Historical records and sources of polycyclic aromatic hydrocarbons (PAHs) and organochlorine pesticides (OCPs) in sediment from a representative plateau lake, China

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HIGHLIGHTS

- The sources of organic contaminants in sediment core were identified.
- Historical changes of PAH and OCP concentrations were reconstructed.
- Organic contaminant concentrations reached peak values in the 1980s and 1990s.
- HCHs and DDTs made up more than 85% of the total OCPs.

GRAPHICAL ABSTRACT
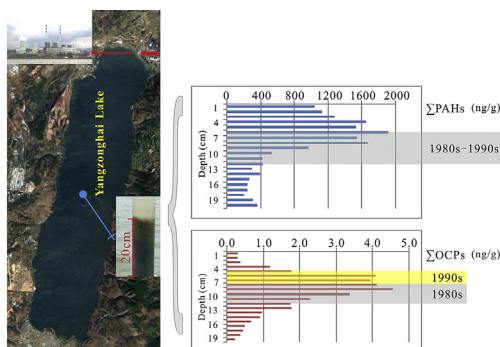
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ABSTRACT

The PAH and OCP concentrations in sediment cores collected from a deep lake were measured and evaluated chronologically. The results indicated that the PAH and OCP concentrations significantly increased from the 1950s to the 1990s and subsequently decreased to recent years. Integrated molecular diagnostic ratios indicated that the predominant petrogenic sources occurred from the 1950s—1980s. Petroleum and fuel combustion dominated the source of contamination more recently as a result of energy structure changes in this region. Additionally, HCHs and DDTs were the dominant OCP compounds, making up a majority of the total OCPs present (>85%). HCHs accounted for a larger ratio of the OCPs between the 1950s and 1980s, suggesting that HCHs were the dominant POPs in this period. DDTs then became dominant in the 1980s and later. High α/γ-HCH ratios suggested that the emission and conversion of local technical HCHs were the predominant HCHs source. The ratios of (DDE + p,p'-DDD)/ DDTs and p,p'-DDT/DDTs indicated that the DDTs mainly originated from historical input. In addition, the dramatic decrease since the 1980s may be the result of China's banning of DDTs. However, DDTs were still present in the 1990s, suggesting DDTs were still used in this region and beyond.

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1. Introduction

Representing important classes of persistent organic pollutants (POPs), polycyclic aromatic hydrocarbons (PAHs) and organochlorine pesticides (OCPs) are identified as toxic chemicals which don't degrade easily in aquatic environment, and have caused increasing worldwide concern (Luzardo et al., 2014; Cetin et al., 2016). PAHs are hydrocarbons with two or more benzene rings, and are regard as one of the most crucial groups of anthropogenic organic contaminants. They are ubiquitous in aquatic ecosystem, and consist of over 100 different chemicals (Hernández-Vega et al., 2017). PAHs originate from a variety of processes, including combustion, slow maturation of organic matter and the short degradation of biogenic precursors (Arias et al., 2010; Li et al., 2010). Sixteen PAH compounds are included in the U.S. Environmental Protection Agency (U.S. EPA) priority pollutant list due to their persistence and long-term toxicity, and their potential mutagenic and carcinogenic effects (Zhi et al., 2015). OCPs were the most extensively used pesticides worldwide from the 1950s. Some OCP compounds are endocrine disruptors, affecting reproductive systems, and disrupting normal endocrine and immune system function (Ene et al., 2012). Certain classes of POPs are fat soluble and resist biological and chemical degradation. As such, they can bring about bioaccumulation in the fatty tissues. Biomagnification then occurs throughout the food chain, leading to adverse health effects for living beings through ingestion, even at low environmental concentrations (Karacık et al., 2013). Because of their ecotoxicity and carcinogenic properties, most OCP compounds have been prohibited or restricted in many countries for a long time (Yamashita et al., 2000; Concha-Graña et al., 2000; Combi et al., 2013). Nevertheless, a considerable number of these organic pollutants still persist in the environment because of a long half-life and illegal production and use (Zhi et al., 2015).

Organic pollutants discharged into the aquatic environment were adsorbed on particulate matter and accumulated into the adipose tissues of organisms, and ultimately deposited into sediments because of their low solubility in water, relatively nonpolar nature, and particulate-oriented behavior. This makes sediments an important reservoir for organic pollutants, and by extension, important archives of environmental information (Thomas et al., 2012). POPs, including PAHs and OCPs, have been introduced into aquatic ecosystem through a variety of processes including urban and agricultural runoff, vehicle exhaust emissions, and fossil fuel spillage (Rinawati et al., 2012). These organic pollution have been released into the aquatic environment and have undergone different physical, chemical, and biological effects, including adsorption, oxidation, photolysis and biodegradation (Sultana et al., 2014; Mahugija et al., 2015). PAHs and OCPs in the sediments provide an ideal archive of historical information about anthropogenic contamination in aquatic ecosystems, and research involving sediments can effectively assess on PAH and OCP contamination in aquatic ecosystems (Veses et al., 2013). Dated sediments are natural tracers, comprehensively recording historical organic contamination processes. Using dated sediment cores is considered as a well-established method to reconstruct the chronology of organic contaminations in aquatic ecosystem (Guo et al., 2010; Li et al., 2015).

China, the biggest developing country, is experiencing rapid growth of population, industry and agriculture, energy consumption and transportation in recent decades. Accordingly, high organic pollutant levels have been detected in lake sediments in China, and attracted significant attention (Qiu et al., 2005; Zhi et al., 2015). However, existing researches mainly focused on developed regions and limited information for POPs in deep plateau lakes in the western China was available. Deep plateau lakes archive the contaminant pollution histories more effectively and faithfully than shallow lakes adjacent to cities owning to less anthropogenic disturbances and stable sedimentary environment. Research on sediments in these lakes can promote the understanding and management of the relationship between environmental quality and anthropogenic activities (Wang et al., 2010a, b). The aims of this study were to: 1) investigate the residual levels and temporal distributions of PAH and OCP in the sediment from a representative plateau lake, 2) identify PAH and OCP sources in the undisturbed sediment profile combined with chronology study, and 3) reconstruct the historical trends related to organic contamination in the lake ecosystem, which reveals trends related to socioeconomic development and energy consumption in the region in turn.

2. Material and methods

2.1. Study area description

Yangzonghai Lake $(24°27'-24°54'N, 102°55'-103°02'E)$ is an important deep plateau lake on the Yunnan-Guizhou Plateau. It is located in southwest China and approximately 36 km from Kunming, the capital city of Yunnan Province, China. The average lake elevation of the lake is approximately 1773 m, with a water area of almost 31 km^2. Yangzonghai Lake is a deep freshwater lake with a maximum length and width of 12.7 and 2.5 km, respectively, and a mean depth of 22 m (Liu et al., 2014). The lake basin occupies 286.0 km^2 and is mainly comprised of carbonate rocks. Lake water is mainly derived from rainfall and underground streams. The Yangzonghai Lake watershed has no naturally occurring surface outflows, and the lake is recharged by rain and the Tangquan River, Yangzong River, and Baiyi River surrounding the lake. The lake's outlet is the Tangdi Canal in the southern part of the lake. Yangzonghai Lake is an important drinking source for Yiliang County, affiliated with Kunming City, and provides water for industry, agriculture, and landscapes (Wang et al., 2010a, b). Because of the subtropical monsoon, the majority of the annual precipitation falls during June to September, and the average rainfall in the basin is approximately 963 mm annually with an average evaporation of 2112 mm.

