070 ng/g dry weight (d.w.) in Dianchi Lake, and from 230 to 12,271 ng/g d.w. in the estuaries. Σ PAHs in sediments from Caohai section were higher than those from Waihai section. The occurrences of PAHs in the Lake were closely related to the distributions of rivers, indicating that the river runoff was an important pathway of PAHs into the Lake. Compared with the US Sediment Quality Guidelines (SQGs), Σ PAHs in most area were below the effect range low (ERL), which implied that the adverse biological effects would occur rarely. The toxic equivalent concentrations of potentially carcinogenic PAHs (TEQ^{arc}) varied from 19 to 967 ng TEQ/g d.w., and the higher values were found in northern Caohai area. The proportions of the toxic equivalent quantity (TEQ^{arc}) to the total TEQs in sediments were all above 96%, suggesting that the carcinogenicity of PAHs could be occurred. Significantly positive correlations between total organic carbon (TOC) and less molecular weight PAHs (2, 3-ring) (LPAHs) were observed in the Lake. Diagnostic ratios showed that the primary source of PAHs in Dianchi Lake and most estuaries is biomass combustion, but is petroleum combustion or petrogenic origin in several other estuaries.

Key words: Polycyclic aromatic hydrocarbons, Distribution, Source, Risk Assessment, Dianchi Lake

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are a kind of typical persistent organic pollutants (POPs) and are ubiquitously distributed in the environment, such as air, water, soil, sediment, plants, animals and human bodies etc. (LaFlamme *et al.*, 1978, Menichini, 1992, Countway *et al.*, 2003, Kuo *et al.*, 2003, Motelay-Massei *et al.*, 2004, Vivesa *et al.*, 2004, Lin *et al.*, 2005). Sources of PAHs could be classified as natural and anthropogenic (Barra *et al.*, 2007). However, most of PAHs in environments are associated with the anthropogenic activities, hence, human production and living activities are generally considered to be the major sources of the compounds (e.g., combustion of fossil fuel, vehicle emissions and power generation, municipal and industrial waste incineration, petroleum

transportation etc.) (Hoffman *et al.*, 1984, Soclo *et al.*, 2000). Once introduced into the water environment, PAHs tend to preferentially accumulate in bottom sediments of estuary and lake because of their high octanol/water partition coefficient (K_{ow}) and low solubility characteristics (Mai *et al.*, 2001, Djomo *et al.*, 2004). PAHs in sediments are mainly bound to natural organic matter which would be considered to significantly affect the distributions of PAHs in sediments (Chefetz *et al.*, 2000, Salloum *et al.*, 2002). Since these compounds are also highly bio-available and lipophilic, PAH-contaminated sediments can adversely affect biota and result in high concentrations in the lipids of organisms (Meador *et al.*, 1995, Yim *et al.*, 2007). Due to their potential carcinogenic, mutagenic or toxic effects to both

*Corresponding author E-mail: xjpan@kmust.edu.cn

terrestrial and aquatic organisms, sixteen PAHs were included in the European Union and US EPA priority pollutant lists (Qiao *et al.*, 2006). To manage and prevent pollution of PAHs, it is essential to understand the pollution levels, distributions and identify the main sources.

Dianchi Lake, adjacent to Kunming City, located in the southwest of China, is the sixth largest freshwater lake in China and the largest freshwater lake in the Yungui Plateau, with an elevation of 1,886 m and a surface area of 300 km². Dianchi Lake is a multi-functional water body mainly used for backup drinking water, industry and agriculture, fisheries, aquaculture, flood control and landscape etc. The Lake was artificially divided into two isolated parts: Waihai section and Caohai section (Fig. 1). Waihai section is the main portion with the surface area of 290 km², mean water depth of 4.4 m, and an only nature outlet (Haikou River). Caohai is more adjacent to Kunming City than

Waihai, and had received large amounts of untreated urban sewage and industrial wastewater before 2002. Xiyuan tunnel is the anthropogenic outlet of Caohai Lake. The effluent of the lake finally flows into Yangtze River, the largest river in China. Dianchi Lake plays an important role in the local socio-economic developments. However, rapid economic development, urbanization, industrialization and agricultural development in Dianchi Lake basin have brought adverse impacts on its ecological environment in recent thirty years. Dianchi Lake has been listed into the focuses of national lake bodies' harnessing in China for its deteriorating water environment. Unfortunately, most studies were mainly focused on the eutrophication, and the limited research on PAHs in Dianchi Lake was conducted by Wu *et al.* (2012). In this paper, the relationship between PAHs and sedimentary organic carbon were investigated through analyzing sediment core samples collected from

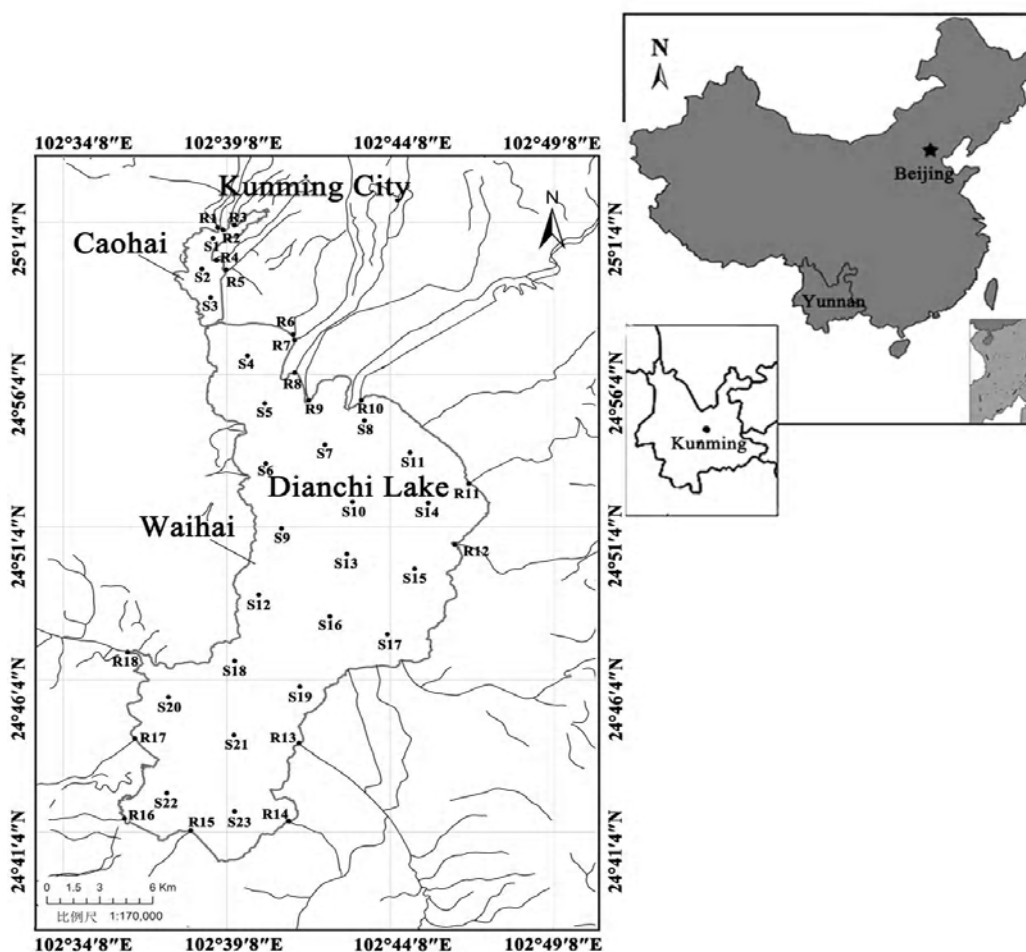


Fig. 1. Map of sampling locations in Dianchi Lake, China
Locations of the sediment samples in Dianchi Lake (S1-S23) and its estuaries (R1-R18)

Dianchi Lake (Wu *et al.*, 2012). However, no comprehensive surveys of PAHs in sediments have been done in Dianchi Lake. Thus, the aims of this study were to investigate the contamination levels, spatial distributions, possible sources and potential toxicity effects of sixteen US EPA's priority pollutants PAHs in surface sediments from Dianchi Lake. The research results may provide theoretical references for environmental managers to reconsider the current regulation for Dianchi Lake.

MATERIALS & METHODS

To identify the contamination levels, distributions and sources of PAHs, surface sediments were collected from the forty-one sampling sites in Dianchi Lake and its estuaries with a stainless steel grab sampler in December 2012. The coordinates of sampling locations were recorded with a global position system (GPS) (Fig. 1). Eight sampling sites were located in Caohai section (S1-S3 in lake area and R1-R5 in estuaries, respectively) and thirty-three sites in Waihai section (S4-S23 in lake area and R6-R18 in estuaries, respectively). The sampling depth of each site was about 5 cm. Surface sediment samples were collected in triplicate from each sampling location during the same period, respectively. All samples were placed in the solvent-washed brown glass (pyrolyzed at 400 °C for 6 h) fitted with aluminum-foil lined cap and were kept at -40 °C until analysis.

The procedures of sample preparation and analysis were performed according to previously reported methods (Wang *et al.*, 2013). Briefly, sediment samples were lyophilized using an Eyela FDU-1200 freeze-drier (Tokyo, Japan). All freeze-dried samples were passed through the sieve (bore diameter: 0.15 mm), ground and homogenized. Samples were extracted using an accelerated solvent extractor (ASE-200, Dionex, USA). 10.0 g sediment sample was weighed and mixed with 2.0 g diatomite (pyrolyzed at 600 °C for 4 h) and 2.0 g anhydrous sodium sulfate (pyrolyzed at 400 °C for 6 h), transferred into 22 mL extraction cell and the surrogates 1, 4-Dichlorobenzene-*d*4, naphthalene-*d*8, phenanthrene-*d*10, chrysene-*d*12 and perylene-*d*12 were added to the samples. The samples were extracted with a mixture of hexane/acetone (1:1 v/v) at 1500 psi and 90 °C with flush percentage of 60% in the extraction cell by static extraction for 6 min. The extraction was carried out in one cycle. After removing water by adding 5.0 g anhydrous sodium sulfate, the extracts were concentrated to 1.0 mL by nitrogen evaporator (Turbo Vap II, Caliper, USA). For elimination of impurities, the extracts were passed through the Silica gel-Florisil composite columns (sequentially filled with 1.0 g Florisil, 0.7 g activated silica gel and 1.0 g anhydrous sodium from bottom to top) pre-

conditioned with 7.0 mL hexane, and the target compounds were eluted with 17.0 mL mixture of hexane/acetone (19:1 v/v). The fractions were finally concentrated to 1.0 mL under a gentle stream of nitrogen for determination.

PAHs identification and quantification were performed by an Agilent 7890 Gas Chromatograph coupled with Agilent 7000 GC/MS Triple Quad, Agilent 7693 Auto Sampler and DB-5 fused silica capillary column (30 m × 0.25 mm × 0.25 μm) operating in the electron ionization (EI) mode. Those samples were injected in the splitless mode with an injection temperature of 280 °C. The oven temperature program was initially set at 50 °C for 3 min, raised to 150 °C at the rate of 25 °C/min, held at this temperature for 3 min, then to 240 °C at the rate of 6 °C/min, held for 5 min, finally to 280 °C at the rate of 16 °C/min, held for 10 min. Ion source temperature was kept at 280 °C and the ionization energy was 70 eV. High-purity helium was used as a carrier gas with a constant flow rate of 1.0 mL/min. The acquisition mode was multiple reaction monitor (MRM) with 2 parent/product ion transitions being monitored for quantification and quality analysis (Wang *et al.*, 2013). All concentrations were expressed on a sediment dry weight basis.