2.2. Sample collection and sampling procedure

Three sediment sample cores (approximately 20 cm) were collected at the centre of Yangzonghai Lake using a columnar sampling instrument in September 2015 (Fig. 1). The sampling cores were sliced into sub-samples at 1 cm intervals. All the sub-samples were immediately placed into sealable plastic bags sterilized with ethylene oxide, placed in an incubator with ice bags, and transported to the laboratory. Two sampling cores were lyophilized and then ground into smaller particles employing agate mortar. The samples were then shaken through a 100 mesh sieve for homogeneity, prior to subsequent experiments. After the samples were vacuum freeze-dried, the remaining sample cores were used to date for sediment.

2.3. Dating

For the dating process, organic matter was removed with 0.5 mol/l HCl. Then approximately 10 g homogenized sub-samples from the Yangzonghai Lake cores were measured to establish the chronology. Sub-samples were analyzed using a high-resolution HPGe gamma-ray spectrometer, equipped with a well-type coaxial low background intrinsic germanium detector to determine of ^{210}Pb, ^{226}Ra and ^{137}Cs activities. Before analyzing the radionuclides, each sub-sample was stored in sealed centrifuge tubes for 15 days, allowing radioactive equilibration of ^{226}Ra and ^{210}Pb. The activities
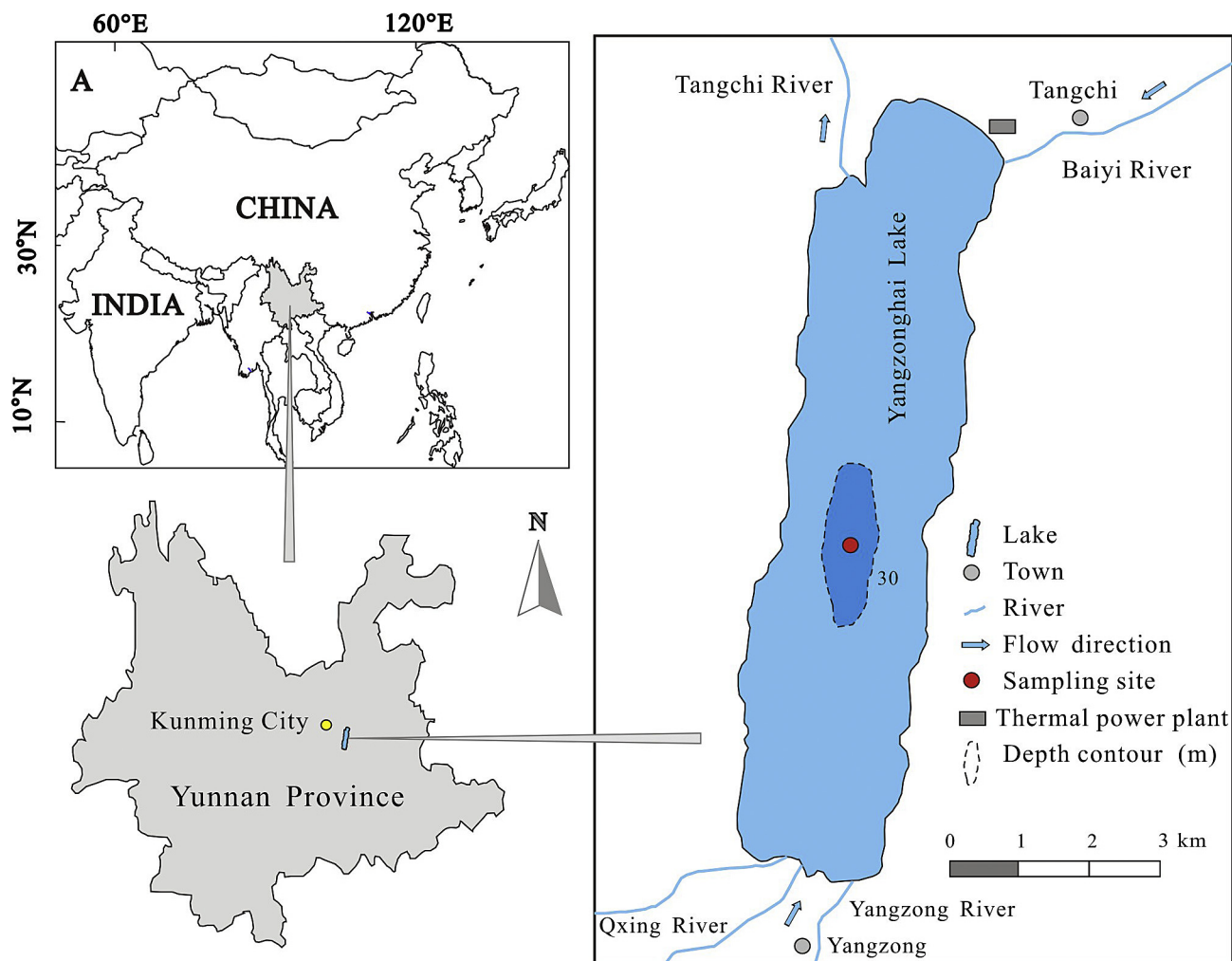
Fig. 1. Location of study area and sampling sites in Yangzonghai Lake.

of ^{210}Pb and ^{226}Ra were assayed using gamma emissions peak values at 46.5 keV and 352 keV, respectively. The activity of ^{137}Cs was acquired by its emissions peak at 662 keV to determine the dating based on ^{210}Pb activity. The detector counting efficiency was performed using reference materials supplied by the International Atomic Energy Agency, based on methods described by Martins et al. (2010). Detection errors were within 10% for both ^{210}Pb and ^{137}Cs.

2.4. Extraction and instrumental analysis of PAHs and OCPs

2.4.1. Reagents and cleaning

The mixed internal standard compounds of OCPs were purchased from Supelco LTD. (Bellefonte, USA), included: α-lindane (α-HCH), β-lindane (β-HCH), γ-lindane (γ-HCH), δ-lindane (δ-HCH), heptachlor, aldrin, heptachlor epoxide, *trans*-chlordane, chlordane, p-p'-DDE, dieldrin, endrin, endosulfan, p-p'-DDD, endrin aldehyde, endosulfan sulfate, p-p'-DDT, endrin ketone and methoxychlor. Simultaneously, a standard material mixture of 16 priority PAHs pollutants was also procured from Supelco LTD, including naphthalene (Nap), acenaphthylene (Ace), acenaphthene (Ac), fluorene (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene (Fluo), 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 (IcdP), dibenzo[a,h]anthracene

(DahA), and benzo[g,h,i]-perylene (BghiP). The solvents, including dichloromethane, hexane, and methanol, were of high-purity chromatographic grade, and other reagents were analytical grade. Stock standard solutions were dissolved in methanol/dichloromethane (1:1, v/v), and then stored at 4 °C prior to use. All glass ware was successively cleaned with methyl alcohol and dichloromethane, and then pyrolyzed at 450 °C in an oven for 4 h prior to extraction.