Sixteen PAH compounds were analyzed: naphthalene (Na), acenaphthylene (Acy), acenaphthene (Ace), fluorene (Flu), anthracene (An), phenanthrene (Ph), fluoranthene (Fl), pyrene (Pyr), benzo[a]anthracene (BaA), chrysene (Chrys), benzo[a]pyrene (BaP), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[g, h, i]perylene (BghiP), indeno[1, 2, 3-c, d]pyrene (IP), and dibenzo[a, h]anthracene (dBanA). Total organic carbon (TOC) in the sediment samples were quantified using a SHIMADZU-TOC-VCPH model analyzer after the removal of carbonates.

For method quality control and assurance, reagent blanks, procedural blanks, spiked blanks and triplicate spiked matrices were analyzed for each batch of samples. No target compounds were detected in the reagents, trace levels of targets were detected in the procedural blanks, the recoveries of sixteen PAHs ranged from 70.4% to 124.7%, and the surrogate recoveries in all samples were from 74.8% to 98.4%. Detection limits were 0.07-0.45 ng/g d.w. for PAHs. The correlation coefficients (R^2) values of calibration curves were above 0.993 with the acceptable RSD values of 1.2%-10.4% for PAHs.

RESULTS & DISCUSSION

The total PAH concentrations (Σ PAHs) in surface sediments from Dianchi Lake and its estuaries ranged from 210 to 11,070 ng/g d.w. and from 230 to 12,271 ng/

g d.w. respectively (Table 1). The highest Σ PAHs concentration in Dianchi Lake was found at S1 located in the north of Caohai section due to the inputs of three heavy polluted rivers: Yunliang River (R1), Xin River (R2) and Dagan River (R3). The corresponding Σ PAHs concentrations in the estuaries of the above mentioned rivers were 12,271 ng/g d.w. (R1), 5,473 ng/g d.w. (R2) and 6,296 ng/g d.w. (R3), respectively (Table 1). Among the higher Σ PAHs, S2 (1,492 ng/g d.w.) and S3 (1,681 ng/g d.w.) were located in the middle and south of the Caohai section, respectively, where the concentrations of Σ PAHs in the estuaries of Xiba River (R4) and Chuanfang River (R5) were 2,512 ng/g d.w. and 787 ng/g d.w., respectively. S4 (2,072 ng/g d.w.), S5 (2,506 ng/g d.w.) and S6 (1,643 ng/g d.w.) were in the north of the Waihai section, where the inputs rivers include Jinjia River (R6: 1,407 ng/g d.w.), Panlong River (R7: 3,709 ng/g d.w.), Daqing River (R8: 6,278 ng/g d.w.), and Hai River (R9: 5,919 ng/g d.w.). S8 (1,344 ng/g d.w.) and S11 (1,413 ng/g d.w.) were in the northeast of the Waihai section near the estuaries of Baoxiang River (R10: 1,825 ng/g d.w.) and Luolong River (R11: 3705 ng/g d.w.), respectively. The lowest Σ PAHs concentration was detected at S9 (210 ng/g d.w.) located in the west of Waihai section near the mountainous area in which there were few anthropogenic sources. Obviously, the contents of PAHs in Dianchi Lake were primarily influenced by the distributions of river and the PAH discharge levels in those region. It indicated that the river runoff was the major input pathway of PAHs into Dianchi Lake.

According to the categories from Baumard et al. (1998), Σ PAHs pollution levels were classified into four categories including low, moderate, high and very high level when Σ PAHs are 0-100, 100-1,000, 1,000-5,000 and >5,000 ng/g d.w., respectively. In this study, 41.5%, 43.9% and 14.6% of all samples could be characterized as moderate, high and very high pollution level, respectively. The sediment samples from Caohai section could be considered as the pollution levels from high to very high, except samples from R5. Except for R8 and R9, the concentrations of PAHs in the rest of sampling sites all exceed or equaled to the moderate level. It was obvious that the PAHs pollution level in sediment from Caohai section was higher than that from Waihai section since there were a large number of enterprises (smelter, pharmaceutical factory, paper mill, cement plant, chemical plant, paint factory, steel plant, and so on) scattering around Caohai section before 2002.

A comparison with those reports on Σ PAHs in surface sediments from different areas was shown in Table 2. The pollution levels were in the moderate to very high in this study. The minimum value was lower than that in Erie Lake, Taihu Lake, Yellow River and

rivers of Tianjing, and the maximum was also lower than that in Nansi Lake, Santander Bay, rivers of Tianjing and Naples' Harbor.

The composition of PAHs in surface sediments is presented in Fig. 2. According to the number of aromatic rings, PAHs were classified into four categories: 2- and 3-ring, 4-ring, 5-ring and 6-ring. As shown in Fig. 2, the 4-ring PAHs were dominant in surface sediments, with a proportion ranging from 33.5% to 66.9%, except the samples from S8, S14, S16, where the 6-ring PAHs were dominant at 41.3%, 38.7% and 58.8%, respectively. The percentage of less molecular weight PAHs (2, 3-ring) LPAHs to the total PAHs ranged from 5.5% to 27.3%. High molecular weight PAHs (4-, 5- and 6-ring) (HPAHs) were the dominant compounds with a contribution of 72.7%-94.5% to the total PAHs.

The identification of PAH sources is crucial to reduce the input of PAHs to the environment. The sources of PAHs could be classified into two groups: pyrogenic (from combustion) and petrogenic (from petrochemicals) (Mai *et al.*, 2002, Zakaria *et al.*, 2002, Stout *et al.*, 2004). Pyrogenic sources include vehicles using gasoline or diesel fuel, industrial operations and power plants using fossil fuels, smelting, waste incinerators and combustion of biomass (grass, wood and coal); petrogenic sources include crude oil and petrochemicals (gasoline, diesel fuel, kerosene, lubricating oil and asphalt) (Boonyatumanond *et al.*, 2006).

In general, the petrogenic sources such as petroleum spills and oil seeps contain predominantly LPAH compounds, whereas the pyrogenic sources (e.g., vehicle exhaust, domestic heating with coal, forest fires) or pyrolytic PAH compounds contain predominantly more of the HPAH species (Irwin *et al.*, 1997, Ünlü *et al.*, 2010). The ratio of Σ LPAHs/ Σ HPAHs has been successfully used to distinguish pyrogenic (<1) and petrogenic (>1) sources of PAHs in many studies (Magi *et al.*, 2002, Qiao *et al.*, 2006; Chen and Chen, 2011). All the ratios of Σ LPAHs/ Σ HPAHs ranged from 0.06 to 0.38 (Table 1), indicating that sedimentary PAHs at these sites had a greater contribution from pyrogenic sources. Vehicle emissions (more than 1.7 million automobiles in Kunming City), wastes from industrial operations (a large number of enterprises such as smelter, pharmaceutical factory, paper mill, cement plant, chemical plant, paint factory and steel plant scattered around the Lake) and forest fires (dry weather in spring and winter often leads to forest fires in the region) could be the main pyrogenic sources.

Besides Σ LPAHs/ Σ HPAHs, some typically PAH isomeric ratios such as Ph/An, Fl/Pyr, BaP/BghiP, BaA/

Table 1. PAH concentrations (ng/g d.w.), selected molecular ratios, TEQ (ng TEQ/g d.w.) and TOC (%) in sediments of Dianchi Lake

Site	Σ PAHs ^a	Σ LPAHs ^b	Σ HPAHs ^c	Σ LPAHs/ Σ HPAHs	An/(Ph+An)	Fl/(Fl+Pyr)	Σ CPAHs ^d	Σ TEQ ^e	Σ TEQ ^{carc}	TOC
S1	11,070	727	10,344	0.07	0.19	0.56	8,518	971	967	15.7
S2	1,492	407	1,085	0.38	0.86	0.63	462	93	90	14.2
S3	1,681	251	1,430	0.18	0.57	0.62	1,119	210	208	28.2
S4	2,072	151	1,922	0.08	0.20	0.62	1,608	193	192	6.1
S5	2,506	163	2,343	0.07	0.20	0.62	2,013	238	237	5.4
S6	1,643	100	1,543	0.06	0.24	0.63	1,314	154	153	6.2
S7	937	89	848	0.10	0.46	0.66	726	100	100	6.0
S8	1,344	108	1,236	0.09	0.21	0.65	1,100	198	197	4.8
S9	210	36	174	0.21	0.32	0.67	139	19	19	2.2
S10	1,138	78	1,060	0.07	0.21	0.65	891	91	91	9.2
S11	1,413	122	1,292	0.09	0.17	0.64	1,105	154	85	4.8
S12	772	77	695	0.11	0.22	0.65	595	85	154	4.0
S13	973	94	879	0.11	0.18	0.67	743	83	83	6.5
S14	661	50	611	0.08	0.25	0.69	538	90	90	5.3
S15	609	52	556	0.09	0.21	0.69	478	64	64	5.7
S16	978	53	924	0.06	0.23	0.67	864	260	260	2.7
S17	645	58	587	0.10	0.23	0.67	497	54	54	6.6
S18	1,088	84	1,004	0.08	0.20	0.67	856	99	99	6.3
S19	817	68	749	0.09	0.21	0.66	649	95	95	6.2
S20	1,072	97	975	0.10	0.19	0.65	813	81	80	7.7
S21	1,134	100	1,034	0.10	0.19	0.64	861	85	85	6.4
S22	752	77	675	0.11	0.23	0.69	588	88	88	8.6
S23	479	57	422	0.14	0.20	0.72	367	50	50	5.1
R1	12,271	1,815	10,456	0.17	0.13	0.33	5,967	790	782	22.9
R2	5,473	836	4,637	0.18	0.16	0.42	2,948	490	487	5.1
R3	6,296	1,457	4,839	0.30	0.19	0.54	3,152	680	675	14.3
R4	2,512	637	1,874	0.34	0.16	0.70	1,203	121	119	20.7
R5	787	127	661	0.19	0.13	0.61	498	108	108	11.9
R6	1,407	273	1,134	0.24	0.12	0.56	780	176	175	16.2
R7	3,709	519	3,189	0.16	0.07	0.45	1,913	175	173	7.6
R8	6,278	1,043	5,235	0.20	0.12	0.42	2,952	262	258	10.3
R9	5,919	1,584	4,336	0.37	0.15	0.69	2,291	142	136	2.8
R10	1,825	302	1,523	0.20	0.20	0.55	922	96	95	1.1
R11	3,705	653	3,052	0.21	0.13	0.39	1,862	449	446	6.9
R12	549	92	457	0.20	0.15	0.55	334	80	79	4.0
R13	230	54	176	0.31	0.12	0.56	130	29	29	2.5
R14	1,899	202	1,698	0.12	0.11	0.50	1,367	138	137	3.3
R15	381	73	308	0.24	0.11	0.55	223	39	39	3.2
R16	387	79	308	0.26	0.10	0.57	230	46	45	7.9
R17	630	100	530	0.19	0.15	0.53	388	87	86	8.7
R18	2,334	472	1,862	0.25	0.11	0.40	1,168	121	120	16.9

^a Sum of concentrations of 16 PAH compounds.