2.4.2. Extraction procedure

After successive ultrasonic cleaning with methanol and dichloromethane for 20 min, silica dioxide and alumina were activated at 450 and 250 °C, respectively, for 12 h respectively, then deactivated with distilled water for another 12 h and stored in a sealed conical flask soaking with dichloromethane to produce alumina-silica gel chromatography columns. An aliquot of 5 g of homogenized sub-sample was mixed with approximately 0.5 g of copper powder (for desulfurization before extraction) and simultaneously extracted with a 100 ml hexane and methanol mixture (1:1, v/v) for 20 min, using an accelerated solvent extraction instrument (Thermo, ASE350, USA). The extracts were subsequently concentrated after vacuum rotary evaporation and cleaned-up the prepared alumina-silica gel chromatography column. Then 30 ml hexane and a 70 ml dichloromethane-hexane mixture (1; 1, v/v) were used to elute the aliphatic and aromatic fractions, respectively

(Yuan et al., 2016). Finally, the eluents were collected into KD-bottles and concentrated to 1 ml with a suitable nitrogen flow to subsequently determine of PAH and OCP concentrations.

2.4.3. PAHs analysis

A high-performance liquid chromatography system (HPLC) (Agilent 1200, USA) was employed to quantitatively determine PAH compounds in sediment extracts. The HPLC had an Agilent 1200 series quaternary pump and diode-array detector (DAD) combining a series-wound fluorescence detector (FLD). A waters PAH C18 chromatographic column (250 mm × 4.6 mm × 5 μm) was used. The determination wavelength for DAD was 238 nm. The wavelengths of excitation (Ex) and emission (Em) were adjusted based on the time program for FLD, i.e., Ex/Em: 280/330 nm from 0 min, 260/380 nm from 9.0 min, 280/450 nm from 11.2 min, 260/380 nm from 12.5 min, 290/410 nm from 19.5 min, and 310/500 nm from 28.0min, respectively. For gradient elution, a mixture of 40% deionized water and 60% acetonitrile was firstly taken as mobile phase. Then, 100% acetonitrile was added, increasing at a linear gradient for 20 min and held for another 10 min. Finally, another mixture of purified water and acetonitrile (4:6, v/v) was added for a balance time for 6 min. The injection volume was 20 μl and the flow rate was 1 ml/min. The temperature of the chromatographic column was maintained at 25 °C throughout the process. Individual PAHs were quantified based on retention time and accomplished by using external standards.

2.4.4. OCPs analysis

The OCP concentrations within each finished extract from the sediments were analyzed using with a gas chromatograph (GC), combining a Ni electron capture detector (GC—ECD) (Agilent 7890A, USA). Analytes were chromatographically resolved on a DB-5MS capillary column (30 m, 0.32 mm i.d., 0.25 mm film thickness). Helium was taken as a carrier gas at 1 ml/min flow. The injector and detector temperatures were maintained at 250 and 320 °C, respectively. The linear oven gradient began at an initial temperature of 60 °C, the temperature was increased to 170 °C at a rate of 10 °C/min (with a holding period of 2 min for equilibrium). The temperature was then increased to 280 °C at 5 °C/min (with a holding period of 3 min), finally reaching to 300 °C at a rate of increase of 15 °C/min. A 1 μl extract was injected into the GC-ECD for subsequent analysis. A total of 19 OCPs were identified using a gas chromatography-mass spectrometry (GC-MS) (Agilent 7890A-5975C, USA) equipped with a DB-5MS capillary column (30 m, 0.32 mm i.d., 0.25 mm film thickness). The operating conditions of GC-MS were the same as GC-ECD. Individual OCP concentrations in samples were identified based on their retention time through the column.

2.5. Quality assurance and quality control

An external standard method was employed to quantify PAH and OCP compounds. Six different linear levels of standard PAH and OCP materials were used to establish the standard curves and the correlation coefficients between the concentration and the peak area reached higher than 0.999 for each compound. Procedural blanks accompanied with the sediment sample extraction procedure for the quality control. Quartz, used as the substitute matrix, was baked at 550 °C for 6 h and spiked with the known concentration of working solutions containing the PAH and OCP standard. Samples were then extracted and analyzed.

Surface sediment sample parameters were extracted using a similar process and measured in triplicate. The results indicated that the relative standard deviations (RSD) were lower than 10% (n = 3). The limits of detection (LD) of individual PAH and OCP

compounds were defined as the target analytes concentrations having peak when signal-to-noise (S/N) ratio was set as 3:1 and ranged from 0.01 to 1.02 ng/g in this study, level less than LD were expressed as not detected (n.d.), with 0 used for statistical purposes. Procedural blanks operation showed no detectable concentrations of PAH and OCP compounds, suggesting that contamination was negligible during sample transport and analysis. PAH and OCP peaks were distinguished based on both the retention time and the spectra of standard ingredients detected on the identical instrument conditions. PAH and OCP recoveries were defined as the ratios of direct injection of extracts and the mixed internal standard compounds. The spiked recoveries of individual PAH and OCP compounds ranged from 89 to 113% and 81—107.7%, respectively, indicating the determination precision is reliable.

2.6. Data analysis

Common statistical parameters, including maximum value, minimum, and mean values in sediments, were computed using the statistical package SPSS 19.0 (SPSS Inc., USA). Correlations among the individual organic contaminants were also calculated using SPSS 19.0 statistical software. A two-tailed test and Pearson correlation coefficient were used to calculate the correlation coefficients between the measured parameters. *P* values less than 0.05 were considered to be statistically significant. Additionally, depositional flux is important for the evaluation of contamination levels. Contaminant concentrations in the sediment core depend on both sources of emissions and sedimentation rates as well as possibly dilution (Guo et al., 2013). Depositional fluxes of PAH and OCP are calculated by combining measured concentrations with densities and sedimentation rates (Lima et al., 2003). In general, the variation in deposition fluxes of PAH and OCP is significantly similar to the concentrations in this study.

3. Results and discussion

3.1. Dating

Radiometric dates were obtained for the sediment core collected from Yangzonghai Lake by analyzing the samples for ^{210}Pb and ^{137}Cs from the bottom to top layer (Fig. 2). The ^{137}Cs concentrations were low (<20Bq/kg) throughout the sediment core, however, the typical chronological time-mark could be identified. The appearance of ^{137}Cs at a sediment depth of approximately 18 cm below the surface corresponded to the year 1952. Further, the ^{137}Cs activity also showed a relatively well-resolved peak at approximately 14 cm below the surface, recording the peak from the atmospheric fall-out from nuclear weapon testing in 1963 (Abril and Brunskill, 2014). The peak in ^{137}Cs activity at approximately 9.5 cm below the surface roughly indicates the maximum fallout from the Chernobyl incident in 1986. The ^{210}Pb activity exponentially decreased with depth ($R^2 = 0.922$) downwards, therefore a constant rate supply (CRS) dating model to determine the ^{210}Pb chronology was applied to date the sediment core, using the ^{137}Cs data to obtain sedimentation rates (Abril, 2004). The average sedimentary rate was calculated as 0.32 cm/a. That is, relative higher than other plateau lakes in western China and suggests that there was more exogenous detritus input into Yangzonghai Lake (Guo et al., 2010; Wang et al., 2010a, b).