^b Sum of concentrations of the low molecular weight PAHs (2, 3-ring).

^c Sum of concentrations of the high molecular weight PAHs (4, 5, 6-ring).

^d Sum of concentrations of the potential carcinogenic PAHs including BaA, Chrys, BaP, BbF, BkF, BghiP, IP and dBanA.

^e The total toxic BaP equivalent for all 16 PAH compounds.

Σ TEQ^{carc}: the total toxic BaP equivalent for potential carcinogenic PAHs.

Table 2. PAH concentrations in sediments from different locations

Location	ΣPAHs (ng/g d.w.)	Contamination level ^a	N ^b	References
Iznik Lake, Turkey	17-835	Low to moderate	12	Ünlü et al. (2010)
Masan Bay, Korea	207-2,670	Moderate to high	24	Yim et al. (2005)
Erie Lake, USA	224-5,304	Moderate to very high	16	Smirnov et al. (1998)
Naples' Harbor, Italy	9-31,774	Low to very high	16	Sprovieri et al. (2007)
Santander Bay, Spain	20-344,600	Low to very high	16	Viguri et al. (2002)
Liaodong Bay, China	144.5-291.7	Low	16	Hu et al. (2011)
Qiantang River, China	91.3-614.4	Low to moderate	15	Chen et al. (2007)
Yangtze River Estuary, China	84.6-620	Low to moderate	16	Hui et al. (2009)
Yellow River, China	464-2,621	Low to high	16	Xu et al. (2007)
Taihu Lake, China	410-5,260	Moderate to very high	35	Qu et al. (2002)
Nansi Lake, China	160-32,600	Moderate to very high	16	Li et al. (2009)
Rivers of Tianjing, China	787-1,943,000	Moderate to very high	16	Shi et al. (2005)
Dianchi Lake, China	210-12,271	Moderate to very high	16	This study

^a Scale of contamination level: low: 0-100 ng g⁻¹ d.w., moderate: >100-1,000 ng g⁻¹ d.w., high: >1,000-5,000 ng g⁻¹ d.w., very high: >5,000 ng g⁻¹ d.w. (Baumard et al. 1998).

^b Number of PAH compounds analyzed in each study.

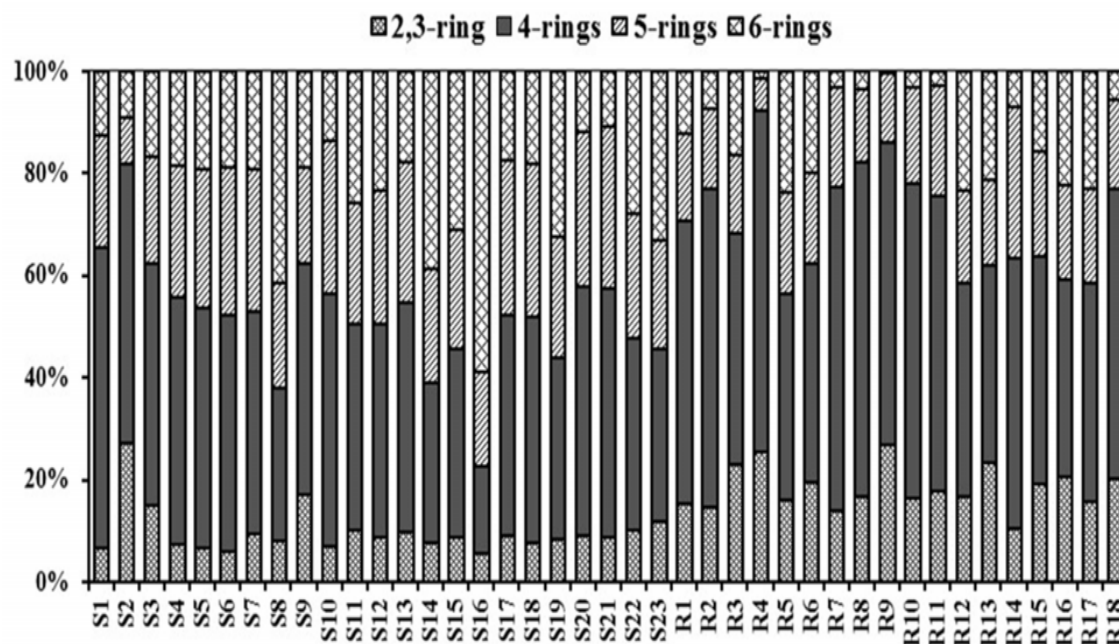


Fig. 2. The composition characteristics of PAHs in sediments

BaA+Chry, An/(Ph+An) and Fl/(Fl+Pyr) have also been widely used as clues to identify the pyrogenic and petrogenic sources of PAHs (Budzinski *et al.*, 1997, Oros and Ross, 2005, Wang *et al.*, 2009). In the present work, molecular diagnostic ratios of An/(Ph+An) and Fl/(Fl+Pyr) were adopted for the identification of PAH sources. The ratio of An/(An+Ph) equal to or greater than 0.1 usually means a dominance of pyrogenic, while below 0.1 usually is considered an indication of petroleum (Yunker *et al.*, 2002). The ratio of Fl/(Fl+Pyr) less than 0.4 suggests petroleum origin, between 0.4 and 0.5 presents the characteristic of petroleum combustion, while greater than 0.5 indicates biomass combustion (Yunker *et al.*, 2002). The ratios of An/(Ph+An) and Fl/(Fl+Pyr) for all samples were calculated (Table 1), and Fl/(Fl+Pyr) versus An/(Ph+An) ratios were plotted (Fig. 3).