3.2. PAH concentrations in sediments

Concentrations and deposition fluxes of selected individual PAH and total PAH compounds (ΣPAHs) in different dates of the lake's sediment core are illustrated in Fig. 3. Except Chr and INP, a
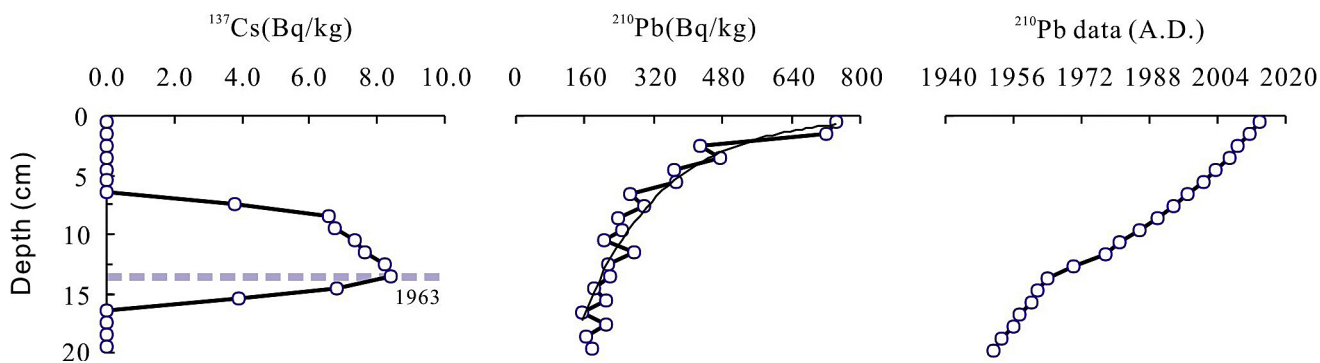
Fig. 2. [137]Cs, ^{210}Pb activities and ^{210}Pb CRS depth versus age model.

total of 14 individual PAH were detected in the sediment profile. PAH concentrations significantly changed from the bottom to the upper layer of the sediment core. Overall increasing trends from the 1950s to the 1990s and then dropped to relatively low concentrations to recent years were shown for ΣPAHs and most individual PAH, simultaneously. The ΣPAHs concentration ranged from 200.7 to 1913.7 ng/g and the fluxes of ΣPAHs varied between 34.2 and 203.5 ng/(cm^2·a). The peak values of ΣPAHs concentration and flux were detected in the 1990s, and lower than that in Dianchi Lake (highest concentration and flux of 4560.8 ng/g and 3128.7 ng/(cm^2·a), respectively, also detected in the 1990s), which is adjacent to Kunming City (Guo et al., 2013). Similar pattern in concentration and flux distributions (initial increase as date increases, followed by a drop until the recent years) were also seen in samples from Erhai Lake, a large shallow lake adjacent to Dali City and close to Yangzonghai Lake (Guo et al., 2013). However, other sampling locations around the world have experienced continuously increasing PAH concentrations in lake sediments (Guo et al., 2010; Sun and Zang, 2013; Yang et al., 2016). The difference in the PAH peaks in sediment cores between remote lakes and those closer to developed region or cities could be attributed to different transportation modes and energy consumption. The highest concentrations of individual PAHs decreased as follows: BbF > DBA > Phen > Nap > BaA > Pyr > BkF > Flu > Ace > BghiP > Ant > Fluo > Ac > BaP. Different variation trend suggested that they came from different sources.

Peak values for all aromatic ring types were detected in the 1990s for all the number of aromatic rings. Fig. 4 presents the ratios of individual PAH with different aromatic rings as a proportion of ΣPAHs. The concentration of 2-ring PAHs decreased from the 1950s to recent years, while 4 and 5-ring PAH concentrations conversely varied. Concentrations of 3-ring PAHs didn't significantly change across the full sediment profile. Concentration of 6-ring PAHs increased between the 1950s and the 1990s and then decreased to recent years. The 2-ring PAHs were present at the highest ratios compared to other PAH compounds, from the 1950s to the 1980s with a subsequent decrease until recent years. Fig. 4 presents the ratios of individual PAH with different aromatic rings as a proportion of ΣPAHs. The ratio of 4-ring PAHs compared to the total increased from the 1990s, and made up the largest values. In addition, the ratio of 5-ring PAHs accounting for ΣPAHs continually increased from the 1950s. 4-ring PAHs increased from the 1950s to the 1990s and then decreased to recent years.

3.3. OCPs concentrations in sediments

Fig. 5 shows the individual OCP and total OCP (ΣOCPs) concentrations and fluxes in the sedimentary core. Of the 19 individual OCPs investigated, only HCHs including α-HCH, β-HCH, γ-HCH and δ-HCH, DDTs (p,p'-DDD and p,p'-DDT), dieldrin and endrin ketone were detected. This suggests these OCP compounds were the predominant contributors of OCPs to the lake. The total OCP concentrations varied between 0.3 and 4.5 g/g, with fluxes ranging
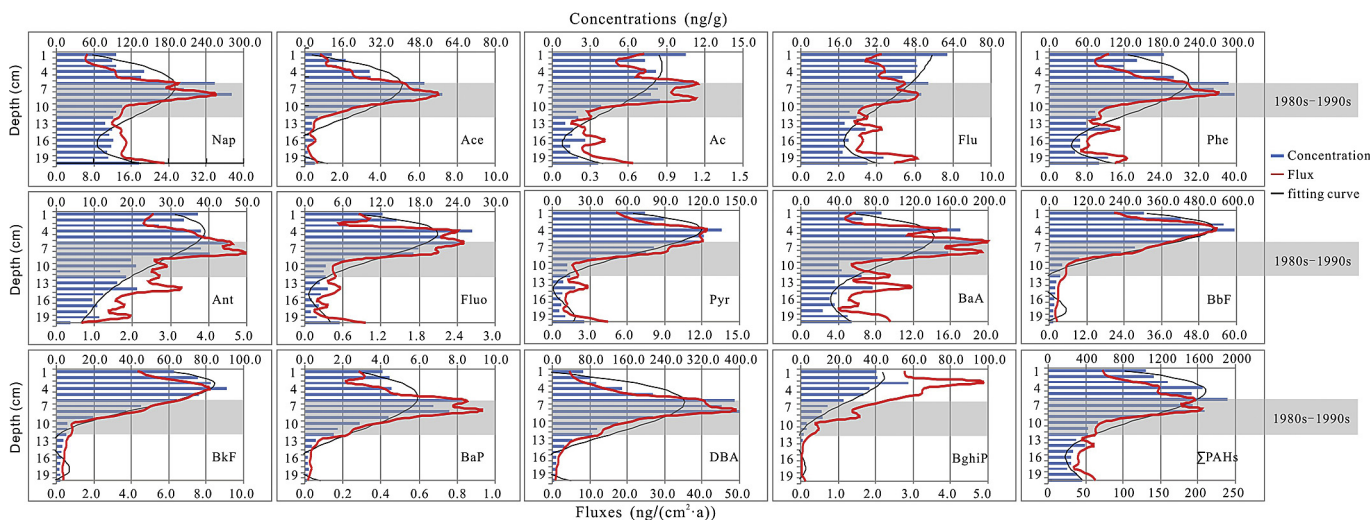

Fig. 3. Concentrations and deposition fluxes of individual PAH compounds and ∑PAHs corresponding to date. Black solid curves represent the fitting curves (polynomial order = 4, R > 0.77) describing the general trends.
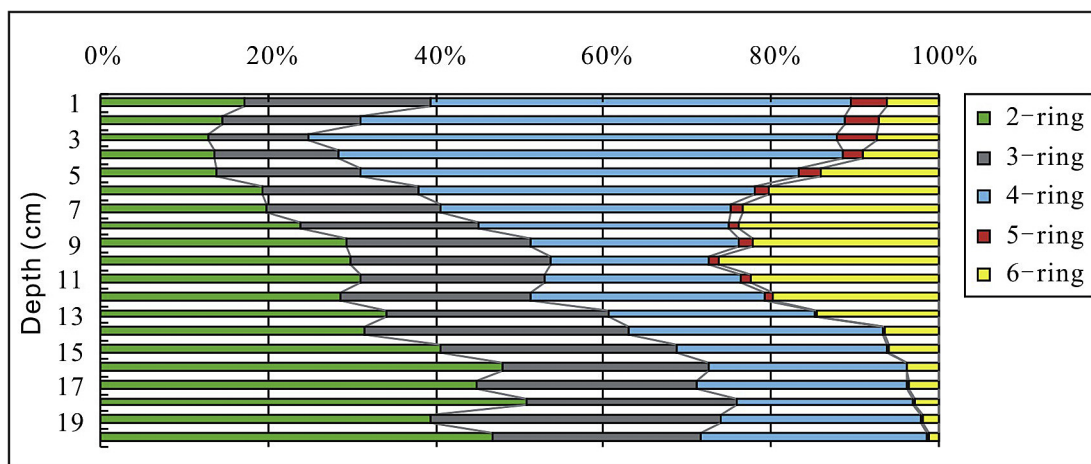
Fig. 4. Relative percentages of PAHs with different rings accounting for ΣPAHs in sediment core.

between 0.02 and 0.6 ng/(cm²·a). HCH isomers (HCHs, equivalent sum of α, β, γ and δ-HCH) ranged from n.d. to 3.5 ng/g and DDT congeners (DDTs, p,p'-DDD + p,p'-DDT) ranged from 0.1 to 1.4 ng/g, respectively. HCHs and DDTs were the predominant contaminants in sediment, making up more than 85% of ΣOCPs. The mean of OCP concentrations were in order as HCHs > DDTs > Dieldrin > Endrin ketone.

Similar to the variations in ΣPAHs across the whole sedimentary profile, ΣOCPs and individual OCP varied significantly: the concentrations increased from the 1950s to the 1990s and then decreased to recent years. Fig. 6 illustrates the ratios of HCHs, DDTs, Dieldrin and Endrin ketone as a proportion of ΣOCPs. The HCHs are present at the highest concentrations, at a proportion of more than 50% from the 1950s to the 1990s, and then significantly decreased until modern times. The DDT values slightly fluctuated until the 1990s, then significantly increasing to more than 70%. Similarly, dieldrin concentrations also first increased and then decreased.

3.4. Source appointment

PAH compounds originating from petrogenic and pyrogenic origins are released into the aquatic ecosystems through various processes, of which anthropogenic deposition is widely regarded as the most significant source (Culotta et al., 2006). Correlations between different PAH compounds detected in this study were listed in Table 1. Generally positive correlations were detected between individual PAH compounds. This suggests that the similar sources contributed to these organic contaminants. The aromatic ring numbers can be employed to diagnose the PAH sources. For example, low-molecular-weight (LMW) PAHs (2–3 ring) are mainly derived from petrogenic sources, such as petroleum discharge and combustion processes at low or moderate temperatures. These processes include biomass and domestic coal combustion. In contrast, high-molecular-weight (HMW) PAHs (4–6 ring) are formed predominantly pyrolytically, from high temperature burning processes, such as vehicular exhaust emission and
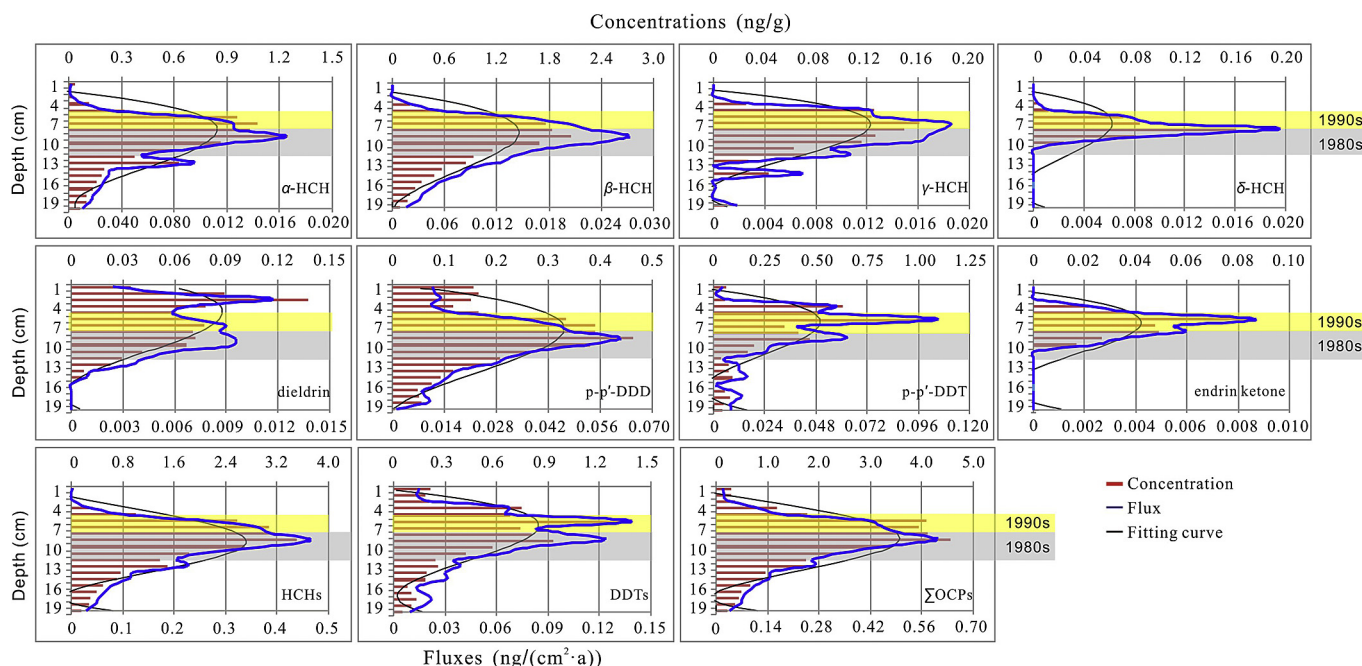