In the Lake, the ratios of An/(Ph+An) were in the range of 0.17-0.86 with an average of 0.27 for all sites (S1-S23), indicating that sedimentary PAHs were mostly of pyrogenic origin. These were further confirmed by the ratios of Fl/(Fl+Pyr) ranged from 0.56-0.72 with an average of 0.65 for all sites. The results showed that the major source of PAHs was derived from biomass combustion in the region, which could be a mirror of the local economic-social development. In a long time, coal has been used as the main energy resource by most of industries and residents in Dianchi catchment. But, coal combustion is the critical source of PAHs which could pose a potential risk to aquatic organisms

and even human. Fortunately, local governments have realized the seriousness of the deterioration of environment, and coal combustion is being replaced by clean energy such as natural gas and electricity step by step.

In the estuaries, the An/(Ph+An) ratios were from 0.07 to 0.20 with an average of 0.13 for all sites (R1-R18), indicating that sedimentary PAHs were mostly of pyrogenic origin for the most estuaries except R7. The Fl/(Fl+Pyr) ratios were from 0.33 to 0.70 with an average of 0.52 for all sites. The estuaries R2, R7, R8 and R18 with the ratios of Fl/(Fl+Pyr) between 0.4 and 0.5 should be largely contaminated by petroleum (vehicular emissions, crude oil, gasoline, fuel oil et al.) combustion, while R1 and R11 less than 0.4 indicated that the main PAH sources were petroleum origin, and the rest of the estuaries greater than 0.5 implied that biomass combustion were the dominant sources. The rivers with the estuaries R10, R12-R17 flow through rural area where the impacts of urbanization and industry were low. Biomass combustion could be the major source of PAHs. While the rest of the rivers flow through the city and rural area where multiple PAHs sources were included. In Dianchi valley, there were no large scale petrochemical plants, therefore, oil seepage was unlikely emitted to the water system. The petrogenic sources could be mainly introduced to the rivers and lake through run-off of street dust which potentially contains petrogenic PAHs (spilled fuel, asphalt and tire-wear materials). Oil spill from the

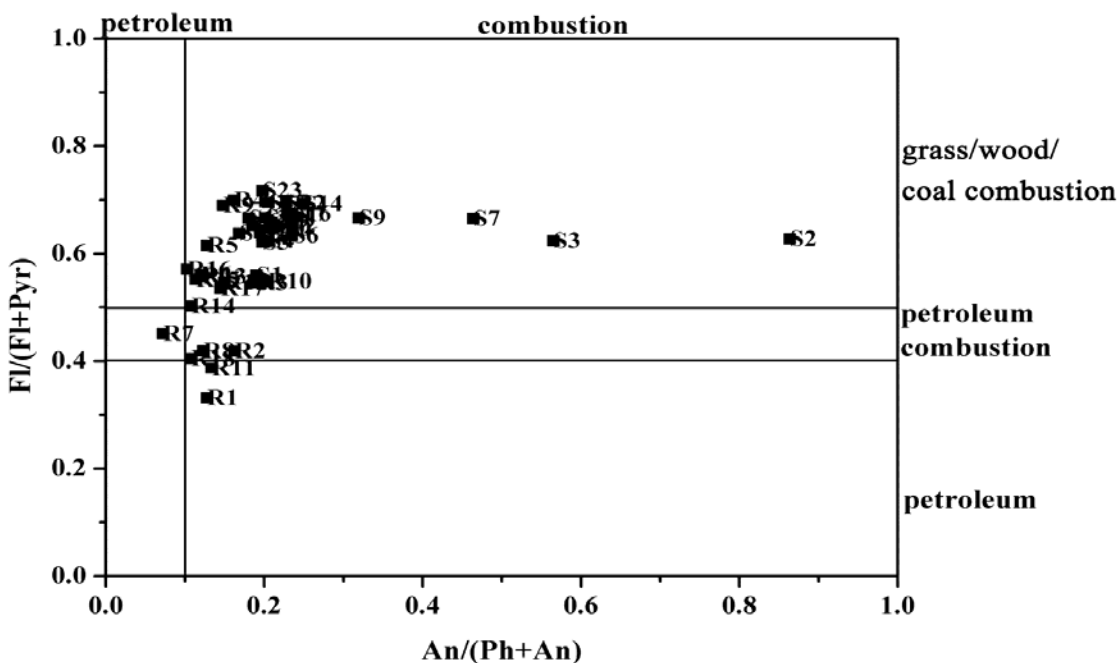


Fig. 3. Plots of the PAH isomeric ratios based on Fl/(Fl+Pyr) versus An/(Ph+An)

boats may be another petrogenic source.

Many studies have shown a positive correlation between concentrations of PAHs and TOC in sediments (Gustafson and Dickhut, 1997, Yang, 2000, Shi *et al.*, 2007, Charriau *et al.*, 2009). TOC was an important factor in controlling the distribution of PAHs in sediments (Boehm and Farrington, 1984, Kim *et al.*, 1999), and high TOC content was associated with high PAHs concentration (Wang *et al.*, 2001). TOC values ranged from 2.19% to 28.23%, with a mean of 7.55% for Dianchi Lake; and from 1.13% to 22.93%, with a mean of 9.24% for the estuaries (Table 1). The relationship between PAHs and TOC were examined as shown in the Table 3.