Fig. 5. Concentrations and deposition fluxes of individual OCP compounds and ∑OCPs corresponding to date. Black solid curves represent the fitting curves (polynomial order = 3, R > 0.67) describing the general trends.
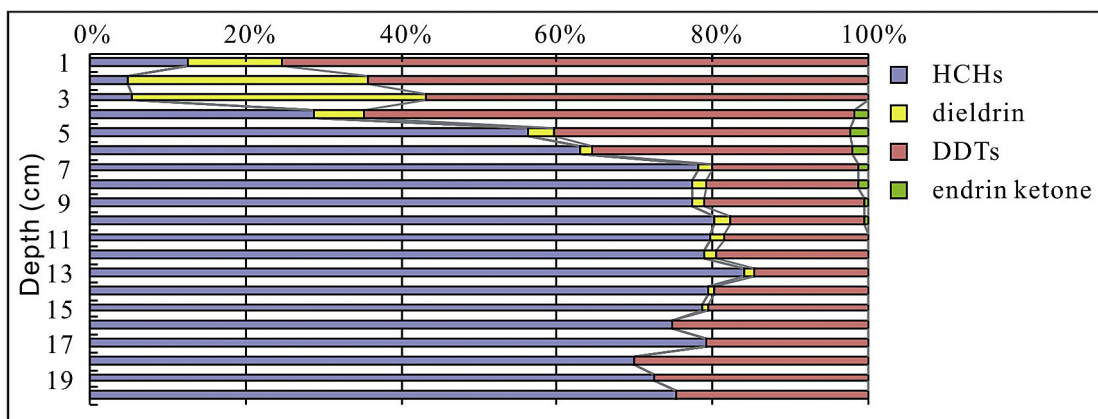
Fig. 6. Relative percentages of OCP compounds accounting for ΣOCPs in sediment core.

industrial coal and petroleum combustion (Arias et al., 2010).

In this study, the proportion of LMW PAHs to ΣPAHs significantly decreased from the 1950s to recent years. In contrast, HMW PAH concentrations followed an inverse pattern, present a proportions of more than 50% from the 1990s to the present (Fig. 4). The proportion of LMW and HMW PAHs in ΣPAHs varied from 21.9 to 51.8% and 24.2–78.1%, with mean values of 52.1 and 47.9%, respectively. Higher proportions of LMW PAHs were seen between the 1950s and the 1990s. Based on a comparison to the HMW PAH compounds, it can be concluded that PAH pollution in Yangzonghai Lake sediments may have originated from petroleum discharge and combustion processes at low or moderate temperatures during the period associated with those core depths. A similar trend was seen in other lakes in western China (Wang et al., 2010a; Guo et al., 2013). Subsequently, the significant increasing trend of HMW PAHs from the 1990s to recent years suggests an enhancement in anthropogenic pyrolysis inputs. This may be the result of increased energy demands from fossil fuels and coal in recent decades.

Additionally, molecular diagnostic ratios of specific PAHs can also provide more detailed information about specific origins in the environment, as molecular ratios change as the composition and burning temperature of organic matter change (Keshavarzifard et al., 2014). For example, molecular diagnostic ratios such as Ant/(Ant + Phe), Flt/(Flt + Pyr), and BaP/BPE have been used to distinguish compositions and possible origins of PAH compounds (Katsoyiannis et al., 2007; Jautzy et al., 2015). In this study, the ratios of Ant/(Ant + Phe), Flt/(Flt + Pyr), and BaP/BPE varied from 0.01 to 0.21, 0.09 to 0.77 and 0.04 to 0.88, respectively. Fig. 7 depicts

the values of Flt/(Flt + Pyr) versus Ant/(Ant + Phe) and Ant/(Ant + Phe) versus LMW/HMW, simultaneously. Ant/(Ant + Phe) ratios less than 0.1 suggest that the PAHs principally originated from petroleum pollution, that is, petrogenic source. Ratios higher than 0.1 are considered to represent combustion sources, i.e., pyrogenic source (Barakat et al., 2011). Flt/(Flt + Pyr) ratios lower than 0.4 are often considered to be typical petroleum contamination. Ratios higher than 0.5 suggest that PAH compounds came primarily from pyrogenic sources, especially grass, wood and coal burning. Values of Flt/(Flt + Pyr) that fall between 0.4 and 0.5 point to the fuel combustion sources (Andersson et al., 2014; Manneh et al., 2016). In general, Flt/(Flt + Pyr) values in sediment core in the Yangzonghai Lake sediment core exceed 0.5 from the 1950s to the 1990s. This suggests a stronger pyrogenic signal. Subsequent values of Flt/(Flt + Pyr) were less than 0.4, from the 1990s to recent years. This indicates the petrogenic inputs. From the 1950s to the 1990s, the majority of Ant/(Ant + Phe) values exceed 0.1. This suggests that the PAH compounds in sediments principally originated from the pyrogenic sources, including fossil fuels and natural source (grass, wood and coal) combustion.

Furthermore, LMW/HMW ratios may also identify the PAH source: values lower than 1 suggest pyrolytic PAHs input, whereas values greater than 1 point to the petrogenic sources. LMW/HMW PAHs ratios in Yangzonghai Lake exceed 1 during the period of the 1950s to the 1990s, showing that early sources of PAHs were petrogenic. LMW/HMW PAHs values in sediments lower than 1 indicate the presence of PAHs with pyrolytic origins, resulting from grass, wood and coal combustion in the early period. Taking into

Table 1
Correlation coefficient matrix for different PAH compounds (n = 20).

	Nap	Ace	Ac	Flu	Phen	Ant	Fluo	Pyr	BaA	BbF	BkF	BaP	DBA	BghiP
Nap	1													
Ace	0.931**	1												
Ac	0.681**	0.756**	1											
Flu	0.608**	0.696**	0.847**	1										
Phen	0.889**	0.918**	0.882**	0.813**	1									
Ant	0.628**	0.733**	0.851**	0.762**	0.883**	1								
Fluo	0.663	0.716**	0.828**	0.772**	0.841**	0.898**	1							
Pyr	0.477*	0.518**	0.779**	0.625**	0.724**	0.877**	0.937**	1						
BaA	0.669**	0.632**	0.581**	0.694**	0.753**	0.768**	0.848**	0.726**	1					
BbF	0.339	0.423	0.751**	0.506*	0.616**	0.811**	0.831**	0.951**	0.505*	1				
BkF	0.341	0.438	0.800**	0.584**	0.642**	0.837**	0.840**	0.949**	0.512*	0.992**	1			
BaP	0.842**	0.925**	0.891**	0.780**	0.963**	0.917**	0.855**	0.752**	0.713**	0.671**	0.697**	1		
DBA	0.928**	0.963**	0.725**	0.608**	0.928**	0.784**	0.733**	0.583**	0.681**	0.474*	0.475*	0.936**	1	
BghiP	0.139	0.234	0.709**	0.427	0.466*	0.688**	0.626**	0.814**	0.244	0.930**	0.944**	0.526*	0.274	1

** Correlation is significant at the 0.01 level (2-tailed). * Correlation is significant at the 0.05 level (2-tailed).
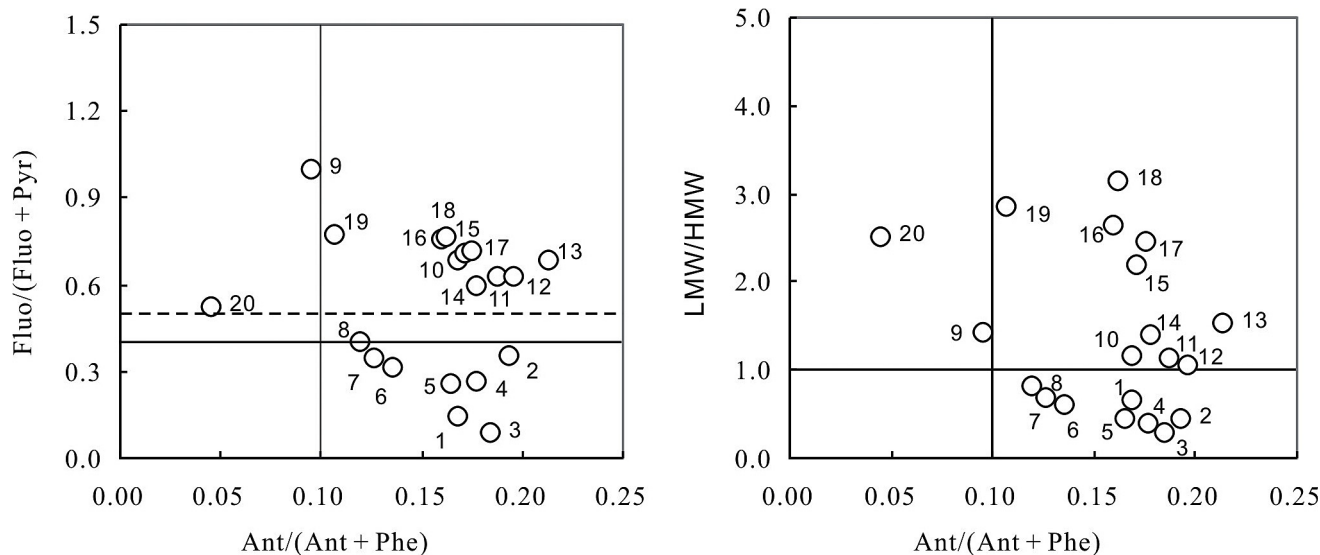
Fig. 7. Different diagnostic ratios of PAHs in sediment core. The number represents the sediment layer.

account of the accuracy of molecular diagnostic ratios of individual PAH compound for the PAH sources identification (Martins et al., 2010), synthetic diagnostic ratios were used in this study. In general, PAHs in sediments of Yangzonghai Lake originally derived from natural sources (grass, wood and coal) combustion. Mixed sources of petroleum, and subsequently fuel combustion dominated the upper layer because of the energy transition from natural sources to oil and natural gas for home and industrial heating, and improved combustion efficiencies especially in power generation (Liu et al., 2009).

Table 2 shows the correlations between different OCP compounds. Generally, significant positive correlation coefficients were seen between individual OCP except dieldrin. This indicates that these OCP compounds had homogeneous origins and transport modes. For OCPs, HCHs and DDTs made up the largest proportions of OCPs (>85%) and were the most important OCP compounds in the sediment core. The composition of HCHs related isomers or DDTs congeners can serve as an indicator to differentiate the origins and fates of HCHs in the environment. Typically, the main sources of HCHs came from the use of technical HCHs, which are generally composes of 60—70% α-HCH, 5—12% β-HCH, 10—15% γ-HCH, and 6—10% δ-HCH (Wu et al., 2010; Sun et al., 2010; Yuan et al., 2013). Individual HCH isomers as a part of the total HCHs in the Yangzonghai Lake sediment core varied from 27.0 to 100%, n.d.-73.5%, n.d.-12.5 and n.d.-5.0% with average values of 43.4, 52.5, 3.3 and 0.8%, respectively. From the 1950s to the 2000s, β-HCH was the

HCH with the highest ratio relative to the other HCH isomers. The isomer δ-HCH was only detected between the 1980s and the 2000s of sediment core and made up the lowest ratios. The isomers β-HCH and γ-HCH were not observed near the top layer of the sediment core.

The isomer α-HCH was also present at a relatively high ratio in HCHs. From the 2000s to recent years, the α-HCH ratio dramatically increases. The preponderance of β-HCH can be attributed to higher partition coefficients, lower vapor pressure, and water solubility relative to other HCH isomers. This makes β-HCH the most persistent and stable for microbial degradation and sediment adsorption, with less evaporative loss in the aquatic environment (Sultana et al., 2014). As such, volatile α-HCH and γ-HCH degraded into β-HCH, and the dominance of β-HCH indicated no recent inputs of technical HCHs. Conversely, the dominance of α-HCH and γ-HCH suggests long-range transport (Meng et al., 2014). Furthermore, the stoichiometric α/γ-HCH ratio is 5:7 in technical HCHs, but tends to increase over time. This is due to the faster degradation of γ-HCH relative to α-HCH (Liu et al., 2010). However, the continued use of pesticides containing lindane (γ-HCH) led to a decline in the α/γ-HCH ratios. Generally speaking, ratios of α/γ-HCH lower than 1 indicated recent lindane (γ-HCH) inputs (Zhang et al., 2009). In this research, α/γ-HCH ratio varied between 2.6 and 22.7 at the layer where γ-HCH was detected. This indicates that HCHs in sediments from the Yangzonghai Lake principally originated from the emission and conversion of local technical HCHs. The presence of

Table 2
Correlation coefficient matrix for different OCP compounds (n = 20).

	α-HCH	β-HCH	γ-HCH	δ-HCH	dieldrin	p-p'-DDD	p-p'-DDT	Endrin ketone	HCHs	DDTs	OCPs
α-HCH	1										
β-HCH	0.982**	1									
γ-HCH	0.879**	0.883**	1								
δ-HCH	0.799**	0.777**	0.779**	1							
dieldrin	0.323	0.286	0.428	0.377	1						
p-p'-DDD	0.928**	0.925**	0.863**	0.769**	0.564**	1					
p-p'-DDT	0.561*	0.503	0.657**	0.553*	0.417	0.530*	1				
Endrin ketone	0.688* *	0.627**	0.792**	0.754**	0.440	0.648**	0.911**	1			
HCHs	0.993**	0.996**	0.899**	0.806**	0.314	0.933**	0.541*	0.672**	1		
DDTs	0.772**	0.727**	0.819**	0.703**	0.530*	0.776**	0.946**	0.924**	0.759**	1	
OCPs	0.983**	0.973**	0.923**	0.822**	0.403	0.942**	0.673**	0.773**	0.985**	0.860**	1

** Correlation is significant at the 0.01 level (2-tailed). * Correlation is significant at the 0.05 level (2-tailed).

dieldrin and DDTs suggests that OCPs were still produced and used for small-scale applications, such as malaria control and dicofol production. This result is supported by the research in other regions (Zhang et al., 2014; Zhi et al., 2015; Nixdorf et al., 2015).

DDT/DDTs ratios can serve as an indicator to distinguish recent sources and the transport process of technical DDTs. High values show recent technical DDT input, while low ratios imply no recent input (Yuan et al., 2016). Technical DDTs is usually composed of 5% p,p'-DDE, <5% p,p'-DDD, and 90% p,p'-DDT (Li et al., 2015). In this study, p,p'-DDD and p,p'-DDT accounted for 11.7 and 11.1–88.9% and 84.4% of total DDTs, with mean values of 50.9 and 49.1%, respectively. DDT could be biodegraded into DDE and DDD on aerobic and anaerobic condition, respectively (Kuranchie-Mensah et al., 2012). DDE concentrations below detection limits in the Yangzonghai Lake sediment core suggest that the historical input parent DDTs degraded into DDD due to the anaerobic conditions at depths greater than 30 m. In addition, the tendency of DDTs congeners to biodegrade can help distinguish the relative contribution of technical DDT. Based on previous studies, values of (DDE + DDD)/DDTs higher than 0.5 indicate a long-term weathering process, and DDE/DDD ratios higher than 1 suggest the dominant aerobic degradation process (Zhou et al., 2006; Li et al., 2015). Values of (DDE + p,p'-DDD)/DDTs lower than 0.5 for sediments from the 1950s to the 1960s and the 1990s to the 2000s indicated there may have been significant DDT parent inputs, or use of other pesticides containing DDTs (Zhao et al., 2009). From the 1960s to the 1990s, the ratio was slightly greater than 0.5. This indicates that DDTs may have primarily originated from microbial degraded DDTs in the sediments. The ratios at the upper layer of the sediment profile which are significantly larger than 0.5 suggests that the DDT primarily originated from DDT-treated agricultural soils in the Yangzonghai Lake catchment and microbial degraded DDTs in the sediments, after the official ban on DDTs (Doong et al., 2002; Wang et al., 2013). Finally, the values of p,p'-DDT/DDTs in sediment core from Yangzonghai Lake varied from 0.11 to 0.88, suggesting that the DDTs in the study area originated from historical input and long-term degradation.