In Dianchi Lake (S1-S23), TOC had significant positive correlations with 2-ring PAHs ($r=0.705, p<0.01, N=23$), 3-ring PAHs ($r=0.566, p<0.01, N=23$) and LPAHs ($r=0.602, p<0.01, N=23$), but no significant correlations with other PAHs and TPAHs. Obviously, TOC was more strongly positively correlated with LPAHs than HPAHs. Moreover, the correlation factors decreased with the increasing of the number of ring. It suggested that TOC played a more important role in controlling the distributions of LPAHs than HPAHs in surface sediments of Dianchi Lake. These results were different from those reported by Wu *et al.* (2012), who found that TOC had significant positive correlations with LPAHs ($r=0.960, p<0.001, N=20$) and HPAHs ($r=0.987, p<0.001, N=20$) in Dianchi Lake core sediments (Wu *et al.*, 2012). Different sampling sites, time and sample

types may be the main reasons result in the difference between research results. Aromatic carbon structure played an important role in the sorption mechanism between TOC and PAHs (Bucheli and Gustafsson, 2000). The structural differences of PAHs may have a significant impact on their relationship with TOC.

In estuaries (R1-R18), TOC had slightly positive correlations with different ring PAHs, and there was no obvious difference in the correlation factors between LPAHs and HPAHs with TOC. These results were different from those in the Lake. Hydraulic power factors, origins and other factors may play a more important role in controlling the distributions of PAHs in surface sediments of estuary than TOC.

Based upon the total content of potentially carcinogenic PAH compounds (CPAHs) (BaA, Chrys, BaP, BbF, BkF, BghiP, IP and dBanA) listed by US EPA (Bojes and Pope, 2007), the potential toxicity of sediments from Dianchi Lake were evaluated. The concentrations of CPAHs (Σ CPAHs) ranged from 139 ng/g d.w. (S9) to 8,518 ng/g d.w. (S1), with a mean of 1,167 ng/g d.w. in Dianchi Lake and from 129 ng/g d.w. (R13) to 5,967 ng/g d.w. (R1), with a mean of 1,574 ng/g d.w. in the estuaries, respectively. The proportions of Σ CPAHs/ Σ PAHs were from 31.0% to 88.3%, with a mean of 75.6% in the Lake, and from 38.7% to 72.0%, with a mean of 54.2% in the estuaries. Chrys, BaF, BbA and BghiP were dominant in CPAHs, with a proportion of 33.5%, 18.7%, 14.0% and 11.9% of the Σ CPAHs,

Table 3. ERL and ERM guideline values of PAHs in surface sediments (ng/g d.w.) (Long *et al.*, 1995; Liu, *et al.* 2009)

	ERL	ERM	Present study			
			Mean	Maximum	ERL	ERM
Na	160	2,100	31	151	-	-
Acy	16	500	10	82	R1-R3, R7-R9, R11, R18	-
Ace	44	640	7	49	R2	-
Flu	19	540	39	243	S1-S5, S12, R1-R11, R14, R18	-
An	853	1,100	43	241	-	-
Ph	240	1,500	198	1,281	S1, R1-R4, R7-R9, R11, R18	-
Fl	600	5,100	286	1,487	S1, R1-R3, R8, R9,	-
Pyr	665	2,600	287	3,001	S1, R1-R3, R7, R8, R11	R1
BaA	261	1,600	188	1,528	S1, S4, S5, R1-R4, R8, R9	-
Chrys	384	2,800	451	3,163	S1, S4, S5, R1-R3, R7-R9, R11, R14, R18	S1
BaP	430	1,600	63	331	-	-
BbF	320	1,880	252	1,719	S1, S4-S6, R1-R3, R7-R9, R14	-
BkF	280	1,620	119	674	S1, R1, R3, R9	-
BghiP	430	1,600	160	893	S1, R3	-
IP	-	-	60	328	-	-
dBanA	63.4	260	52	234	S1, S3, S5, S8, S16, R1-R3, R6	-
? PAHs	4,022	4,4792	2,246	15,405	S1, R1, R3, R8, R9	-

respectively. The concentration distribution of CPAHs was plotted based upon the analysis of GIS interpolation, and the darker color means the higher Σ CPAHs value, as shown in the Fig. 4. Obviously, high Σ CPAHs mainly occurred in the north of Caohai section and the northeast of Waihai section.

The toxic equivalency factor (TEF) method has been successfully developed to evaluate the potential toxicity of PAHs in sediment, and the toxicity is expressed relative to BaP, the reference standard (Delistraty, 1997, Sprovieri *et al.*, 2007). BaP-like toxicity or toxic equivalent (TEQ) for PAH compounds can be calculated using the following equation:

$$TEQ = \sum PAH_i \times TEF_i \quad (1)$$

where, PAH_i is the concentration of PAH congener i (ng/g.d.w.); TEF_i is the toxic equivalency factor for PAH congener i . TEF_i for Na, Ace, Acy, Flu, Ph, An, Fl, Pyr, BaA, Chrys, BbF, BkF, BaP, IP, dBanA and BghiP are 0.001, 0.001, 0.001, 0.001, 0.001, 0.01, 0.001, 0.001, 0.1, 0.01, 0.1, 0.1, 1, 0.1, 1 and 0.01, respectively (Nisbet and LaGoy, 1992, US EPA, 1993).