3.5. Historical pollution procedure

Sediments are an important sink, which can sensitively record the historical process associated with organic contaminant and regional energy structure change. Obvious peak periods of PAH and OCP concentrations in the sediment core from Yangzonghai Lake were measured in the 1990s (see Fig. 2). This peak period was later than was seen in Tokyo Bay, where similar contaminant levels were correlated with the 1970s and the early 1980s, when consumption of fossil fuel was globally increasing (Yamashita et al., 2000). This lag may have been caused by uneven regional economic development. The lower layer of the sediment core, from the 1950s to the 1980s, had relatively consistently low concentrations of individual PAH and a higher proportion of LMW PAHs. This may reflect the fact that biomass was a primary resource for burning before the 1980s in the Yangzonghai Lake Basin. In turn, the increase in the proportion of HMW PAHs points to the occurrence of fossil fuel combustion in the lake basin associated with the start of industrial activities in China in the 1950s (Wang et al., 2010a; Bigus et al., 2014).

The proportion of HMW PAH concentrations to ΣPAHs dramatically increased during time period encompassing the 1980s to the 1990s, indicating the extensive input of petroleum and industrial coal combustion as a result of the initiation of the "Reform and Open" Policy, starting in 1978 (Guo et al., 2006). During this period, China, including this region, experienced rapid development and subsequent dramatic fuel requirements and organic

contaminant discharges. Notably, ΣPAHs and HMW PAH concentrations, as well as the proportion of HMW PAHs, significantly decreased starting in the 2000s. This trend was also seen in Dianchi Lake, which is adjacent to Yangzonghai Lake, in a survey completed by Guo et al. (2013). However, this pattern was not seen in other lake sediments in western China (Guo et al., 2010). These results may be due to improved fuel combustion technologies associated with coal and petroleum in the past two decades, even as coal consumption was increasing overall in Yangzonghai Basin.

As the largest developing country, China has well-developed agricultural and industrial sectors. It was once a main producer and consumer of OCPs and initiated HCH use in the 1950s (Qiu et al., 2005; Yang et al., 2015), which correspond to bottom of the sediment profile in Yangzonghai Lake. The results indicated that HCHs and DDTs were extensively applied starting in the 1950s and reaching a peak in the 1980s. Additionally, the detected concentrations in the 1950s suggested that HCHs and DDTs were applied during an earlier period than dieldrin and endrin ketone in the study area. This result was similar to research done by Zhang et al. (2011) in a Bay located in southeast China. HCHs including β-HCH, γ-HCH and δ-HCH were not detected in upper layer of the sediment core. This absence corresponds with the ban of technical mixtures of HCH starting in the 1980s. The detection of α-HCH as the predominant HCH isomer without β-HCH in the later period indicates that α-HCH was transported upward through resuspension and bioturbation (Wang et al., 2008; Yuan et al., 2013). This mechanism may have resulted in the endogenesis release of α-HCH because of the instability of α-HCH in aquatic ecosystem even the external input has been cut down. Owning to the most carcinogenic effect in HCH isomers, the α-HCH pollution levels may induce high ecotoxicity for the lake ecosystem (Doong et al., 2002).

In addition, DDTs, including p,p'-DDD and p,p'-DDT, were detected from the 1950s and reached high concentrations in the 1980s. Levels remained high to the 1990s. The continuous increasing trend indicates that DDTs were widely used in Yangzonghai Lake Basin. A subsequently significant decrease up to recent years was likely associated with the banning of DDTs in China starting in 1983. Similar to Dianchi Lake, and in contrast to other developed regions with peaks in the 1960–1970s (Guo et al., 2013), the high levels with later peaks and an extended period of presence suggests that DDT and HCH use were more extensive and continuous in western China. Additionally, in contrast with Taihu Lake and Daya Bay in more developed regions in China, where continuous HCH and DDT increases were detected (Wang et al., 2008; Wu et al., 2010), the pattern of initial increasing concentrations and then decreasing concentrations in the study area suggests that the official ban of OCPs resulted in better outcomes in the developing region. It is particularly worthwhile to note that DDTs remained in the sediment core later than the 1990s, suggesting that they were continuously used in Yangzonghai Lake Basin for various agricultural or medicinal purposes (He et al., 2014). Qiu et al. (2005) also reported that DDTs were still produced and used in China until 2002. In general, while OCP compounds have been restricted and banned for approximately three decades in China, their residues in sediments might pose potential secondary pollution to water through runoff discharge and desorption (Meng et al., 2014).

4. Conclusion

The total of PAH and OCP concentrations in the sediment core profile from Yangzonghai Lake were 200.7–1913.7 ng/g and 0.3–4.5 ng/g, respectively. Significant increasing from the bottom to middle layer and subsequent decreasing upwards in concentrations were detected. This indicates that PAH and OCP inputs peaked in the 1980s with rapid regional development, and then declined

up to the present. Combined with molecular diagnostic ratios of Flt/(Flt + Pyr), Ant/(Ant + Phe) and LMW/HMW, the LHW PAHs accounted for a proportion of total PAHs exceeding 50%. This suggests that burned biomass (grass, coal, and wood) dominated the bottom to the middle segment of the core, corresponding to the 1950s—1980s timeframe. After this point, petroleum and fuel combustion dominated use, based on the increasing ratio of HMW PAHs. This shift was due to changes in energy structure and improved combustion efficiencies. Additionally, of the 6 detected individual OCP compounds in the sediment core, HCHs and DDTs made up more than 85% of the total OCP contaminants. HCHs accounted for a larger proportion than OCPs from the 1950s to 1990s. This layer corresponds to deposits made from the 1950s to the 1990s, and suggests that HCHs were the dominant OCPs in this period. High α/γ-HCH ratios indicate that emissions and conversion of local technical HCHs were dominant sources of contaminants in Yangzonghai Lake. The ratios of (DDE + p,p'-DDD)/DDTs and p,p'-DDT/DDTs in the sediment core suggest that the DDTs in the research area came from historical inputs. In addition, DDTs were detected from the bottom of the sediment core, reaching a peak value in the 1990s. This point aligns with the point in time when HCHs and DDTs were banned in China. The detected DDT values then generally decreased up to the present time. However, the continuous increasing ratios accounting for OCPs from the 1990s indicated that DDTs were widely used in Yangzonghai Lake Basin.

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