In this study, sixteen PAH TEQs and eight CPAH TEQs (TEQ^{carc}) of all samples were calculated as presented in Table 1. The total TEQ values ranged from 19 to 971 ng TEQ/g d.w., and the highest value was found at S1. The TEQ^{carc} values varied from 19 to 967 ng TEQ/g.d.w., with a proportion of above 96% of the total TEQ, which showed that the potential toxicity of PAHs in sediments could be represented by TEQ^{carc} . The higher TEQ^{carc} values were presented at S1, R1,

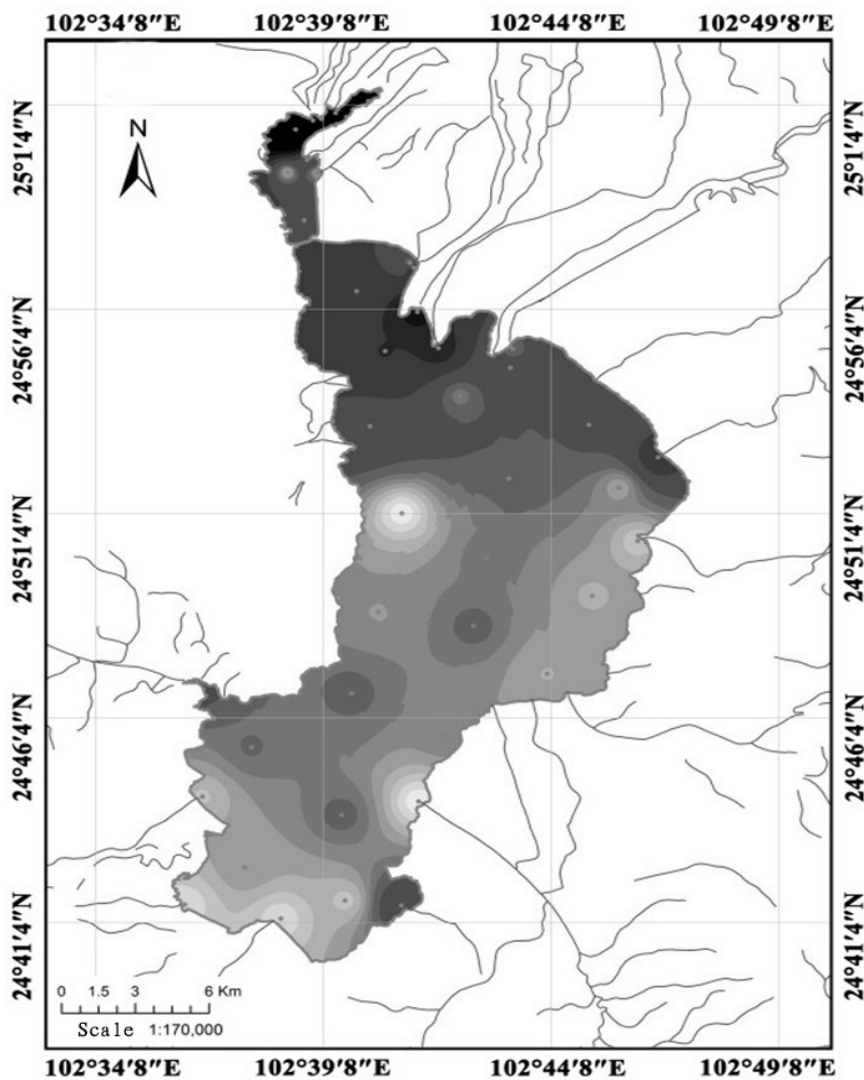


Fig. 4. Distribution characteristics of Σ CPAHs in Dianchi Lake

R2, R3 and R11, with the values greater than 400 ng TEQ/g d.w., while for the most sites (51.2%) the values were below 100 ng TEQ/g d.w.. Compared with other literatures, the TEQ^{carc} in this study were less than those reported in Shipping area of Naples Harbor, Italy (45-3,578 ng TEQ/g d.w.) (Savinov *et al.*, 2003) and Kaohsiung Harbor, Taiwan (55-1,964 ng TEQ/g d.w.) (Chen and Chen, 2011), while higher than those in Kola Bay (71-583 ng TEQ/g d.w.) and Korsfjord of Barents Sea, Russia (18-60 ng TEQ/g d.w.) (Savinov *et al.*, 2003). dBanA, BaP, BbF and BaA were dominant carcinogenic PAH compounds, with the contribution of 31.2%, 29.8%, 15.1% and 10.4% to the TEQ^{carc}, respectively. Sediments are a potential source of toxicity to aquatic organisms (Liu *et al.*, 2009). As a sediment quality guideline (SQG), the effect range-low (ERL) and effect range-median (ERM) had been developed to quantitatively assess the adverse biological effects in sediments (Long *et al.*, 1995). Each individual PAH was separated into three concentration ranges which were rarely (<ERL), occasionally (\geq ERL and <ERM) and frequently (\geq ERM) associated with adverse biological toxicity effects (Long *et al.*, 1995).

As shown in the mean Σ PAHs was below the ERL value. The Σ PAHs at S1, R1, R3, R8 and R9 were between the ERL and ERM, which demonstrated that adverse biological toxicity effect would occur occasionally. While Σ PAHs were below the ERL for the rest of sites, suggesting that adverse biological toxicity effects would occur rarely in most area.

CONCLUSION

PAHs in surface sediments from forty-one sites in Dianchi Lake and estuaries around Dianchi Lake were systematically investigated. The results suggested that Σ PAHs in sediments from Caohai section were higher than those from Waihai section, and the river runoff was an important input pathway of PAHs into the Lake. According to SQGs, adverse biological effects caused by PAHs would occur rarely in most area of the Lake. High values of TEQ^{carc}/TEQ showed that the potential toxicity of PAHs in sediments could be represented by TEQ^{carc} in the Lake. Significantly positive correlations between TOC and LPAHs suggested that TOC played a more important role in controlling the distributions of LPAHs than HPAHs in surface sediments of Dianchi Lake. Sources identification suggested that PAHs in Dianchi Lake and majority of estuaries were dominated by the biomass combustion.

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